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# IIT Chemistry

Topic-wise  
Solved Questions

39 years' solved questions  
**1978-2016**

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Education

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**McGraw Hill Education (India) Private Limited**  
NEW DELHI

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**IIT Chemistry Topic-wise Solved Questions**

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# PREFACE

*IIT Chemistry: Topic-wise Solved Questions* provides a collection of solved questions in Chemistry from past IIT question papers, arranged systematically according to the various topics in the subject. This new edition contains IIT question papers from the last 39 years, i.e., **from 1978 to 2016**. Such a compilation would enable the reader to pick and choose a particular topic and get a collection of actual questions asked in the examination over the past three decades. The solutions to JEE Advanced 2016 question papers are given at the end of the book.

The questions have been categorised as:

## **Straight Objective Type**

It contains multiple choice questions having exactly one correct answer.

## **Multiple Correct Choice Type**

It contains multiple choice questions having one or more than one correct answer.

## **Fill in the Blanks Type**

It contains questions in which given statements are to be completed to make them true by filling appropriate word(s) in blanks.

## **True/False Type**

Statements in this type of questions are to be labeled as true or false as may be appropriate.

## **Matrix Match Type**

Each question in this category contains statements given in 2 columns. Statements in the first column have to be matched with statements in the second.

## **Linked Comprehension Type**

Each question in this category contains a paragraph followed by questions. Each question has four choices out of which exactly one is correct.

## **Reasoning Type**

Each Question in this category contains Statement -1 and Statement-2

Write (a) if both the statements are True and Statement-2 is the correct explanation of Statement-1

Write (b) if both the statements are True but Statement-2 is not the correct explanation of Statement-1.

Write (c) if Statement-1 is True and Statement-2 is False.

Write (d) if Statement-1 is False and Statement-2 is True.

## **Short Answer Type**

Answers have been provided to all the questions and hints and solutions have been provided to selected questions.

## **Subjective Type**

Answers have been provided to all the questions and hints and solutions have been provided to selected questions.

We hope that this collection of questions would provide adequate practice for aspirants in solving actual problems asked in the exam.

We sincerely wish all aspirants the best in their endeavours.



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# THE CONCEPTS OF ATOMS AND MOLECULES

1

## Straight Objective Type

1. 27 g of Al will react completely with
  - (a) 8 g of O<sub>2</sub>
  - (b) 16 g of O<sub>2</sub>
  - (c) 24 g of O<sub>2</sub>
  - (d) 32 g of O<sub>2</sub>
  - (e) 40 g of O<sub>2</sub>

(1978)
2. 10 g of CaCO<sub>3</sub> contains
  - (a) 10 mol of CaCO<sub>3</sub>
  - (b) 1 mol of Ca
  - (c)  $6 \times 10^{22}$  atoms of Ca
  - (d) 0.1 g equivalent of Ca
  - (e) None of these

(1978)
3. Which of the following has highest mass?
  - (a) 20 g phosphorus
  - (b) 5 mol of water
  - (c) 2 equivalent of Na<sub>2</sub>CO<sub>3</sub>
  - (d)  $12 \times 10^{24}$  atoms of hydrogen

(1978)
4. 2.76 g of silver carbonate, on being strongly heated, yields a residue weighing
  - (a) 2.16 g
  - (b) 2.48 g
  - (c) 2.32 g
  - (d) 2.64 g

(1979)
5. A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by mass. The ratio of their numbers of molecules is
  - (a) 1 : 4
  - (b) 1 : 8
  - (c) 7 : 32
  - (d) 3 : 16

(1979)
6. The largest number of molecules is in
  - (a) 36 g of water
  - (b) 28 g of carbon monoxide
  - (c) 46 g of ethyl alcohol
  - (d) 54 g of nitrogen pentoxide

(1979)
7. M is the molar mass of KMnO<sub>4</sub>. The equivalent mass of KMnO<sub>4</sub> when it is converted into K<sub>2</sub>MnO<sub>4</sub> is
  - (a) M
  - (b) M/3
  - (c) M/5
  - (d) M/7

(1980)
8. White phosphorus reacts with caustic soda. The products are PH<sub>3</sub> and NaH<sub>2</sub>PO<sub>4</sub>. The reaction is an example of
  - (a) oxidation
  - (b) reduction
  - (c) oxidation-reduction
  - (d) neutralization

(1980)
9. If 0.5 mol of BaCl<sub>2</sub> is mixed with 0.20 mol of Na<sub>3</sub>PO<sub>4</sub>, the maximum amount of Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> that can be formed is
  - (a) 0.70 mol
  - (b) 0.50 mol
  - (c) 0.20 mol
  - (d) 0.10 mol

(1981)
10. One mole of N<sub>2</sub>H<sub>4</sub> loses 10 mol of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of nitrogen in Y? (There is no change in the oxidation state of hydrogen.)
  - (a) -1
  - (b) -3
  - (c) +3
  - (d) +5

(1981)

11. HBr and HI can reduce sulphuric acid, HCl can reduce  $\text{KMnO}_4$  and HF can reduce  
 (a)  $\text{H}_2\text{SO}_4$       (b)  $\text{KMnO}_4$       (c)  $\text{K}_2\text{Cr}_2\text{O}_7$       (d) none of these      (1981)
12. A solution of sodium metal in liquid ammonia is strongly reducing agent due to the presence of  
 (a) sodium atoms      (b) sodium hydride  
 (c) sodium amide      (d) solvated electrons      (1981)
13. The oxidation number of carbon in  $\text{CH}_2\text{O}$  is  
 (a) -2      (b) +2      (c) 0      (d) +4      (1982)
14. The brown ring complex compound is formulated as  $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})^+]\text{SO}_4$ . The oxidation state of iron is  
 (a) 1      (b) 2      (c) 3      (d) 0      (1984)
15. The equivalent mass of  $\text{MnSO}_4$  is half its molar mass when it is converted to  
 (a)  $\text{Mn}_2\text{O}_3$       (b)  $\text{MnO}_2$       (c)  $\text{MnO}_4^-$       (d)  $\text{MnO}_4^{2-}$       (1988)
16. The oxidation number of phosphorus in  $\text{Ba}(\text{H}_2\text{PO}_2)_2$  is  
 (a) +3      (b) +2      (c) +1      (d) -1      (1990)
17. The reaction which proceeds in the forward direction is  
 (a)  $\text{Fe}_2\text{O}_3 + 6\text{HCl} = 2\text{FeCl}_3 + 3\text{H}_2\text{O}$       (b)  $\text{NH}_3 + \text{H}_2\text{O} + \text{NaCl} = \text{NH}_4\text{Cl} + \text{NaOH}$   
 (c)  $\text{SnCl}_4 + \text{Hg}_2\text{Cl}_2 = \text{SnCl}_2 + 2\text{HgCl}_2$       (d)  $2\text{CuI} + \text{I}_2 + 4\text{K}^+ = 2\text{Cu}^{2+} + 4\text{KI}$       (1991)
18. The oxidation states of the most electronegative element in the products of the reaction,  $\text{BaO}_2$  with dil.  $\text{H}_2\text{SO}_4$  are  
 (a) 0 and -1      (b) -1 and -2      (c) -2 and 0      (d) -2 and +1      (1991)
19. For the redox reaction  $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$   
 the correct coefficients of the reactants for the balanced reaction are
- |                  |                             |              |                  |                             |              |
|------------------|-----------------------------|--------------|------------------|-----------------------------|--------------|
| $\text{MnO}_4^-$ | $\text{C}_2\text{O}_4^{2-}$ | $\text{H}^+$ | $\text{MnO}_4^-$ | $\text{C}_2\text{O}_4^{2-}$ | $\text{H}^+$ |
| (a) 2            | 5                           | 16           | (b) 16           | 5                           | 2            |
| (c) 5            | 16                          | 2            | (d) 2            | 16                          | 5            |
- (1993)
20. An example of a reversible reaction is  
 (a)  $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{NaI}(\text{aq}) = \text{PbI}_2(\text{s}) + 2\text{NaNO}_3(\text{aq})$   
 (b)  $\text{AgNO}_3(\text{aq}) + \text{HCl}(\text{aq}) = \text{AgCl}(\text{s}) + \text{HNO}_3(\text{aq})$   
 (c)  $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) = 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$   
 (d)  $\text{KNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) = \text{KCl}(\text{aq}) + \text{NaNO}_3(\text{aq})$       (1985)
21. The number of moles of  $\text{KMnO}_4$  that will be needed to react completely with one mole of ferrous oxalate in acidic solution is  
 (a) 3/5      (b) 2/5      (c) 4/5      (d) 1      (1997)
22. The number of moles of  $\text{KMnO}_4$  that will be needed to react with one mole of sulphite ion in acidic solution is  
 (a) 2/5      (b) 3/5      (c) 4/5      (d) 1      (1997)
23. The normality of 0.3 M phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is,  
 (a) 0.1      (b) 0.9      (c) 0.3      (d) 0.6      (1999)
24. The oxidation number of sulphur in  $\text{S}_8$ ,  $\text{S}_2\text{F}_2$ ,  $\text{H}_2\text{S}$  respectively, are  
 (a) 0, +1 and -2      (b) +2, +1 and -2  
 (c) 0, +1 and +2      (d) -2, +1 and -2      (1999)

25. Amongst the following, identify the species with an atom in +6 oxidation state.

- (a)  $\text{MnO}_4^-$       (b)  $\text{Cr}(\text{CN})_6^{3-}$       (c)  $\text{NiF}_6^{2-}$       (d)  $\text{CrO}_2\text{Cl}_2$       (2000)

26. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is

- (a) 40 mL      (b) 20 mL      (c) 10 mL      (d) 4 mL      (2001)

27. The reaction,  $3\text{ClO}_3^-(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + 2\text{Cl}^-(\text{aq})$ , is an example of

- |                                 |                            |
|---------------------------------|----------------------------|
| (a) oxidation reaction          | (b) reduction reaction     |
| (c) disproportionation reaction | (d) decomposition reaction |
- (2001)

28. In the standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  using  $\text{K}_2\text{Cr}_2\text{O}_7$  by iodometry, the equivalent mass of  $\text{K}_2\text{Cr}_2\text{O}_7$  is

- |                    |                        |
|--------------------|------------------------|
| (a) (molar mass)/2 | (b) (molar mass)/6     |
| (c) (molar mass)/3 | (d) same as molar mass |
- (2001)

29. How many moles of electrons weigh one kilogram?

- |  |  |
|--|--|
| (a) $6.023 \times 10^{23}$               | (b) $\frac{1}{9.108} \times 10^{31}$           |
| (c) $\frac{6.023}{9.108} \times 10^{54}$ | (d) $\frac{1}{9.108 \times 6.023} \times 10^8$ |
- (2002)

30. Which of the following has maximum number of atoms?

- |   |  |
|---|--|
| (a) 24 g of C ( $M = 12 \text{ g mol}^{-1}$ ) | (b) 23 g of Na ( $M = 23 \text{ g mol}^{-1}$ )   |
| (c) 48 g of S ( $M = 32 \text{ g mol}^{-1}$ ) | (d) 108 g of Ag ( $M = 108 \text{ g mol}^{-1}$ ) |
- (2003)

31. The pair of the compounds in which both the metals are in the highest possible oxidation state is

- |   |  |
|---|--|
| (a) $[\text{Fe}(\text{CN})_6]^{4-}$ , $[\text{Co}(\text{CN})_6]^{3-}$ | (b) $[\text{Co}(\text{CN})_6]^{3-}$ , $\text{Ni}(\text{CO})_4$ |
| (c) $\text{TiO}_2$ , $\text{MnO}_2$                                   | (d) $\text{CrO}_2\text{Cl}_2$ , $\text{MnO}_4^-$               |
- (2004)

32. Which of the following is not oxidised by  $\text{O}_3$ ?

- |                              |                     |
|------------------------------|---------------------|
| (a) KI                       | (b) $\text{KMnO}_4$ |
| (c) $\text{K}_2\text{MnO}_4$ | (d) $\text{FeSO}_4$ |
- (2005)

33. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is

- (a) 3      (b) 4      (c) 5      (d) 6      (2007)

34. Given that the abundances of isotopes  $^{54}\text{Fe}$ ,  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$  are 5%, 90% and 5%, respectively, the relative atomic mass of Fe is

- (a) 55.85      (b) 55.95      (c) 55.75      (d) 56.05      (2009)

35. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

- |   |  |
|---|--|
| (a) II, III in haematite and III in magnetite | (b) II, III in haematite and II in magnetite   |
| (c) II in haematite and II, III in magnetite  | (d) III in haematite and II, III in magnetite. |
- (2011)

36. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?

- |  |  |
|--|--|
| (a) $\text{HNO}_3$ , NO, $\text{NH}_4\text{Cl}$ , $\text{N}_2$ | (b) $\text{HNO}_3$ , NO, $\text{N}_2$ , $\text{NH}_4\text{Cl}$ |
| (c) $\text{HNO}_3$ , $\text{NH}_4\text{Cl}$ , NO, $\text{N}_2$ | (d) NO, $\text{HNO}_3$ , $\text{NH}_4\text{Cl}$ , $\text{N}_2$ |
- (2012)

## Multiple Correct-Choice Type

1. Many elements have non-integral atomic masses because
  - they have isotopes
  - their isotopes have non-integral masses
  - their isotopes have different masses
  - the constituents-neutrons, protons and electrons-combine to give fractional masses.(1984)
2. Reduction of the metal centre in aqueous permanganate ion involves
 

(a) 3 electrons in neutral medium	(b) 5 electrons in neutral medium
(c) 3 electrons in alkaline medium	(d) 5 electrons in acidic medium

(2011)
3. For the reaction:  

$$\text{I}^- + \text{ClO}_3^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$$
 the correct statement(s) in the balanced equation is/are
 

(a) Stoichiometric coefficient of $\text{HSO}_4^-$ is 6.	(b) Iodide is oxidised
(c) Sulphur is reduced	(d) $\text{H}_2\text{O}$ is one of the products.

(2014)

## Fill-in-the-Blanks Type

1. The modern atomic mass unit is based on the mass of \_\_\_\_\_. (1980)
2. The lowest possible oxidation state of nitrogen is \_\_\_\_\_. (1980)
3. The mass of  $1 \times 10^{22}$  molecules of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is \_\_\_\_\_. (1991)
4. The compound Y,  $\text{Ba}_2\text{Cu}_3\text{O}_7$ , which shows superconductivity, has copper in oxidation state \_\_\_\_\_. Assume that the rare earth element yttrium is in its usual +3 oxidation state. (1994)
5. 3 g of a salt of relative molar mass 30 is dissolved in 250 g of water. The molality of the solution is \_\_\_\_\_. (1983)

## Integer Answer Type

1. The oxidation number of Mn in the product of alkaline oxidative fusion of  $\text{MnO}_2$  is \_\_\_\_\_. (2009)
2. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is \_\_\_\_\_. (2010)
3. Among the following, the number of elements showing only one non-zero oxidation state is \_\_\_\_\_.  
 O, Cl, F, N, P, Sn  
 Tl, Na, Ti (2010)
4. Silver (molar mass = 108 g mol<sup>-1</sup>) has a density of 10.5 g cm<sup>-3</sup>. The number of silver atoms on a surface of area  $10^{-12}$  m<sup>2</sup> can be expressed in scientific notation as  $y \times 10^x$ . The value of x is \_\_\_\_\_. (2010)
5. The difference in the oxidation numbers of the two types of sulphur atom in  $\text{Na}_2\text{S}_4\text{O}_6$  is \_\_\_\_\_. (2011)
6. Reaction of  $\text{Br}_2$  with  $\text{Na}_2\text{CO}_3$  in aqueous solution gives sodium bromide and sodium bromate with evolution of  $\text{CO}_2$  gas. The number of sodium bromide molecules involved in the balanced chemical equation is \_\_\_\_\_. (2011)
7. The volume (in mL) of 0.1 M  $\text{AgNO}_3$  required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$  as silver chloride is close to \_\_\_\_\_. (2011)
8. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL<sup>-1</sup>. The molar mass of HCl is 36.5 g mol<sup>-1</sup>. The volume in mL of stock solution required to prepare a 200 mL solution of 0.4 M HCl is \_\_\_\_\_. (2012)
9. If the value of Avogadro constant is  $6.023 \times 10^{23}$  mol<sup>-1</sup> and the value of Boltzmann constant is  $1.380 \times 10^{-23}$  J K<sup>-1</sup>, then the number of significant digits in the calculated value of the universal gas constant is \_\_\_\_\_. (2014)

### True/False Type

1. Vapour density of a gas is twice its relative molar mass. (1978)
2. A molal solution contains one mole of solute in 100 g of solution. (1978)
3. At a given temperature and pressure equal masses of different gases contain the same number of molecules. (1978)
4. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (1985)

### Reasoning Type

1. Given below are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code among A, B, C and D which are defined below.

#### Code

- (a) Both S and E are true, and E is the correct explanation of S.
- (b) Both S and E are true but E is not the correct explanation of S.
- (c) S is true but E is false.
- (d) S is false but E is true.

#### STATEMENT (S)

In the titration of  $\text{Na}_2\text{CO}_3$  with HCl using methyl orange indicator the volume of acid required at the equivalence point is twice that of the acid required using phenolphthalein as the indicator.

#### EXPLANATION (E)

Two moles of HCl are required for the complete neutralization of one mole of  $\text{Na}_2\text{CO}_3$ .

### Short Answer Type

1. Determine the oxidation numbers of all atoms in the following.
 

(i) $\text{S}_2\text{O}_3^{2-}$	(ii) $\text{BaO}_2$	(iii) $\text{LiH}$
(iv) $\text{C}_2\text{O}_4^{2-}$	(v) $\text{N}_2\text{H}_4$	

(1978)
2. What is the valency of Mn in the following compounds?
 

(a) $\text{MnO}_2$	(b) $\text{MnSO}_4$	(c) $\text{K}_2\text{MnO}_4$	(d) $\text{K}_3\text{MnF}_6$
--------------------	---------------------	------------------------------	------------------------------

(1978)
3. Give the oxidation number (with sign) of the element in bold letters in the following equations:
 

(i) $8\text{KClO}_3 + 24\text{HCl} \rightarrow 8\text{KCl} + 12\text{H}_2\text{O} + 9\text{Cl}_2 + 6\text{ClO}_2$	
(ii) $3\text{I}_2 + 6\text{NaOH} \rightarrow \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$	

(1979)
4. Calculate the equivalent mass of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{KBrO}_3$  in the following equations.
 

(i) $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$	
(ii) $\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$	

(1979)
5. Find the equivalent mass of  $\text{H}_3\text{PO}_4$  in the reaction
 
$$\text{Ca(OH)}_2 + \text{H}_3\text{PO}_4 \rightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}$$
(1980)

**6.** Complete, if necessary, and balance the following equations.

- (i)  $\text{Cr}_2\text{O}_7^{2-} + \text{HNO}_2 + \text{H}^+ \rightarrow \text{_____} + \text{NO}_3^- + \text{H}_2\text{O}$
- (ii)  $\text{Ag} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{Ag}^+ + \text{_____} + \text{H}_2\text{O}$
- (iii)  $\text{H}_2\text{O}_2 + \text{ClO}_2 + \text{OH}^- \rightarrow \text{_____} + \text{O}_2 + \text{H}_2\text{O}$

(1978)

**7.** Balance the following equations.

- (i)  $\text{MnO}_2 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{MnCl}_2 + \text{Cl}_2$
- (ii)  $\text{CO} + \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} + \text{CO}_2$
- (iii)  $\text{PI}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + \text{HI}$
- (iv)  $\text{Cl}_2 + \text{IO}_3^- + \text{OH}^- \rightarrow \text{IO}_4^- + \text{Cl}^- + \text{H}_2\text{O}$
- (v)  $\text{HNO}_3 + \text{HI} \rightarrow \text{NO} + \text{I}_2 + \text{H}_2\text{O}$
- (vi)  $\text{HgS} + \text{HCl} + \text{HNO}_3 \rightarrow \text{H}_2\text{HgCl}_4 + \text{NO} + \text{S} + \text{H}_2\text{O}$

(1978)

**8.** Complete and balance the equations.

- (i)  $\text{KNO}_3 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \text{ (conc.)} \rightarrow$
- (ii)  $\text{H}_2\text{S} + \text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow$
- (iii)  $\text{KI} + \text{H}_2\text{SO}_4 \text{ (conc.)} \xrightarrow{\text{heat}}$
- (iv)  $\text{Mg}_3\text{N}_2 + \text{H}_2\text{O} \rightarrow$
- (v)  $\text{Al} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow$

(1980)

**9.** Balance the following equations.

- (i)  $\text{Cu}_2\text{O} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$
- (ii)  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}$
- (iii)  $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 + \text{OH}^- \rightarrow \text{CHI}_3 + \text{HCO}_2^- + \text{I}^- + \text{H}_2\text{O}$

(1981)

**10.** Complete and balance the following equations.

- |  |  |
|--|--|
| (i) $\text{Zn} + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NH}_4^+$ | (ii) $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_4\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{Cr}^{3+}$ |
| (iii) $\text{HNO}_3 + \text{HCl} \rightarrow \text{NO} + \text{Cl}_2$      | (iv) $\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{Ce}^{4+}$                              |
| (v) $\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^-$     |  |

(1983)

**11.** Complete and balance the following equations.

- (i)  $\text{Mn}^{2+} + \text{PbO}_2 \rightarrow \text{MnO}_4^- + \text{Pb}^{2+} + \text{H}_2\text{O}$
- (ii)  $\text{S} + \text{OH}^- \rightarrow \text{S}^{2-} + \text{S}_2\text{O}_3^{2-}$
- (iii)  $\text{ClO}_3^- + \text{I}^- + \text{H}_2\text{SO}_4 \rightarrow \text{Cl}^- + \text{HSO}_4^- + \text{I}_2$
- (iv)  $\text{Ag}^+ + \text{AsH}_3 \rightarrow \text{H}_3\text{AsO}_3 + \text{H}^+ + \text{Ag}$

(1986)

## Subjective Type

**1.** Naturally occurring boron contains two isotopes whose relative atomic masses are 10.01 and 11.01. The relative atomic mass of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. (1978)

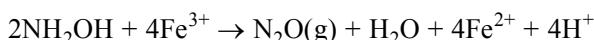
**2.** From 200 mg of  $\text{CO}_2$ ,  $10^{21}$  molecules are removed. How many moles of  $\text{CO}_2$  are left? (1978)

**3.** On dissolving 2.0 g of a metal in sulphuric acid, 4.51 g of the metal sulphate was formed. The specific heat capacity of the metal is  $0.057 \text{ cal g}^{-1}$ . What is the valency of the metal and its exact relative atomic mass? (1978)

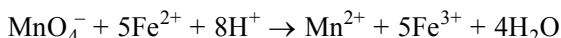
**4.** What are the molarity and molality of a 13% solution (by mass) of sulphuric acid? Its density is  $1.09 \text{ g mL}^{-1}$ . To what volume should 100 mL of this acid be diluted in order to prepare a 1.5 N solution? (1978)

**5.** Two litres of  $\text{NH}_3$  at  $30^\circ\text{C}$  and at 0.20 atm pressure neutralized 134 mL of a sulphuric acid solution. Calculate the normality of the acid. (1978)

6. What mass of AgCl will be precipitated when a solution containing 4.77 g of NaCl is added to a solution containing 5.77 g of AgNO<sub>3</sub>? (1978)
7. A bottle of commercial sulphuric acid (density, 1.787 g/mL) is labelled as 86% by mass. What is the molarity of the acid? What volume of the acid has to be used to make 1 litre of 0.2 M H<sub>2</sub>SO<sub>4</sub>? (1979)
8. 1 g of Mg is burnt in a closed vessel which contains 0.5 g of O<sub>2</sub>.
  - (i) Which reactant is left in excess?
  - (ii) Find the mass of excess reactant?
  - (iii) What volume of 0.5 N H<sub>2</sub>SO<sub>4</sub> will dissolve the residue in the vessel? (1980)
9. 0.5 g of fuming H<sub>2</sub>SO<sub>4</sub> (oleum) is diluted with water. This solution is completely neutralized by 26.7 mL of 0.4 M NaOH. Find the percentage of free SO<sub>2</sub> in the sample of oleum. (1980)
10. A 1.0 g sample of H<sub>2</sub>O<sub>2</sub> solution containing X % H<sub>2</sub>O<sub>2</sub> by mass requires X cm<sup>3</sup> of a KMnO<sub>4</sub> solution for complete oxidation under acidic conditions. Calculate the normality of KMnO<sub>4</sub> solution. (1981)
11. Hydroxylamine reduces iron(III) according to the equation



Iron(II) thus produced is estimated by titration with a standard permanganate solution. The reaction is



A 10 mL sample of hydroxylamine solution was diluted to 1 litre. 50 mL of this diluted solution was boiled with excess of iron(III) solution. The resulting solution required 12 mL of 0.02 M KMnO<sub>4</sub> solution for complete oxidation of iron(II). Calculate the mass of hydroxylamine in one litre of the original solution. (1982)

12. A mixture weighing 4.08 g of BaO and unknown carbonate XCO<sub>3</sub> was heated strongly. The residue weighed 3.64 g. This was dissolved in 100 mL of 1 N HCl. The excess acid required 16 mL of 2.5 N NaOH solution for complete neutralization. Identify the metal M. (1983)
  13. A solution containing  $2.68 \times 10^{-3}$  mol of A<sup>n+</sup> ions requires  $1.61 \times 10^{-3}$  mol of MnO<sub>4</sub><sup>-</sup> for the oxidation of A<sup>n+</sup> to AO<sub>3</sub><sup>-</sup> in acidic medium. What is the value of n? (1984)
  14. Five mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 L. Thirty mL of this acid solution exactly neutralizes 42.9 mL of sodium carbonate solution containing 1 g of Na<sub>2</sub>CO<sub>3</sub> · 10 H<sub>2</sub>O in 100 mL of water. Calculate the mass of SO<sub>4</sub> units in the solution. (1985)
  15. (i) What is the mass of sodium bromate and molarity of solution necessary to prepare 85.5 mL of 0.672 N solution when the half-cell reaction is BrO<sub>3</sub><sup>-</sup> + 6H<sup>+</sup> + 6e<sup>-</sup> → Br<sup>-</sup> + 3H<sub>2</sub>O?  
(ii) What would be the mass as well as molarity if the half-cell reaction is 2BrO<sub>3</sub><sup>-</sup> + 12H<sup>+</sup> + 10e<sup>-</sup> → Br<sub>2</sub> + 6H<sub>2</sub>O? (1987)
  16. A sample of hydrazine sulphate (N<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>) was dissolved in 100 mL of water. 10 mL of this solution was made to react with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of M/50 potassium permanganate solution. Estimate the mass of hydrazine sulphate in one litre of the solution.
- Reactions:  $4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{Fe}^{2+} + 4\text{H}^+$
- $$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \quad (1988)$$
17. A mixture of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (oxalic acid) and NaHC<sub>2</sub>O<sub>4</sub> weighing 2.02 g was dissolved in water and the solution made up to one litre. Ten millilitres of the solution required 3.0 mL of 0.1 N sodium hydroxide solution for complete neutralization. In another experiment 10.0 mL of the same solution, in hot dilute sulphuric acid medium, required 4.0 mL of 0.1 N KMnO<sub>4</sub> solution for complete reaction. Calculate the masses of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and NaHC<sub>2</sub>O<sub>4</sub> in the mixture. (1990)
  18. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600 °C until the mass of the residue was constant. If the loss in mass is 28.0 per cent, find the masses of lead nitrate and sodium nitrate in the mixture. (1990)

19. A solution of 0.2 g of a compound containing  $\text{Cu}^{2+}$  and  $\text{C}_2\text{O}_4^{2-}$  ions on titration with 0.02 M  $\text{KMnO}_4$  in presence of  $\text{H}_2\text{SO}_4$  consumes 22.6 mL of the oxidant. The resultant solution is neutralized with  $\text{Na}_2\text{CO}_3$ , acidified with dilute acetic acid and treated with excess KI. The liberated iodine requires 11.3 mL of 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution for complete reduction. Find out the mole ratio of  $\text{Cu}^{2+}$  to  $\text{C}_2\text{O}_4^{2-}$  in the compound. Write down the balanced redox reactions involved in the above titration. (1991)
20. A 1.0 g sample of  $\text{Fe}_2\text{O}_3$  solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration. (1991)
21. One gram of commercial  $\text{AgNO}_3$  is dissolved in 50 mL of water. It is treated with 50 mL of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with M/10  $\text{KIO}_3$  solution in presence of 6 M HCl till all  $\text{I}^-$  ions are converted into  $\text{ICl}$ . It requires 50 mL of M/10  $\text{KIO}_3$  solution. Twenty milliliters of the same stock solution of KI requires 30 mL of M/10  $\text{KIO}_3$  under similar conditions. Calculate the percentage of  $\text{AgNO}_3$  in the sample. (Reaction:  $\text{KIO}_3 + 2\text{KI} + 6\text{HCl} \rightarrow 3\text{ICl} + 3\text{KCl} + 3\text{H}_2\text{O}$ ) (1992)
22. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is heated till the evolution of  $\text{CO}_2$  ceases. The volume of  $\text{CO}_2$  at 750 mmHg pressure and at 298 K is measured to be 123.9 mL. A 1.5 g of the sample requires 150 mL of M/10 HCl for complete neutralization. Calculate the percentage composition of the components of the mixture. (1992)
23. Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25.0 mL of 0.10 M chromic sulphate solution, precipitation of lead sulphate takes place. What amount of lead sulphate is formed? Also, calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. (1993)
24. A  $20.0 \text{ cm}^3$  mixture of CO,  $\text{CH}_4$  and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be  $13.0 \text{ cm}^3$ . A further contraction of  $14.0 \text{ cm}^3$  occurs when the residual gas is treated with KOH solution. Find out the composition of gaseous mixture in terms of volume percentage. (1995)
25.  $8.0575 \times 10^{-2} \text{ kg}$  of Glauber's salt is dissolved in water to obtain  $1 \text{ dm}^3$  of a solution of density  $1077.2 \text{ kg m}^{-3}$ . Calculate the molarity, molality and mole fraction of  $\text{Na}_2\text{SO}_4$  in the solution. (1994)
26. A sample of hard water contains 96 ppm of  $\text{SO}_4^{2-}$  and 183 ppm of  $\text{HCO}_3^-$ , with  $\text{Ca}^{2+}$  as the only cation. How many moles of CaO will be required to remove  $\text{HCO}_3^-$  from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual  $\text{Ca}^{2+}$  ions? (Assume  $\text{CaCO}_3$  to be completely insoluble in water.) If the  $\text{Ca}^{2+}$  ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH? (One ppm means one part of the substance in one million part of water, mass/mass.) (1997)
27. One litre of a mixture of  $\text{O}_2$  and  $\text{O}_3$  at STP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the mass per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assume that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? (1997)
28. An aqueous solution containing 0.10 g  $\text{KIO}_3$  (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated  $\text{I}_2$  consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution. (1998)
29. A 3.00 g sample containing  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and an inert impure substance, is treated with excess KI solution in presence of dilute  $\text{H}_2\text{SO}_4$ . The entire iron is converted into  $\text{Fe}^{2+}$  along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution requires 11.0 mL of 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution to reduce the iodine present. A 50 mL of the diluted solution, after complete extraction of the iodine requires 12.80 mL of 0.25 M  $\text{KMnO}_4$  solution in dilute  $\text{H}_2\text{SO}_4$  medium for the oxidation of  $\text{Fe}^{2+}$ . Calculate the percentages of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the original sample. (1996)

30. A  $5.0\text{ cm}^3$  solution of  $\text{H}_2\text{O}_2$  liberates  $0.508\text{ g}$  of iodine from an acidified KI solution. Calculate the strength of  $\text{H}_2\text{O}_2$  solution in terms of volume strength at STP. (1995)
31. How many millilitres of  $0.5\text{ M H}_2\text{SO}_4$  are needed to dissolve  $0.5\text{ g}$  of copper(II) carbonate? (1999)
32. A plant virus is found to consist of uniform cylindrical particles of  $150\text{ \AA}$  in diameter and  $5000\text{ \AA}$  long. The specific volume of the virus is  $0.75\text{ cm}^3/\text{g}$ . If the virus is considered to be a single particle, find its molar mass. (1999)
33. Hydrogen peroxide solution ( $20\text{ mL}$ ) reacts quantitatively with a solution of  $\text{KMnO}_4$  ( $20\text{ mL}$ ) acidified with dilute  $\text{H}_2\text{SO}_4$ . The same volume of the  $\text{KMnO}_4$  solution is just decolourised by  $10\text{ mL}$  of  $\text{MnSO}_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $\text{MnO}_2$ . The brown precipitate is dissolved in  $10\text{ mL}$  of  $0.2\text{ M}$  sodium oxalate under boiling condition in the presence of dilute  $\text{H}_2\text{SO}_4$ . Write the balanced equations involved in the reactions and calculate the molarity of  $\text{H}_2\text{O}_2$ . (2001)
34. What is molarity of water at  $4\text{ }^\circ\text{C}$ ? (2003)

## ANSWERS

### **Straight Objective Type**

- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (c)  | 3. (c)  | 4. (a)  | 5. (c)  | 6. (a)  |
| 7. (a)  | 8. (c)  | 9. (d)  | 10. (c) | 11. (d) | 12. (d) |
| 13. (c) | 14. (a) | 15. (b) | 16. (c) | 17. (a) | 18. (b) |
| 19. (a) | 20. (d) | 21. (a) | 22. (a) | 23. (d) | 24. (a) |
| 25. (d) | 26. (a) | 27. (c) | 28. (b) | 29. (d) | 30. (a) |
| 31. (d) | 32. (b) | 33. (d) | 34. (b) | 35. (d) | 36. (b) |

### **Multiple Correct-Choice Type**

1. (a), (c)    2. (a), (d)    3. (a), (b), (d)

### **Fill-in-the-Blanks Type**

1.  $^{12}\text{C}$     2. -3    3.  $4.134\text{ g}$     4. +7/3    5.  $0.4\text{ mol kg}^{-1}$

### **Integer Answer Type**

- |      |      |      |      |      |      |
|------|------|------|------|------|------|
| 1. 6 | 2. 3 | 3. 2 | 4. 7 | 5. 5 | 6. 5 |
| 7. 6 | 8. 8 | 9. 4 |      |      |      |

### **True/False Type**

1. False    2. False    3. False    4. False

### **Reasoning Type**

1. (b)

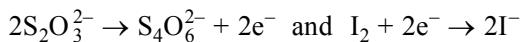
### **Short Answer Type**

- |                      |                    |
|----------------------|--------------------|
| 1. (i) S + 2; O - 2, | (ii) Ba +2; O - 1, |
| (iii) Li + 1; H - 1  | (iv) N - 1; H + 1  |
| 2. (i) + 4,          | (ii) + 2,          |
| (iii) + 6,           | (iv) + 3           |

3. (i) Cl in  $\text{KClO}_3$  + 5; Cl in  $\text{Cl}_2$  0; Cl in  $\text{ClO}_2$  + 4

(ii) I in  $\text{I}_2$  0; I in  $\text{NaIO}_3$  + 5; I in  $\text{NaI}$  - 1

4. (i) The basic reactions are

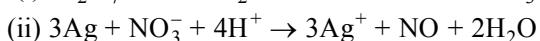
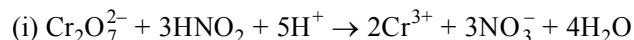


Since  $2\text{e}^-$  are involved for two  $\text{S}_2\text{O}_3^{2-}$  species, the equivalent mass of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  will be equal to its molar mass.

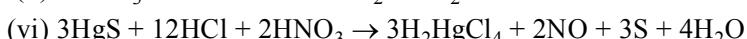
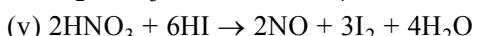
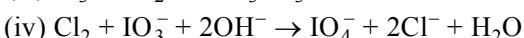
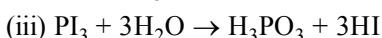
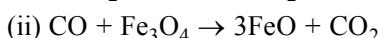
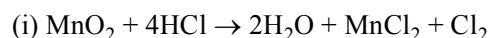
(ii) Since six electrons are involved, the equivalent mass of  $\text{KBrO}_3$  will be its molar mass divided by six.

5. Since two hydrogen ions are involved in the neutralization reaction, the equivalent mass of  $\text{H}_3\text{PO}_4$  is equal to its molar mass divided by two.

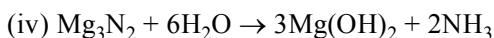
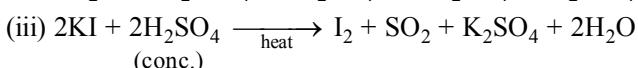
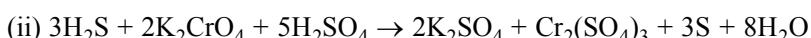
6. The balanced equations are



7. The balanced equations are

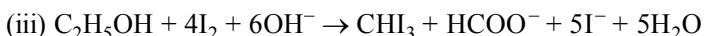
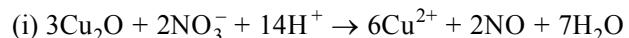


8. The balanced equations are

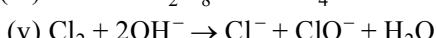
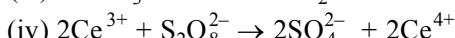
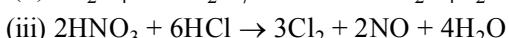
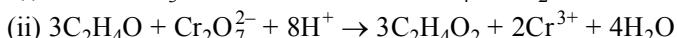


(v) A thin layer of  $\text{Al}_2\text{O}_3$  is deposited on the surface of aluminium.

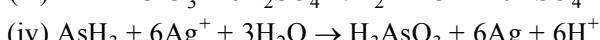
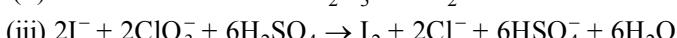
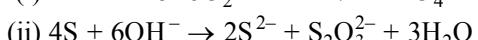
9. The balanced equations are



10. (i)  $4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$



11. (i)  $2\text{Mn}^{2+} + 5\text{PbO}_2 + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + 5\text{Pb}^{2+} + 2\text{H}_2\text{O}$



## Subjective Type

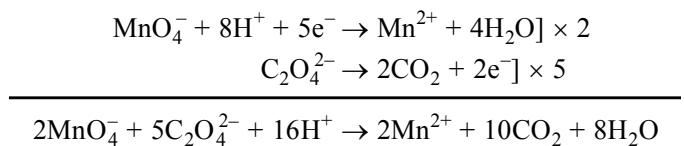
1. 20% of relative atomic mass 10.01 and 80% of relative atomic mass 11.01
2.  $2.885 \times 10^{-3}$  mol
3. Valency = 3; relative atomic mass = 114.57
4. 192.8 mL
5. 0.12 N
6. 4.87 g
7. 12.8 mL
8. Mg; 0.25 g; 125 mL
9. 8.78%
10. 0.588 N
11. 39.6 g
12. Ca
13. 2
14. 6.528 g
15. 1.446 g; 1.735 g
16. 6.5 g
17. 0.9 g; 1.12 g
18. 3.32 g; 1.68 g
19. 1/2
20. 6
21. 85%
22. 26.5% Na<sub>2</sub>CO<sub>3</sub>; 42.0% NaHCO<sub>3</sub>; 31.5% Na<sub>2</sub>SO<sub>4</sub>
23.  $7.5 \times 10^{-3}$  of PbSO<sub>4</sub>; 0.0536 M of Pb<sup>2+</sup>; 0.0714 M of Cr<sup>3+</sup>; 0.3214 M of NO<sub>3</sub><sup>-</sup>
24. 50% of CO; 20% of CH<sub>4</sub>; 30% He
25. 0.25 mol dm<sup>-3</sup>; 0.24 mol kg<sup>-1</sup>; 0.0043 of Na<sub>2</sub>SO<sub>4</sub>
26. 10<sup>-3</sup> mol L<sup>-1</sup> of Ca<sup>2+</sup>, pH = 2.7
27. 6.575 mass % of O<sub>3</sub>;  $1.205 \times 10^{21}$  of photons
28. 0.0623 mol L<sup>-1</sup>
29. 34.8% of Fe<sub>3</sub>O<sub>4</sub>; 49.3% of Fe<sub>2</sub>O<sub>3</sub>
30. 4.48
31. 8.1 mL
32.  $7.1 \times 10^7$  g mol<sup>-1</sup>
33. 0.1 mol L<sup>-1</sup>
34. 55.56 mol L<sup>-1</sup>

## HINTS AND SOLUTIONS

### Straight Objective Type

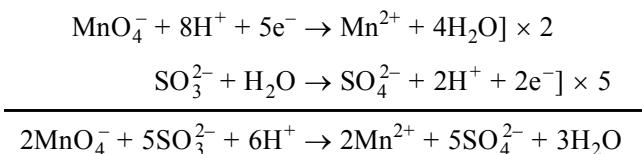
9. The reaction is  $3\text{BaCl}_2 + 2\text{Na}_3\text{PO}_4 \rightarrow \text{Ba}_3(\text{PO}_4)_2 + 6\text{NaCl}$ . Hence  
 $3 \text{ mol BaCl}_2 \equiv 2 \text{ mol Na}_3\text{PO}_4$  and thus  $0.5 \text{ mol BaCl}_2 \equiv (2/3) (0.5 \text{ mol Na}_3\text{PO}_4) \equiv 0.33 \text{ mol Na}_3\text{PO}_4$   
 $2 \text{ mol Na}_3\text{PO}_4 \equiv 3 \text{ mol BaCl}_2$  and thus  $0.2 \text{ mol Na}_3\text{PO}_4 \equiv (3/2) (0.2 \text{ mol BaCl}_2) \equiv 0.1 \text{ mol BaCl}_2$   
 Obviously, Na<sub>3</sub>PO<sub>4</sub> is the limiting reagent. Hence  
 $2 \text{ mol Na}_3\text{PO}_4 \equiv 1 \text{ mol Ba}_3(\text{PO}_4)_2$  and thus  $0.2 \text{ mol Na}_3\text{PO}_4 \equiv 0.1 \text{ mol Ba}_3(\text{PO}_4)_2$
10.  $2\overset{-4}{\text{N}} \text{ in } \text{N}_2\text{H}_4 \xrightarrow{-10e^-} 2\overset{+6}{\text{N}}$  in Y. Oxidation state of N in Y is +3
11. F<sup>-</sup> is most stable species amongst Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>. It does not reduce none of the three species H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.
12. Sodium in liquid ammonia is strongly reducing agent due to the presence of solvated electrons.
13. We have  $x + 2(+1) + (-2) = 0$ . This gives  $x = 0$ .
14. The oxidation state of iron in [Fe(H<sub>2</sub>O)<sub>5</sub>(NO)]<sup>2+</sup> is +1.
15. The oxidation states of Mn<sup>2+</sup> are Mn<sup>+2</sup>; Mn<sup>+3</sup>; Mn<sup>+4</sup>; MnO<sub>2</sub><sup>+7</sup>; MnO<sub>4</sub><sup>-</sup>; MnO<sub>4</sub><sup>2-</sup>  
 When MnSO<sub>4</sub> is changed to MnO<sub>2</sub>, the change in oxidation state is +2. Hence, equivalent mass of MnSO<sub>4</sub> will be half of its molar mass.

16. For the species  $\text{H}_2\text{PO}_2^-$ , we have  $2(+1) + x + 2(-2) = -1 \Rightarrow x = +1$
17. The reactions b to d have tendencies to proceed from right side to left side. The reaction a proceeds in the forward direction.
18. The reaction is  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
The oxidation states of most electronegative atom in the products (which is oxygen) are  $-2$  and  $-1$ , respectively.
19. The balanced equation can be obtained as follows.



21. The reaction is
- $$3\text{MnO}_4^- + 5\text{Fe}(\text{C}_2\text{O}_4) + 24\text{H}^+ \rightarrow 3\text{Mn}^{2+} + 5\text{Fe}^{3+} + 10\text{CO}_2 + 12\text{H}_2\text{O}$$
- $$\begin{aligned} 3 \text{ mol MnO}_4^- &\equiv 5 \text{ mol Fe}(\text{C}_2\text{O}_4) \\ \frac{3}{5} \text{ mol MnO}_4^- &\equiv 1 \text{ mol Fe}(\text{C}_2\text{O}_4) \end{aligned}$$

22. The reaction of  $\text{MnO}_4^-$  and  $\text{SO}_3^{2-}$  in acidic medium is derived as follows:



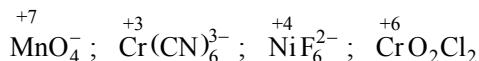
Hence,  $2 \text{ mol MnO}_4^- \equiv 5 \text{ mol SO}_3^{2-}$ ,  
i.e.,  $\frac{2}{5} \text{ mol MnO}_4^- \equiv 1 \text{ mol SO}_3^{2-}$

23. Phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is a dibasic acid,  $\text{HPO}(\text{OH})_2$ . Hence,  $0.3 \text{ M H}_3\text{PO}_3$  will be  $2 \times 0.3 \text{ N acid}$ .
24. The oxidation number of sulphur in elemental sulphur is zero.

The oxidation numbers in  $\text{S}_2\text{F}_2$  are  $\begin{array}{cccc} -1 & +1 & +1 & -1 \\ \text{F} & - & \text{S} & - \text{F} \end{array}$

The oxidation numbers in  $\text{H}_2\text{S}$  are  $\begin{array}{ccc} +1 & -2 & +1 \\ \text{H} & - & \text{S} & - \text{H} \end{array}$

25. The oxidation states of the central atom in the given species are

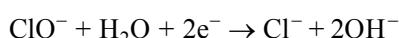


26. Normality of oxalic acid =  $\frac{(6.3 \text{ g}/63 \text{ g eq}^{-1})}{(0.25 \text{ L})} = 0.4 \text{ N}$

Volume of NaOH solution required to neutralise 10 mL of oxalic acid solution is

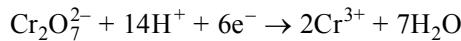
$$V = \frac{(10 \text{ mL})(0.4 \text{ N})}{(0.1 \text{ N})} = 40 \text{ mL}$$

27. The oxidation number of Cl in  $\text{ClO}^-$ ,  $\text{ClO}_3^-$  and  $\text{Cl}^-$  are  $+1$ ,  $+5$  and  $-1$ , respectively. In the given reaction, Cl in  $\text{ClO}^-$  undergoes oxidation as well as reduction reactions as given in the following.



Hence, the given reaction is an example of disproportionation reaction.

28. The reaction undergone by  $\text{Cr}_2\text{O}_7^{2-}$  ions is



$$29. n = \frac{N}{N_A} = \frac{m/m_e}{N_A} = \frac{m}{m_e N_A} = \frac{(1\text{ kg})}{(9.108 \times 10^{-31}\text{ kg})(6.023 \times 10^{23}\text{ mol}^{-1})} = \frac{10^8}{9.108 \times 6.023} \text{ mol}$$

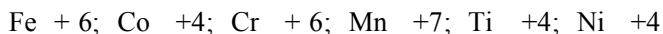
30. We have

$$N(\text{C}) = \frac{m}{M} N_A = \frac{24}{12\text{ g mol}^{-1}} (6.023 \times 10^{23}\text{ mol}^{-1}) = 12.023 \times 10^{23}$$

$$N(\text{Na}) = N(\text{Ag}) = 6.023 \times 10^{23}$$

$$N(\text{S}) = 9.035 \times 10^{23}$$

31. The highest oxidation states of the given metals are as follows:



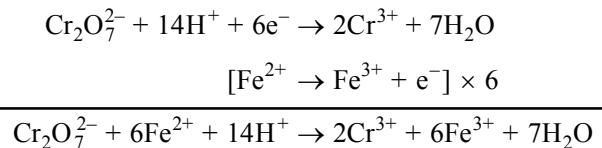
In the given species the oxidation states of metals are:



Hence, the species  $\text{CrO}_2\text{Cl}_2$  and  $\text{MnO}_4^-$  have metals in the highest oxidation states.

32. Mn in  $\text{MnO}_4^-$  exists in its maximum oxidation state of VII. It cannot be oxidised further.

33. The involved reactions are



For 1 mol of  $\text{K}_2\text{Cr}_2\text{O}_7$ , 6 mol of Mohr's salt is oxidised.

34. The relative atomic mass of an element is the weighted average of relative atomic masses of its constituent isotopes. Hence

$$A_r = \frac{5 \times 54 + 90 \times 56 + 5 \times 57}{100} = 55.95$$

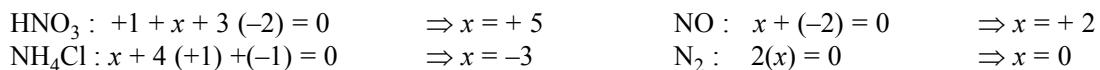
35. Haematite is  $\text{Fe}_2\text{O}_3$  and magnetite is  $\text{Fe}_3\text{O}_4$ .

The oxidation state of Fe in  $\text{Fe}_2\text{O}_3$  is +III.

The magnetite ore is  $\text{FeO} \cdot \text{Fe}_2\text{O}_3 (\equiv \text{Fe}_3\text{O}_4)$ .

The oxidation states of Fe in this ore are +II (in  $\text{FeO}$ ) and +III (in  $\text{Fe}_2\text{O}_3$ ).

36. The oxidation states of nitrogen in the given compounds are as follows.

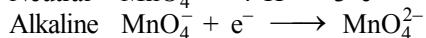
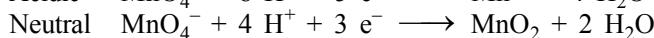
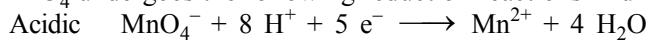


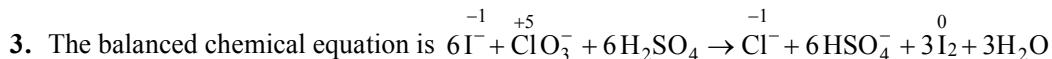
Thus, the decreasing oxidation numbers of nitrogen is  $\text{HNO}_3$ , NO,  $\text{N}_2$  and  $\text{NH}_4\text{Cl}$ .

Therefore, the choice (b) is correct.

### Multiple Correct-Choice Type

2.  $\text{MnO}_4^-$  undergoes the following reduction reactions in different media.





The species undergoing change in oxidation number are:

Iodine from  $-1$  to  $0$

Chlorine from  $+5$  to  $-1$

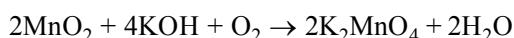
Hence, iodine is oxidised and chlorine is reduced.

### Fill-in-the-Blanks Type

3. Mass of  $1 \times 10^{22}$  molecules of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  =  $\frac{249.0 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \times 10^{22} = 4.134 \text{ g}$

### Integer Answer Type

1. The reaction is



The oxidation number of Mn in  $\text{K}_2\text{MnO}_4$  is  $+6$  (since  $2(+1) + x + 4(-2) = 0$  gives  $x = +6$ ). Therefore, the correct answer is **6**.

2. The average titre value is obtained by adding the given values divided by the number of values. The final answer in adding will include the uncertainty equal to the maximum uncertainty present in the given titre values. Division by 3 involves exact quantity. Thus, the final average value will include as many significant digits as present in a value having minimum significant digits which is equal to three (in the values  $25.2 \text{ mL}$  and  $25.0 \text{ mL}$ ).

Hence, the number of significant digits in the average titre value will be equal to **three**.

3. F has only one oxidation state of  $-1$

Na has only one oxidation state of  $+1$

Hence, the correct answer is **two**.

4. Molar volume of Ag,  $V_m = \frac{M}{\rho} = \frac{108 \text{ g mol}^{-1}}{10.5 \text{ g cm}^{-3}} = 10.286 \text{ cm}^3 \text{ mol}^{-1}$

$$\text{Volume of one atom of silver, } v = \frac{V_m}{N_A} = \frac{10.286 \text{ cm}^3 \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.708 \times 10^{-23} \text{ cm}^3$$

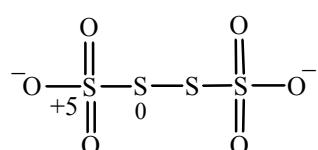
$$\text{Radius of one atom of silver, } r = \left( \frac{3v}{4\pi} \right)^{1/3} = \left( \frac{3 \times 1.708 \times 10^{-23} \text{ cm}^3}{4 \times 3.14} \right)^{1/3} = 1.60 \times 10^{-8} \text{ cm}$$

Number of Ag atoms having surface area of  $10^{-12} \text{ m}^2$  ( $= 10^{-8} \text{ cm}^2$ ) is

$$n = \frac{A}{\pi r^2} = \frac{10^{-8} \text{ cm}^2}{(3.14)(1.60 \times 10^{-8} \text{ cm})^2} = 1.244 \times 10^7$$

Hence, the value of  $x$  is **seven**.

5. The structure of  $\text{S}_4\text{O}_6^{2-}$  is



The oxidation numbers of two types of S are  $+5$  and  $0$ . Thus, their difference is **five**. Hence, the correct answer is **5**.

6. The reaction is  $3\text{Br}_2 + 3\text{Na}_2\text{CO}_3 \rightarrow 5\text{NaBr} + \text{NaBrO}_3 + \text{CO}_2$

Hence, the stoichiometric number of NaBr is 5.

7. Amount of  $\text{Cl}^-$  which can be precipitated as  $\text{AgCl}$  in the given volume of the complex is

$$\begin{aligned} n &= 2 (V M) = 2(30 \times 10^{-3} \text{ L}) (0.01 \text{ mol L}^{-1}) \\ &= 60 \times 10^{-5} \text{ mol} \end{aligned}$$

Volume of  $\text{AgNO}_3$  required for the precipitation is

$$\begin{aligned} V &= \frac{n}{M} = \frac{60 \times 10^{-5} \text{ mol}}{0.1 \text{ mol L}^{-1}} = 60 \times 10^{-4} \text{ L} \\ &= 6 \text{ mL} \end{aligned}$$

8. Amount of HCl required to prepare 200 mL (= 0.2 L) solution of 0.4 M HCl is

$$n = MV = (0.4 \text{ mol L}^{-1}) (0.2 \text{ L}) = 0.08 \text{ mol}$$

Mass of HCl required to prepare the said solution is

$$m = nM_m = (0.08 \text{ mol}) 36.5 \text{ g mol}^{-1} = 2.92 \text{ g.}$$

Mass of HCl solution containing 2.92 g of HCl is

$$m_1 = \left( \frac{\text{mass of solution}}{\text{mass of HCl}} \right) (m) = \left( \frac{100 \text{ g}}{29.2 \text{ g}} \right) (2.92 \text{ g}) = 10 \text{ g}$$

$$\text{Volume of HCl solution required to prepare the given HCl solution is } V = \frac{m_1}{\rho} = \frac{10 \text{ g}}{1.25 \text{ g mL}^{-1}} = 8 \text{ mL}$$

Therefore, the correct answer is 8.

9. Both the numbers  $6.023 \times 10^{23}$  and  $1.380 \times 10^{-23}$  have four significant digits, the universal gas constant  $R(=N_A k)$  will have four significant digits.

## Subjective Type

1. Let  $x$  be the percentage of isotope of relative atomic mass 10.01. We will have

$$10.81 = \frac{(10.01)x + (11.01)(100-x)}{100}$$

Solving for  $x$ , we get  $x = 20$ . Hence, 20% of isotopes of relative atomic mass 10.01 and 80% of isotopes of relative atomic mass 11.01 are present in naturally occurring boron.

2. Amount of  $\text{CO}_2$  in 200 mg is

$$n = \frac{m}{M} = \frac{200 \times 10^{-3} \text{ g}}{44 \text{ g mol}^{-1}} = 4.5455 \times 10^{-3} \text{ mol}$$

Molecules of  $\text{CO}_2$  are

$$\begin{aligned} N &= nN_A = (4.5455 \times 10^{-3} \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= 2.7373 \times 10^{21} \end{aligned}$$

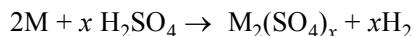
After removing  $10^{21}$  molecules, the amount of  $\text{CO}_2$  left is

$$n = \frac{(2.7373 - 1) \times 10^{21}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 2.885 \times 10^{-3} \text{ mol}$$

3. Since the product of relative atomic mass and specific heat capacity is approximate  $6.4 \text{ cal g}^{-1}$ , we have

$$\text{Approximate relative atomic mass of element} = \frac{6.4 \text{ cal g}^{-1}}{0.057 \text{ cal g}^{-1}} = 112.28$$

Let  $x$  be the valency of M in the metal sulphate. Its reaction with  $\text{H}_2\text{SO}_4$  may be written as



We will have

$$\frac{2M_r + x(96)}{2M_r} = \frac{4.51}{2} \quad \text{i.e.} \quad \frac{2 \times 112.28 + 96x}{2 \times 112.28} = \frac{4.51}{2}$$

Solving for  $x$ , we get

$$x = \frac{4.51 \times 2 \times 112.28 - 2 \times 2 \times 112.28}{2 \times 96} = 2.94$$

Hence, the correct valency of M is 3 and its correct atomic mass is

$$M_r = \left( \frac{3}{2.94} \right) (112.28) = 114.57$$

4. Since the density of solution is  $1.09 \text{ g mL}^{-1}$  ( $= 1090 \text{ g L}^{-1}$ ), it implies that the mass of 1 L of sulphuric acid solution is 1090 g.

Since the mass percent of sulphuric acid is 13%, the mass of sulphuric acid in 1 L of solution is

$$m_2 = \left( \frac{3}{100} \right) (1090 \text{ g}) = 141.7 \text{ g}$$

Amount of sulphuric acid is

$$n_2 = \frac{m_2}{M_2} = \frac{141.7 \text{ g}}{98 \text{ g mol}^{-1}} = 1.446 \text{ mol}$$

Hence, molarity of sulphuric acid solution is

$$M = \frac{n_2}{V} = \frac{1.446 \text{ mol}}{1 \text{ L}} = 1.446 \text{ mol L}^{-1}$$

Mass of water in 1 L solution is

$$m_1 = 1090 \text{ g} - 141.7 \text{ g} = 948.3 \text{ g}$$

Hence, molality of sulphuric acid solution is

$$m = \frac{n_2}{m_1} = \frac{1.446 \text{ mol}}{948.3 \times 10^{-3} \text{ kg}} = 1.525 \text{ mol kg}^{-1}$$

To prepare 1.5 N  $\text{H}_2\text{SO}_4$ , we will have

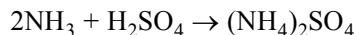
$$(100 \text{ mL}) (2 \times 1.446 \text{ N}) = V(1.5 \text{ N})$$

$$\text{or} \quad V = \frac{2 \times 1.446}{1.5} \times 100 \text{ mL} = 192.8 \text{ mL}$$

5. Amount of  $\text{NH}_3$  is

$$n = \frac{pV}{RT} = \frac{(0.20 \text{ atm})(2 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})} = 0.0161 \text{ mol}$$

The reaction between  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  is



Amount of  $\text{H}_2\text{SO}_4$  to neutralize 0.0161 mol of  $\text{NH}_3$  will be

$$n_2 = \frac{0.0161 \text{ mol}}{2} = 0.00805 \text{ mol}$$

Molarity of  $\text{H}_2\text{SO}_4$  is

$$M = \frac{n_2}{V} = \frac{0.00805 \text{ mol}}{134 \times 10^{-3} \text{ L}} = 0.06 \text{ M}$$

Normality of  $\text{H}_2\text{SO}_4$  is

$$N = (2 \text{ eq mol}^{-1}) (0.06 \text{ mol L}^{-1}) = 0.12 \text{ N}$$

6. Amount of  $\text{NaCl} = \frac{4.77 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.0815 \text{ mol}$

$$\text{Amount of } \text{AgNO}_3 = \frac{5.77 \text{ g}}{169.9 \text{ g mol}^{-1}} = 0.0340 \text{ mol}$$

Since the amount of  $\text{AgNO}_3$  is less than that of  $\text{NaCl}$ , the whole of  $\text{AgNO}_3$  will be practically precipitated as  $\text{AgCl}$ . Hence

$$\text{Mass of } \text{AgCl} \text{ precipitated} = (0.0340 \text{ mol}) (143.4 \text{ g mol}^{-1}) = 4.87 \text{ g}$$

7. Mass of 1000 mL of the given acid solution = 1787 g

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in the solution} = (1787 \text{ g}) (0.86) = 1536.8 \text{ g}$$

$$\text{Amount of } \text{H}_2\text{SO}_4 = \frac{1536.8 \text{ g}}{98 \text{ g mol}^{-1}} = 15.68 \text{ mol}$$

$$\text{Molarity of } \text{H}_2\text{SO}_4 \text{ solution} = \frac{15.68 \text{ mol}}{1 \text{ L}} = 15.68 \text{ M}$$

To make 1 L of 0.2 M  $\text{H}_2\text{SO}_4$ , we have

$$V(15.68 \text{ M}) = (1 \text{ L}) (0.2 \text{ M})$$

$$\text{This gives } V = \frac{(1 \text{ L})(0.2 \text{ M})}{(15.68 \text{ M})} = 0.0128 \text{ L} = 12.8 \text{ mL}$$

8. The burning of Mg is represented as  $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$

$$\text{Initial amount of Mg} = \frac{1}{24 \text{ g mol}^{-1}} = 0.04167 \text{ mol}$$

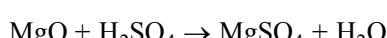
$$\text{Initial amount of O}_2 = \frac{0.5 \text{ g}}{32 \text{ g mol}^{-1}} = 0.015625 \text{ mol}$$

Since 2 mol of Mg is burnt in 1 mol of  $\text{O}_2$ , it follows that Mg will be left in excess.

$$\text{Amount of MgO formed} = 2 \times 0.015625 \text{ mol} = 0.03125 \text{ mol}$$

$$\text{Mass of Mg left in excess} = (0.04167 \text{ mol} - 0.03125 \text{ mol}) (24 \text{ g mol}^{-1}) = 0.25 \text{ g}$$

The dissolution of  $\text{MgO}$  in  $\text{H}_2\text{SO}_4$  is represented as

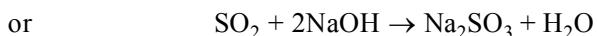
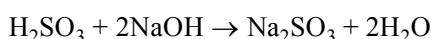
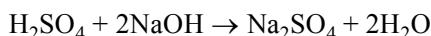


To dissolve 0.03125 mol of MgO, the same amount of H<sub>2</sub>SO<sub>4</sub> will be required. The corresponding volume of H<sub>2</sub>SO<sub>4</sub> (which is 0.5 N, i.e. 0.25 M) may be computed from the expression

$$V(0.25 \text{ M}) = 0.03125 \text{ mol}$$

which gives  $V = 0.125 \text{ L} = 125 \text{ mL}$

**9.** The neutralization reactions are



$$\text{Amount of NaOH consumed} = (26.7 \times 10^{-3} \text{ L}) (0.4 \text{ mol L}^{-1}) = 0.01068 \text{ mol}$$

$$\text{Combined amount of H}_2\text{SO}_4 \text{ and SO}_2 = \frac{0.01068 \text{ mol}}{2} = 0.00534 \text{ mol}$$

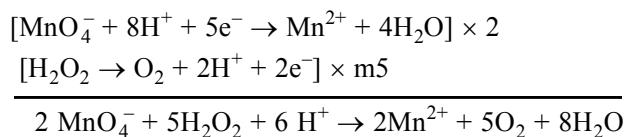
Let  $x$  be the mass of SO<sub>2</sub> in 0.5 g of oleum. We will have

$$\frac{x}{64 \text{ g mol}^{-1}} + \frac{0.5 \text{ g} - x}{98 \text{ g mol}^{-1}} = 0.00534 \text{ mol}$$

Solving for  $x$ , we get  $x = 0.044 \text{ g}$

$$\text{Percentage of SO}_2 = (0.044/0.5) \times 100 = 8.78$$

**10.** The equations involved are



From this equation, we find that

$$\text{Equivalent mass of H}_2\text{O}_2, M_{\text{eq}} = \frac{\text{Molar mass of H}_2\text{O}_2}{2 \text{ eq mol}^{-1}} = \frac{34 \text{ g mol}^{-1}}{2 \text{ eq mol}^{-1}} = 17 \text{ g eq}^{-1}$$

$$\text{Mass of H}_2\text{O}_2 \text{ in the given } 1.0 \text{ g sample, } m_{\text{eq}} = \frac{X}{100} \times 1.0 \text{ g}$$

Amount (in equivalents) of H<sub>2</sub>O<sub>2</sub> in the given 1.0 g sample is

$$n_{\text{eq}} = \frac{m}{M_{\text{eq}}} = \frac{(X/100) \text{ g}}{17 \text{ g eq}^{-1}} = \frac{X}{17 \times 100} \text{ eq} \quad (1)$$

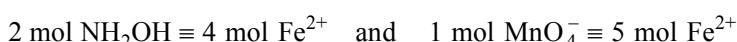
If  $N_{\text{KMnO}_4}$  is the normality of KMnO<sub>4</sub>, the amount (in equivalents) of KMnO<sub>4</sub> consumed is

$$n'_{\text{eq}} = V_{\text{KMnO}_4} N_{\text{KMnO}_4} = \left( \frac{X}{1000} \text{ L} \right) N_{\text{KMnO}_4} \quad (2)$$

Equating Eqs (1) and (2), we get

$$\left( \frac{X}{1000} \text{ L} \right) N_{\text{KMnO}_4} = \frac{X}{17 \times 100} \text{ eq} \quad \text{or} \quad N_{\text{KMnO}_4} = \frac{10}{17} \text{ eq L}^{-1} = 0.588 \text{ eq L}^{-1}$$

**11.** From the given chemical equations, we find that



Amount of  $\text{MnO}_4^-$  consumed in the oxidation of iron(II)

$$= VM = (12 \text{ mL}) (0.02 \text{ M}) = \left(\frac{12}{1000} \text{ L}\right) (0.02 \text{ mol L}^{-1}) = \frac{12 \times 0.02}{1000} \text{ mol}$$

Since 1 mol  $\text{MnO}_4^- \equiv 5 \text{ mol Fe}^{2+}$ , we have

$$\text{Amount of Fe}^{2+} \text{ formed by the reduction of Fe}^{3+} \text{ by NH}_2\text{OH} = (5) \left(\frac{12 \times 0.02}{1000}\right) \text{ mol}$$

Now since 2 mol  $\text{NH}_2\text{OH} \equiv 4 \text{ mol Fe}^{2+}$ , we have

$$\text{Amount of NH}_2\text{OH present in 50 mL of diluted solution} = \left(\frac{2}{4}\right) (5) \left(\frac{12 \times 0.02}{1000}\right) \text{ mol}$$

$$\text{Amount of NH}_2\text{OH present in 1 L of diluted solution} = \left(\frac{1000}{50}\right) \left(\frac{2}{4}\right) (5) \left(\frac{12 \times 0.02}{1000}\right) \text{ mol}$$

Amount of  $\text{NH}_2\text{OH}$  present in 1 L of undiluted solution

$$= \left(\frac{1000}{10}\right) \left(\frac{1000}{50}\right) \left(\frac{2}{4}\right) (5) \left(\frac{12 \times 0.02}{1000}\right) \text{ mol} = 1.2 \text{ mol}$$

Mass of  $\text{NH}_2\text{OH}$  present in 1 L of undiluted solution =  $(1.2 \text{ mol}) (33 \text{ g mol}^{-1}) = 39.6 \text{ g}$ .

12. On heating, we have  $\text{XCO}_3 \rightarrow \text{XO} + \text{CO}_2$

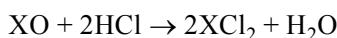
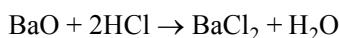
The loss of mass ( $= 4.08 \text{ g} - 3.64 \text{ g} = 0.44 \text{ g}$ ) is due to the removal of  $\text{CO}_2$ . Thus

$$\text{Amount of CO}_2 \text{ released} = \frac{0.44 \text{ g}}{44 \text{ g mol}^{-1}} = 10^{-2} \text{ mol}$$

Hence, Amount of  $\text{XO} = 10^{-2} \text{ mol}$

$$\begin{aligned} \text{Now, Mass of BaO in the mixture after heating} &= 3.64 \text{ g} - (10^{-2} \text{ mol}) (M_{\text{XO}}) \\ &= 3.64 \text{ g} - (10^{-2} \text{ mol}) (M_X + 16 \text{ g mol}^{-1}) \\ &= 3.48 \text{ g} - (10^{-2} \text{ mol}) (M_X) \end{aligned}$$

From the dissolution reactions



we conclude that

$$\text{Amount of HCl consumed for the dissolution process} = 2 \left[ \frac{3.48 \text{ g} - (10^{-2} \text{ mol}) M_X}{M_{\text{BaO}}} + 10^{-2} \text{ mol} \right]$$

Amount of HCl taken for the dissolution process

$$= (100 \text{ mL}) (0.1 \text{ M}) = \left(\frac{100}{1000} \text{ L}\right) (1 \text{ mol L}^{-1}) = 0.1 \text{ mol}$$

$$\text{Amount of remaining HCl} = 0.1 \text{ mol} - 2 \left[ \frac{3.48 \text{ g} - (10^{-2} \text{ mol}) M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol} \right]$$

Since the remaining HCl required 16 mL of 2.5 M NaOH ( $= \frac{16}{1000} \times 2.5 \text{ mol}$ ) for complete neutralization,

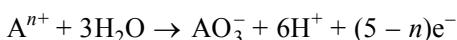
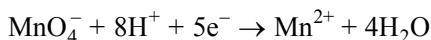
we would have

$$\frac{16 \times 2.5}{1000} \text{ mol} = 0.1 \text{ mol} - 2 \left[ \frac{3.48 \text{ g} - (10^{-2} \text{ mol}) M_X}{154 \text{ g mol}^{-1}} + 10^{-2} \text{ mol} \right]$$

This gives  $M_X = \frac{\left( \frac{16 \times 2.5}{1000} - 0.1 + 2 \times 10^{-2} \right) \left( \frac{154}{2} \right) \text{ g} + 3.48 \text{ g}}{(10^{-2} \text{ mol})} = 40 \text{ g mol}^{-1}$

Hence, the element X is Ca.

**13.** From the chemical equations



we write

Amount of electrons involved in reducing the given amount of  $\text{MnO}_4^- = 5 \times 1.61 \times 10^{-3} \text{ mol}$

Amount of electrons involved in oxidizing the given amount of  $\text{A}^{n+} = (5-n) \times 2.68 \times 10^{-3} \text{ mol}$

Equating these two, we get

$$5 \times 1.61 \times 10^{-3} \text{ mol} = (5-n) \times 2.68 \times 10^{-3} \text{ mol}$$

Hence,  $n = \frac{5(2.68 - 1.61)}{2.68} = \frac{5 \times 1.07}{2.68} \approx 2$ .

**14.** Let  $V$  be the volume of sulphuric acid taken while mixing the given acids. We will have Amount of  $\text{H}^+$  in 2 L of acids solution

$$= (5 \text{ mL}) (8 \text{ M}) + (4.8 \text{ mL}) (5 \text{ M}) + (V) (2 \times 17 \text{ M})$$

$$= \left( \frac{5}{1000} \text{ L} \right) (8 \text{ mol L}^{-1}) + \left( \frac{4.8}{1000} \text{ L} \right) (5 \text{ mol L}^{-1}) + (V) (2 \times 17 \text{ mol L}^{-1})$$

$$= \left( \frac{1}{1000} \right) \left[ 5 \times 8 + 4.8 \times 5 + \left( \frac{V}{\text{mL}} \right) (2 \times 17) \right] \text{ mol} = \left( \frac{1}{1000} \right) \left[ 64 + 34 \left( \frac{V}{\text{mL}} \right) \right] \text{ mol}$$

$$\text{Amount of H}^+ \text{ in } 30 \text{ mL of acids solution} = \left( \frac{30}{2000} \right) \left( \frac{1}{1000} \right) \left[ 64 + 34 \left( \frac{V}{\text{mL}} \right) \right] \text{ mol} \quad (1)$$

Mass of sodium carbonate neutralized by 30 mL of acids solution

$$= \left( \frac{1 \text{ g}}{100 \text{ mL}} \right) (42.9 \text{ mL}) = \frac{42.9}{100} \text{ g}$$

$$\text{Amount of sodium carbonate neutralized} = \frac{(42.9/100) \text{ g}}{286 \text{ g mol}^{-1}} = \frac{42.9}{100 \times 286} \text{ mol} \quad (2)$$

From the chemical equation  $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  we find that 1 mol  $\text{CO}_3^{2-} \equiv 2 \text{ mol H}^+$ . Hence, from Eqs. (1) and (2), we write

$$2 \left( \frac{42.9}{100 \times 286} \right) = \left( \frac{30}{2000} \right) \left( \frac{1}{1000} \right) \left[ 64 + 34 \left( \frac{V}{\text{mL}} \right) \right]$$

which gives  $\frac{V}{\text{mL}} = \frac{1}{34} \left[ 2 \left( \frac{42.9}{100 \times 286} \right) \left( \frac{2000}{30} \right) \left( \frac{1000}{1} \right) - 64 \right] = 4$

i.e.,  $V = 4 \text{ mL}$

Finally,

Mass of  $\text{SO}_4$  unit in 4 mL of 17 M  $\text{H}_2\text{SO}_4$  solution  
 $= (4 \text{ mL}) (17 \text{ mol L}^{-1}) (96 \text{ g mol}^{-1})$   
 $= \left(\frac{4}{1000}\right) (17) (96) \text{ g} = 6.528 \text{ g.}$

15. (i) Since 6 electrons are involved in the half-cell reaction, we would have

$$\text{Molarity of } \text{BrO}_3^- = \frac{0.672}{6} \text{ M}$$

Amount of  $\text{BrO}_3^-$  in 85.5 mL of bromate solution

$$= VM = (85.5 \text{ mL}) \left(\frac{0.672}{6} \text{ M}\right) = \left(\frac{85.5}{1000} \text{ L}\right) \left(\frac{0.672}{6} \text{ mol L}^{-1}\right) = \left(\frac{85.5}{1000}\right) \left(\frac{0.672}{6}\right) \text{ mol}$$

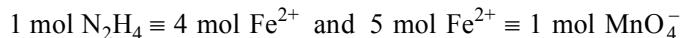
$$\text{Mass of } \text{NaBrO}_3 \text{ in 85.5 mL of solution} = \left(\frac{85.5}{1000}\right) \left(\frac{0.672}{5}\right) (151) \text{ g} = 1.446 \text{ g}$$

- (ii) Since 5 electrons per  $\text{BrO}_3^-$  ion are involved in the half-cell reaction, we would have

$$\text{Molarity of } \text{BrO}_3^- = \frac{0.672}{5} \text{ M}$$

$$\text{Mass of } \text{NaBrO}_3 \text{ in 85.5 mL of solution} = \left(\frac{85.5}{1000}\right) \left(\frac{0.672}{5}\right) (151) \text{ g} = 1.735 \text{ g.}$$

16. From the given chemical equations, we find that



Amount of  $\text{KMnO}_4$  in 20 mL of M/50 solution

$$= VM = (20 \text{ mL}) \left(\frac{1}{50} \text{ M}\right) = \left(\frac{20}{1000} \text{ L}\right) \left(\frac{1}{50} \text{ mol L}^{-1}\right) = \frac{20}{1000 \times 50} \text{ mol}$$

$$\text{Amount of equivalent } \text{Fe}^{2+} \text{ ions} = 5 \left(\frac{20}{1000 \times 50}\right) \text{ mol}$$

$$\text{Amount of equivalent } \text{N}_2\text{H}_4 = \left(\frac{1}{4}\right) (5) \left(\frac{20}{1000 \times 50}\right) \text{ mol}$$

The above amount is present in 10 mL of the solution. Hence,

$$\text{Amount of } \text{N}_2\text{H}_6\text{SO}_4 \text{ present in 1 L solution} = \left(\frac{1000}{10}\right) \left(\frac{1}{4}\right) (5) \left(\frac{20}{1000 \times 50}\right) \text{ mol}$$

$$\text{Mass of } \text{N}_2\text{H}_6\text{SO}_4 \text{ present in 1 L solution} = \left(\frac{1000}{10}\right) \left(\frac{1}{4}\right) (5) \left(\frac{20}{1000 \times 50}\right) (130) \text{ g} = 6.5 \text{ g}$$

17. Let  $x$  be the mass of oxalic acid in 2.02 g of the mixture. We will have

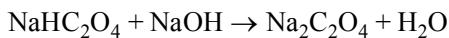
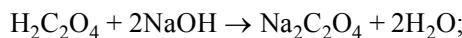
$$\text{Molarity of oxalic acid} = \frac{n}{V} = \frac{(x/90 \text{ g mol}^{-1})}{1 \text{ L}} = \frac{x}{90 \text{ g}} \text{ mol L}^{-1}$$

$$\text{Molarity of NaHC}_2\text{O}_4 = \frac{(2.02 \text{ g} - x)/112 \text{ g mol}^{-1}}{1 \text{ L}} = \frac{(2.02 \text{ g} - x)}{(112 \text{ g})} \text{ mol L}^{-1}$$

$$\begin{aligned}\text{Amount of oxalic acid in 10 mL solution} &= VM = \left( \frac{10}{1000} \text{ L} \right) \left( \frac{x}{90 \text{ g}} \text{ mol L}^{-1} \right) \\ &= \left( \frac{10}{1000} \right) \left( \frac{x}{90 \text{ g}} \right) \text{ mol}\end{aligned}$$

$$\text{Amount of NaHC}_2\text{O}_4 \text{ in 10 mL solution} = \left( \frac{10}{1000} \right) \left( \frac{2.02 \text{ g} - x}{112 \text{ g}} \right) \text{ mol}$$

Now from the neutralization reactions



we find that 1 mol  $\text{H}_2\text{C}_2\text{O}_4 \equiv 2$  mol NaOH and 1 mol  $\text{NaHC}_2\text{O}_4 \equiv 1$  mol NaOH

Hence,

$$\text{Amount of NaOH equivalent to H}_2\text{C}_2\text{O}_4 = 2 \left( \frac{10}{1000} \right) \left( \frac{x}{90 \text{ g}} \right) \text{ mol}$$

$$\text{Amount of NaOH equivalent to NaHC}_2\text{O}_4 = \left( \frac{10}{1000} \right) \left( \frac{2.02 \text{ g} - x}{112 \text{ g}} \right) \text{ mol}$$

Total amount of NaOH equivalent to 10 mL solution containing  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{NaHC}_2\text{O}_4$

$$= \left[ 2 \left( \frac{10}{1000} \right) \left( \frac{x}{90 \text{ g}} \right) + \left( \frac{10}{1000} \right) \left( \frac{2.02 \text{ g} - x}{112 \text{ g}} \right) \right] \text{ mol}$$

This amount will be equal to the amount of NaOH present in 3.0 mL of 0.1 N NaOH solution. Hence,

$$2 \left( \frac{10}{1000} \right) \left( \frac{x}{90 \text{ g}} \right) + \left( \frac{10}{1000} \right) \left( \frac{2.02 \text{ g} - x}{112 \text{ g}} \right) = \left( \frac{3.0}{1000} \right) (0.1)$$

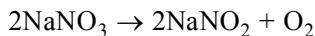
Solving for  $x$ , we get  $x = 0.9 \text{ g}$

Hence, in the original mixture, we have

$$\text{Mass of oxalic acid} = 0.9 \text{ g}$$

$$\text{Mass of NaHC}_2\text{O}_4 = 2.02 \text{ g} - 0.9 \text{ g} = 1.12 \text{ g}.$$

18. Let  $x$  be the mass of lead nitrate in the mixture. Heating the mixture results into the following reactions.



$$\text{Hence, Mass of PbO obtained} = \frac{2 M_{\text{PbO}}}{2 M_{\text{Pb}(\text{NO}_3)_2}} \times x = \frac{223}{331} x$$

$$\text{Mass of NaNO}_2 \text{ obtained} = \frac{2 M_{\text{NaNO}_2}}{2 M_{\text{NaNO}_3}} (5.0 \text{ g} - x) = \left( \frac{69}{85} \right) (5.0 \text{ g} - x)$$

$$\text{Total mass of residue} = \frac{223}{331} x + \frac{69}{85} (5.0 \text{ g} - x)$$

Since there occurs 28 per cent loss in mass, we would have

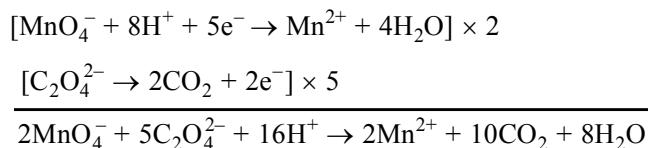
$$\frac{223}{331}x + \frac{69}{85}(5.0\text{ g} - x) = \frac{100 - 28}{100} \times 5.0\text{ g}$$

Solving for  $x$ , we get  $x = 3.32\text{ g}$

Hence, Mass of lead nitrate =  $3.32\text{ g}$

Mass of sodium nitrate =  $(5.0 - 3.32)\text{ g} = 1.68\text{ g}$ .

- 19.** The chemical equations involved in the titration of  $\text{C}_2\text{O}_4^{2-}$  with  $\text{MnO}_4^-$  are:



From this equation, we conclude  $2\text{ mol MnO}_4^- \equiv 5\text{ mol C}_2\text{O}_4^{2-}$

Hence,

$$\begin{aligned} \text{Amount of C}_2\text{O}_4^{2-} \text{ in the solution} &= \left(\frac{5}{2}\right)(22.6\text{ mL})(0.02\text{ M}) \\ &= \left(\frac{5}{2}\right)\left(\frac{22.6}{1000}\text{ L}\right)(0.02\text{ mol L}^{-1}) = 0.00113\text{ mol} \end{aligned}$$

The chemical equations involved during the treatment of KI and the titration with  $\text{Na}_2\text{S}_2\text{O}_3$  are



From these equations, we conclude



$$\begin{aligned} \text{Now, Amount of S}_2\text{O}_3^{2-} \text{ consumed} &= (11.3\text{ mL})(0.05\text{ M}) = \left(\frac{11.3}{1000}\text{ L}\right)(0.05\text{ mol L}^{-1}) \\ &= \left(\frac{11.3}{1000}\right)(0.05) \text{ mol} = 0.000565\text{ mol} \end{aligned}$$

Amount of  $\text{Cu}^{2+}$  equivalent to the above amount of  $\text{S}_2\text{O}_3^{2-} = 0.000565\text{ mol}$

$$\text{Hence, } \frac{\text{Amount of Cu}^{2+}}{\text{Amount of C}_2\text{O}_4^{2-}} = \frac{0.000565}{0.00113} = \frac{1}{2}$$

- 20.** We have

$$\text{Mass of Fe}_2\text{O}_3 \text{ in the sample} = (1.0\text{ g}) \left(\frac{55.2}{100}\right) = 0.552\text{ g}$$

$$\text{Molar mass of Fe}_2\text{O}_3 = 159.8\text{ g mol}^{-1}$$

$$\text{Amount of Fe}_2\text{O}_3 = \frac{0.552\text{ g}}{159.8\text{ g mol}^{-1}} = 3.454 \times 10^{-3}\text{ mol}$$

$$\text{Amount of Fe}^{3+} \text{ ions} = 2 \times 3.454 \times 10^{-3}\text{ mol}$$

On reduction, we have

$$\text{Amount of Fe}^{2+} \text{ ions} = 2 \times 3.454 \times 10^{-3} \text{ mol}$$

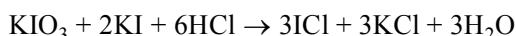
$$\text{Molarity of Fe}^{2+} \text{ ions} = \frac{2 \times 3.454 \times 10^{-3} \text{ mol}}{100 \times 10^{-3} \text{ L}} = 6.908 \times 10^{-2} \text{ mol L}^{-1}$$

If  $z$  is the number of electrons taken by the oxidant, we will have

$$(25.0 \text{ mL}) (6.908 \times 10^{-2} \text{ mol L}^{-1}) (1 \text{ eq mol}^{-1}) = (17.0 \text{ mL}) (0.0167 \text{ mol L}^{-1}) (z \text{ eq mol}^{-1})$$

$$\text{which gives } z = \frac{25.0 \times 6.908 \times 10^{-2}}{17 \times 0.0167} = 6.$$

- 21.** It is given that 20 mL of stock solution of KI requires 30 mL of M/10 KIO<sub>3</sub> solution to convert I<sup>-</sup> ions into ICl according to the reaction



For 50 mL of KI solution, the required volume of KIO<sub>3</sub> solution would be

$$\frac{30 \text{ mL of KIO}_3 \text{ solution}}{20 \text{ mL of KI solution}} \times 50 \text{ mL of KI solution} = 75 \text{ mL of KIO}_3 \text{ solution}$$

After treating 50 mL of KI solution with 1 g AgNO<sub>3</sub> sample, the volume of KIO<sub>3</sub> solution used is 50 mL. This means KI equivalent to 25 mL of KIO<sub>3</sub> solution is used in precipitating out Ag<sup>+</sup> ions from 50 mL of KI solution.

$$\begin{aligned} \text{Amount of KIO}_3 \text{ in 25 mL of M/10 KIO}_3 \text{ solution} &= (25 \text{ mL}) \left( \frac{1}{10} \text{ M} \right) \\ &= \left( \frac{25}{1000} \text{ L} \right) \left( \frac{1}{10} \text{ mol L}^{-1} \right) = 0.0025 \text{ mol} \end{aligned}$$

$$\text{Amount of KI equivalent to this amount} = 2 \times 0.0025 \text{ mol}$$

$$\text{Mass of AgNO}_3 \text{ precipitated out} = 2 \times 0.0025 \times 170 \text{ g} = 0.85 \text{ g}$$

$$\text{Per cent of AgNO}_3 \text{ in the sample} = \frac{0.85 \text{ g}}{1.0 \text{ g}} \times 100 = 85.$$

- 22.** The evolution of CO<sub>2</sub> on heating the mixture is due to the reaction



From the liberated volume of CO<sub>2</sub>, we calculate

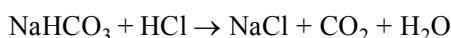
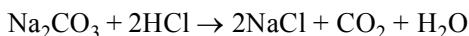
$$\text{Amount of liberated CO}_2 = \frac{pV}{RT} = \frac{\{(750/760) \text{ atm}\} (0.1239 \text{ L})}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) (298 \text{ K})} = 0.005 \text{ mol.}$$

From the chemical equation given above, we conclude that

$$\text{Amount of NaHCO}_3 \text{ present in 2.0 g sample of the mixture} = 2 \times 0.005 \text{ mol} = 0.01 \text{ mol}$$

$$\text{Mass of NaHCO}_3 \text{ present in the mixture} = (0.01 \text{ mol}) (84 \text{ g mol}^{-1}) = 0.84 \text{ g}$$

The treatment of the mixture with HCl solution would cause the following neutralization reactions.



Now, 1.5 g of the sample required 150 mL of M/10 HCl. For 2.0 g of the sample, volume of HCl required would be 200 mL. Hence,

$$\text{Amount of HCl in } 200 \text{ mL of M/10 HCl} = (200 \text{ mL})(0.1 \text{ mol L}^{-1}) = \left(\frac{200}{1000} \text{ L}\right)(0.1 \text{ mol L}^{-1}) = 0.02 \text{ mol}$$

Since the mixture contains 0.01 mol of  $\text{NaHCO}_3$ , 0.01 mol out of 0.02 mol would be consumed for the neutralization of  $\text{NaHCO}_3$ . The remaining 0.01 mol will be used for the neutralization of  $\text{Na}_2\text{CO}_3$ . From the chemical equation given above, we conclude that

$$\text{Amount of } \text{Na}_2\text{CO}_3 \text{ present in the } 2.0 \text{ g sample of the mixture} = \left(\frac{0.01 \text{ mol}}{2}\right) = 0.005 \text{ mol}$$

$$\text{Mass of } \text{Na}_2\text{CO}_3 \text{ present in } 2.0 \text{ g sample of the mixture} = (0.005 \text{ mol}) (106 \text{ g mol}^{-1}) = 0.53 \text{ g}$$

$$\text{Hence, Mass per cent of } \text{Na}_2\text{CO}_3 = \left(\frac{0.53 \text{ g}}{2.0 \text{ g}} \times 100\right) = 26.5$$

$$\text{Mass per cent of } \text{NaHCO}_3 = \left(\frac{0.84 \text{ g}}{2.0 \text{ g}} \times 100\right) = 42.0$$

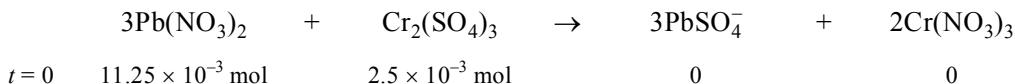
$$\text{Mass per cent of } \text{Na}_2\text{SO}_4 = 100 - (26.5 + 42.0) = 31.5.$$

23. To start with, we have

$$\text{Amount of } \text{Pb}(\text{NO}_3)_2 = MV = (0.25 \text{ mol L}^{-1})(45 \times 10^{-3} \text{ L}) = 11.25 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } \text{Cr}(\text{SO}_4)_3 = (0.1 \text{ mol L}^{-1})(25 \times 10^{-3} \text{ L}) = 2.5 \times 10^{-3} \text{ mol}$$

The reaction occurring is



In the above reaction,  $\text{Cr}_2(\text{SO}_4)_3$  has the limiting concentration. Hence, it will be consumed completely.

$$\text{Thus, Amount of } \text{Pb}(\text{NO}_3)_2 \text{ left} = 11.25 \times 10^{-3} \text{ mol} - 3 \times 2.5 \times 10^{-3} \text{ mol} = 3.75 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } \text{PbSO}_4 \text{ precipitated} = 3 \times 2.5 \times 10^{-3} \text{ mol} = 7.5 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } \text{Cr}(\text{NO}_3)_3 \text{ formed} = 2 \times 2.5 \times 10^{-3} \text{ mol} = 5.0 \times 10^{-3} \text{ mol}$$

Now the volume of the system after mixing  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cr}_2(\text{SO}_4)_3$  solutions becomes 70.0 mL ( $= 45.0 \text{ mL} + 25.0 \text{ mL}$ ). Hence,

$$[\text{Pb}(\text{NO}_3)_2] = \frac{3.75 \times 10^{-3} \text{ mol}}{70 \times 10^{-3} \text{ L}} = 0.0536 \text{ M} \quad \text{and} \quad [\text{Cr}(\text{NO}_3)_3] = \frac{5.0 \times 10^{-3} \text{ mol}}{70 \times 10^{-3} \text{ L}} = 0.0714 \text{ M}$$

Assuming  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  completely dissociated, we will have

$$[\text{Pb}^{2+}] = 0.0536 \text{ M}$$

$$[\text{Cr}^{3+}] = 0.0714 \text{ M}$$

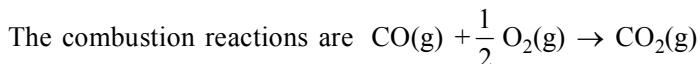
$$[\text{NO}_3^-] = (2 \times 0.0536 + 3 \times 0.0714) \text{ M} = 0.3214 \text{ M}$$

$$\text{Amount of } \text{PbSO}_4 \text{ formed} = 7.5 \times 10^{-3} \text{ mol.}$$

24. Let  $V_1$ ,  $V_2$  and  $V_3$  be the respective partial volumes of CO,  $\text{CH}_4$  and He in the given 20.0 cm<sup>3</sup> of the mixture.

$$\text{Hence, } V_1 + V_2 + V_3 = 20.0 \text{ cm}^3$$

(1)



Hence,  $V_1 \text{ volume CO} \equiv \frac{V_1}{2} \text{ volume O}_2 \equiv V_1 \text{ volume CO}_2$

$$V_2 \text{ volume CH}_4 \equiv 2V_2 \text{ volume O}_2 \equiv V_2 \text{ volume CO}_2$$

Since there is no volume change due to the replacement of CO into CO<sub>2</sub> and CH<sub>4</sub> into CO<sub>2</sub>, the volume change is due to the consumption of O<sub>2</sub>. Hence,

$$\frac{V_1}{2} + 2V_2 = 13.0 \text{ cm}^3 \quad (2)$$

The treatment of residual gases with KOH solution would cause the absorption of CO<sub>2</sub>(g). Hence,

$$V_1 + V_2 = 14.0 \text{ cm}^3 \quad (3)$$

Solving V<sub>1</sub>, V<sub>2</sub> and V<sub>3</sub> from Eqs (1) to (3), we get V<sub>1</sub> = 10.0 cm<sup>3</sup>, V<sub>2</sub> = 4.0 cm<sup>3</sup>, and V<sub>3</sub> = 6.0 cm<sup>3</sup>

Hence, Volume percentage of CO =  $\frac{10.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 50$

Volume percentage of CH<sub>4</sub> =  $\frac{4.0 \text{ cm}^3}{20.0 \text{ cm}^3} \times 100 = 20$

Volume percentage of He = 100 – (50 + 20) = 30.

**25.** Glauber's salt is NaSO<sub>4</sub> · 10H<sub>2</sub>O.

$$\begin{aligned} \text{Molar mass of Glauber's salt} &= \{2 \times 23.00 + 32.1 + 4 \times 16.0 + 10(2 \times 1.01 + 16.0)\} \text{ g mol}^{-1} \\ &= 322.3 \text{ g mol}^{-1} \end{aligned}$$

$$\text{Amount of Glauber's salt dissolved, } n_2 = \frac{m}{M} = \frac{8.0575 \times 10^{-2} \text{ kg}}{322.3 \times 10^{-3} \text{ kg mol}^{-1}} = 0.25 \text{ mol}$$

$$\text{Mass of } 1 \text{ dm}^3 \text{ solution} = \rho V = (1077.2 \text{ kg m}^{-3})(10^{-3} \text{ m}^3) = 1.0772 \text{ kg}$$

$$\begin{aligned} \text{Mass of Na}_2\text{SO}_4 \text{ in } 1 \text{ dm}^3 \text{ solution,} &= n_2 M_{\text{Na}_2\text{SO}_4} = (0.25 \text{ mol})(2 \times 23 + 32.10 + 4 \times 16.0) \text{ g mol}^{-1} \\ &= 35.525 \text{ g} = 3.5525 \times 10^{-2} \text{ kg} \end{aligned}$$

$$\text{Mass of solvent in } 1 \text{ dm}^3 \text{ solution} = (1.0772 - 3.5525 \times 10^{-2}) \text{ kg} = 1.0417 \text{ kg}$$

$$\text{Molarity of solution} = \frac{n_2}{V} = \frac{0.25 \text{ mol}}{1 \text{ dm}^3} = 0.25 \text{ mol dm}^{-3}$$

$$\text{Molality of solution} = \frac{n_2}{m_{\text{solvent}}} = \frac{0.25 \text{ mol}}{1.0417 \text{ kg}} = 0.24 \text{ mol kg}^{-1}$$

$$\text{Amount of solvent in } 1 \text{ dm}^3 \text{ solution, } n_1 = \frac{1.0417 \times 10^3 \text{ g}}{18 \text{ g mol}^{-1}} = 57.87 \text{ mol}$$

$$\text{Mole fraction of Na}_2\text{SO}_4 \text{ in solution, } \frac{n_1}{n_1 + n_2} = \frac{0.25}{0.25 + 57.87} = 0.0043$$

**26.** In 10<sup>6</sup> g (= 1000 kg) of the given hard water, we will have

$$\text{Mass of SO}_4^{2-} \text{ ions} = 96 \text{ g}$$

$$\text{Mass of HCO}_3^- \text{ ions} = 183 \text{ g}$$

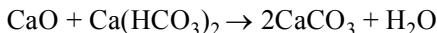
Thus      Amount of SO<sub>4</sub><sup>2-</sup> ions =  $\frac{96 \text{ g}}{96 \text{ g mol}^{-1}} = 1 \text{ mol}$

$$\text{Amount of } \text{HCO}_3^- \text{ ions} = \frac{183 \text{ g}}{61 \text{ g mol}^{-1}} = 3 \text{ mol}$$

These ions are present as  $\text{CaSO}_4$  and  $\text{Ca}(\text{HCO}_3)_2$ .

Hence, Amount of  $\text{Ca}^{2+}$  ions =  $(1 + 1.5)$  mol =  $2.5$  mol.

The addition of  $\text{CaO}$  causes the following reaction:

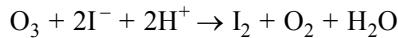


To remove  $1.5$  mol of  $\text{Ca}(\text{HCO}_3)_2$ ,  $1.5$  mol of  $\text{CaO}$  will be required in the treated water. After this, the solution contains only  $\text{CaSO}_4$ . Thus,  $1$  mol of  $\text{Ca}^{2+}$  ions will be present in  $10^6$  g of water. Hence, its concentration will be  $40$  ppm. Molarity of  $\text{Ca}^{2+}$  ions in the treated water will be  $10^{-3}$  mol L $^{-1}$ . If the  $\text{Ca}^{2+}$  ions are exchanged by  $\text{H}^+$  ions, then

$$\text{Molarity of } \text{H}^+ \text{ in the treated water} = 2 \times 10^{-3} \text{ M.}$$

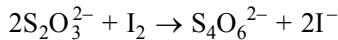
$$\text{Thus, } \text{pH} = -\log(2 \times 10^{-3}) = 2.7$$

27. The reaction of  $\text{O}_3$  with  $\text{I}^-$  in acidic medium is



$$\text{Hence, } 1 \text{ mol O}_3 \equiv 1 \text{ mol I}_2$$

The reaction of  $\text{I}_2$  with  $\text{S}_2\text{O}_3^{2-}$  is



$$\text{Hence, } 2 \text{ mol S}_2\text{O}_3^{2-} \equiv 1 \text{ mol I}_2$$

$$\text{Amount of S}_2\text{O}_3^{2-} \text{ consumed} = (40 \times 10^{-3} \text{ L}) \left( \frac{1}{10} \text{ mol L}^{-1} \right) = 40 \times 10^{-4} \text{ mol}$$

$$\text{Thus } 40 \times 10^{-4} \text{ mol S}_2\text{O}_3^{2-} \equiv 20 \times 10^{-4} \text{ mol I}_2 \equiv 20 \times 10^{-4} \text{ mol O}_3$$

$$\text{Mass of O}_3 \text{ present in 1 L of mixture} = (20 \times 10^{-4} \text{ mol}) (48 \text{ g mol}^{-1}) = 9.6 \times 10^{-2} \text{ g}$$

Total amount of  $\text{O}_2$  and  $\text{O}_3$  present in 1 L of mixture at STP is

$$n_{\text{total}} = \frac{pV}{RT} = \frac{(1 \text{ atm})(1 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1})(273 \text{ K})} = 4.462 \times 10^{-2} \text{ mol}$$

Hence,

$$\text{Amount of O}_2 \text{ present in 1 L of mixture} = (4.462 \times 10^{-2} - 20 \times 10^{-4}) \text{ mol} = 4.262 \times 10^{-2} \text{ mol}$$

$$\text{Mass of O}_2 \text{ present in 1 L of mixture} = (4.262 \times 10^{-2} \text{ mol}) (32 \text{ g mol}^{-1}) = 1.364 \text{ g}$$

$$\text{Mass percent of O}_3 \text{ in the mixture} = \frac{9.6 \times 10^{-2}}{9.6 \times 10^{-2} + 1.364} \times 100 = 6.575$$

$$\text{Amount of photons required to decompose O}_3 = \text{Amount of O}_3 = 20 \times 10^{-4} \text{ mol}$$

$$\text{Number of photons required} = (20 \times 10^{-4} \text{ mol}) (6.022 \times 10^{23} \text{ mol}^{-1}) = 1.204 \times 10^{21}$$

28. The reaction between  $\text{KIO}_3$  and  $\text{KI}$  is  $\text{KIO}_3 + 5\text{KI} + 6\text{HCl} \rightarrow 6\text{KCl} + 3\text{H}_2\text{O} + 3\text{I}_2$

$$\text{The reaction of I}_2 \text{ with thiosulphate ion is } 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$$

From these reactions, we can write

$$1 \text{ mol KIO}_3 \equiv 3 \text{ mol I}_2 \text{ and } 1 \text{ mol I}_2 \equiv 2 \text{ mol S}_2\text{O}_3^{2-}$$

From the given mass of  $\text{KIO}_3$ , we get

$$\text{Amount of KIO}_3 = \frac{0.10 \text{ g}}{214.0 \text{ g mol}^{-1}} = 4.6729 \times 10^{-4} \text{ mol}$$

$$\text{Amount of I}_2 \text{ generated} = 3 \times 4.6729 \times 10^{-4} \text{ mol}$$

$$\text{Amount of S}_2\text{O}_3^{2-} \text{ consumed} = 2(3 \times 4.6729 \times 10^{-4} \text{ mol}) \quad (1)$$

Let  $M$  be the molarity of thiosulphate solution. From the given volume of thiosulphate solution, we get

$$\text{Amount of S}_2\text{O}_3^{2-} \text{ consumed} = MV = M(45.0 \times 10^{-3} \text{ L}) \quad (2)$$

Equating Eqs (1) and (2), we get

$$\text{i.e. } M(45.0 \times 10^{-3} \text{ L}) = 2(3 \times 4.6729 \times 10^{-4} \text{ mol})$$

$$M = \frac{2(3 \times 4.6729 \times 10^{-4} \text{ mol})}{45.0 \times 10^{-3} \text{ L}} = 0.0623 \text{ mol L}^{-1}$$

**29.** The reactions with KI solution in acidic medium are



The reaction involving  $\text{I}_2$  and  $\text{S}_2\text{O}_3^{2-}$  is  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$

From this equation, we conclude  $2 \text{ mol S}_2\text{O}_3^{2-} \equiv 1 \text{ mol I}_2$

Amount of  $\text{S}_2\text{O}_3^{2-}$  in 11.0 mL of 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution

$$= (11.0 \times 10^{-3} \text{ L})(0.5 \text{ mol L}^{-1}) = 5.5 \times 10^{-3} \text{ mol}$$

Amount of  $\text{I}_2$  equivalent to the above amount of  $\text{S}_2\text{O}_3^{2-}$

$$= \frac{1}{2}(5.5 \times 10^{-3} \text{ mol}) = 2.75 \times 10^{-3} \text{ mol}$$

The above iodine is present in 20 mL of the solution. Hence,

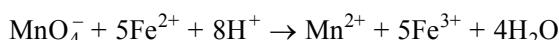
Amount of  $\text{I}_2$  liberated in 100 mL solution

$$= 5 \times 2.75 \times 10^{-3} \text{ mol} = 13.75 \times 10^{-3} \text{ mol}$$

If  $n_1$  and  $n_2$  are the respective amounts of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  present in the given 3.00 g sample, then from Eqs (1) and (2), we can write

$$n_1 + n_2 = 13.75 \times 10^{-3} \text{ mol} \quad (3)$$

Now from the chemical equation



we can write  $1 \text{ mol MnO}_4^- \equiv 5 \text{ mol Fe}^{2+}$

Amount of  $\text{MnO}_4^-$  in 12.80 mL of 0.25 M  $\text{KMnO}_4$  solution

$$= (12.80 \times 10^{-3} \text{ L})(0.25 \text{ mol L}^{-1}) = 3.2 \times 10^{-3} \text{ mol}$$

Amount of  $\text{Fe}^{2+}$  equivalent to the above amount of

$$\text{MnO}_4^- \text{ ions} = 5 \times 3.2 \times 10^{-3} \text{ mol} = 16.0 \times 10^{-3} \text{ mol}$$

This amount of  $\text{Fe}^{2+}$  ions is present in 50 mL of the solution. Hence,

Amount of  $\text{Fe}^{2+}$  ions in 100 mL solution =  $2 \times 16.0 \times 10^{-3} \text{ mol}$

From Eqs. (1) and (2), we can now write

$$3n_1 + 2n_2 = 32.0 \times 10^{-3} \text{ mol} \quad (4)$$

Solving for  $n_1$  and  $n_2$  from Eqs (3) and (4), we get

$$n_1 = 4.5 \times 10^{-3} \text{ mol} \quad \text{and} \quad n_2 = 9.25 \times 10^{-3} \text{ mol}$$

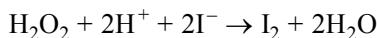
$$\begin{aligned}\text{Mass of Fe}_3\text{O}_4 \text{ in } 3.00 \text{ g sample} &= (4.5 \times 10^{-3} \text{ mol}) (232 \text{ g mol}^{-1}) \\ &= 1.044 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Mass of Fe}_2\text{O}_3 \text{ in } 3.00 \text{ g sample} &= (9.25 \times 10^{-3} \text{ mol}) (160 \text{ g mol}^{-1}) \\ &= 1.48 \text{ g}\end{aligned}$$

$$\text{Mass per cent of Fe}_3\text{O}_4 \text{ in the sample} = \frac{1.044}{3} \times 100 = 34.8$$

$$\text{Mass per cent of Fe}_2\text{O}_3 \text{ in the sample} = \frac{1.48}{3} \times 100 = 49.3$$

**30.** The involved reaction is



$$\text{Hence } 1 \text{ mol H}_2\text{O}_2 \equiv 1 \text{ mol I}_2$$

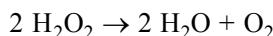
$$\text{Amount of I}_2 \text{ liberated} = \frac{0.508 \text{ g}}{(2 \times 127) \text{ g mol}^{-1}} = 2 \times 10^{-3} \text{ mol}$$

Thus

$$\text{Amount of H}_2\text{O}_2 \text{ in } 5.0 \text{ cm}^3 \text{ solution} = 2 \times 10^{-3} \text{ mol}$$

$$\text{Molar concentration of H}_2\text{O}_2 = \frac{2 \times 10^{-3} \text{ mol}}{5 \times 10^{-3} \text{ L}} = 0.4 \text{ mol L}^{-1}$$

The volume strength of H<sub>2</sub>O<sub>2</sub> is based on the reaction



$$\text{Thus } 2 \text{ mol H}_2\text{O}_2 \equiv 1 \text{ mol O}_2 \equiv 22.4 \text{ L O}_2 \text{ at STP}$$

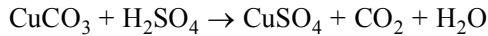
Now 2 molar solution of H<sub>2</sub>O<sub>2</sub> has volume strength of 22.4.

$$\text{Hence, } 0.4 \text{ molar solution of H}_2\text{O}_2 \text{ has volume strength of } \frac{22.4}{2 \text{ M}} \times 0.4 \text{ M} = 4.48$$

$$\begin{aligned}\text{31. Molar mass of CuCO}_3 &= (63.5 + 12 + 3 \times 16) \text{ g mol}^{-1} \\ &= 123.5 \text{ g mol}^{-1}\end{aligned}$$

$$\text{Amount of given CuCO}_3 = \frac{0.5 \text{ g}}{123.5 \text{ g mol}^{-1}} = 4.05 \times 10^{-3} \text{ mol}$$

The dissolution reaction is



From the stoichiometric coefficients, we can write

Amount of H<sub>2</sub>SO<sub>4</sub> required for dissolution of the given mass of CuCO<sub>3</sub>,

$$n = 4.05 \times 10^{-3} \text{ mol}$$

Volume of 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing  $4.05 \times 10^{-3}$  mol of H<sub>2</sub>SO<sub>4</sub>

$$= \frac{n}{M} = \frac{4.05 \times 10^{-3} \text{ mol}}{0.5 \text{ mol L}^{-1}} = 8.1 \times 10^{-3} \text{ L} = 8.1 \text{ mL}$$

**32.** Radius of the cylindrical particle is

$$r = \frac{150 \times 10^{-8} \text{ cm}}{2} = 75 \times 10^{-8} \text{ cm}$$

Length of the cylindrical particle is

$$l = 5000 \times 10^{-8} \text{ cm}$$

Volume of the cylindrical particle is

$$\begin{aligned} V &= \pi r^2 l = (3.14) (75 \times 10^{-8} \text{ cm})^2 (500 \times 10^{-8} \text{ cm}) \\ &= 8.83 \times 10^{-17} \text{ cm}^3 \end{aligned}$$

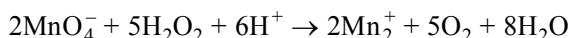
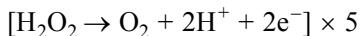
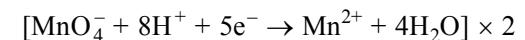
Mass of the cylindrical particle is

$$m = \frac{V}{\rho} = \frac{8.83 \times 10^{-17} \text{ cm}^3}{0.75 \text{ cm}^3/\text{g}} = 1.18 \times 10^{-16} \text{ g}$$

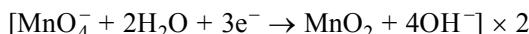
Molar mass of the cylindrical particle is

$$\begin{aligned} M &= m N_A = (1.18 \times 10^{-16} \text{ g}) (6.023 \times 10^{23} \text{ mol}^{-1}) \\ &= 7.1 \times 10^7 \text{ g mol}^{-1} \end{aligned}$$

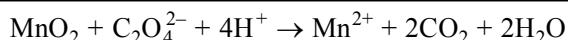
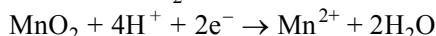
33. In acidic medium,  $\text{MnO}_4^-$  oxidises  $\text{H}_2\text{O}_2$  to  $\text{O}_2$ . The involved reactions are



In neutral medium, the reactions of  $\text{MnO}_4^-$  with  $\text{Mn}^{2+}$  are as follows.



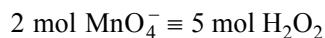
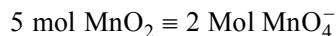
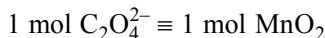
The dissolution of  $\text{MnO}_2$  in sodium oxalate in acidic medium involves the following reactions.



Amount of oxalate used in dissolving  $\text{MnO}_2$  is

$$\begin{aligned} n_1 &= V_1 M_1 = (10 \text{ mL}) (0.2 \text{ M}) \\ &= (10 \text{ mL}) \left( \frac{0.2 \text{ mol}}{1000 \text{ mL}} \right) = 2 \times 10^{-3} \text{ mol} \end{aligned}$$

From the reactions given above, we conclude that



$$\text{Hence, } 2 \times 10^{-3} \text{ mol C}_2\text{O}_4^{2-} \equiv 2 \times 10^{-3} \text{ mol MnO}_2 \equiv \frac{2}{5} (2 \times 10^{-3} \text{ mol MnO}_4^-)$$

$$= \frac{5}{2} \left[ \frac{2}{5} (2 \times 10^{-3} \text{ mol H}_2\text{O}_2) \right]$$

that is,

$2 \times 10^{-3}$  mol of  $\text{H}_2\text{O}_2$  was present in 20 mL of hydrogen peroxide solution. Hence, its molarity is

$$M = \frac{n}{V} = \frac{2 \times 10^{-3} \text{ mol}}{20 \times 10^{-3} \text{ L}} = 0.1 \text{ mol L}^{-1}$$

34. By definition, molarity is the amount of substance (i.e. number of moles) per liter of the solution. To calculate molarity of water, we take 1 L of water and find out the amount of water in this volume. We know that the density of water at  $4^\circ\text{C}$  is  $1 \text{ g mL}^{-1}$ . Hence, the mass of 1 L of water is

$$m = \rho V = (1 \text{ g mL}^{-1}) (1000 \text{ mL}) = 1000 \text{ g}$$

The amount of water in this mass is

$$n = \frac{m}{M} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.56 \text{ mol}$$

Hence, the molarity of water at  $4^\circ\text{C}$  is  $55.56 \text{ mol L}^{-1}$ .



# **GASEOUS, LIQUID AND SOLID STATES**

2

## **SECTION - I GASEOUS STATE**

## **Straight Objective Type**



21. The rms speed of hydrogen is  $\sqrt{7}$  times the rms speed of nitrogen. If  $T$  is the temperature of the gas, then

- |                       |                                |
|-----------------------|--------------------------------|
| (a) $T(H_2) = T(N_2)$ | (b) $T(H_2) > T(N_2)$          |
| (c) $T(H_2) < T(N_2)$ | (d) $T(H_2) = \sqrt{7} T(N_2)$ |
- (2000)

22. A real gas is expected to behave more or less ideally at

- |                                       |   |
|---------------------------------------|---|
| (a) low temperature and low pressure  | (b) low temperature and high pressure         |
| (c) high temperature and low pressure | (d) high temperature and high pressure (1999) |

23. The compression factor of a gas is less than unity at STP. Therefore

- |                            |                               |
|----------------------------|-------------------------------|
| (a) $V_m > 22.4 \text{ L}$ | (b) $V_m < 22.4 \text{ L}$    |
| (c) $V_m = 22.4 \text{ L}$ | (d) $V_m \geq 44.8 \text{ L}$ |
- (2000)

24. Equal masses of methane and hydrogen are mixed in an empty container at 25 °C. The fraction of the total pressure exerted by hydrogen is

- |         |         |         |           |
|---------|---------|---------|-----------|
| (a) 1/2 | (b) 8/9 | (c) 1/9 | (d) 16/17 |
|---------|---------|---------|-----------|
- (1984)

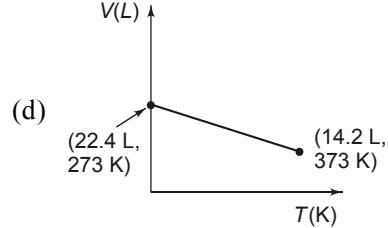
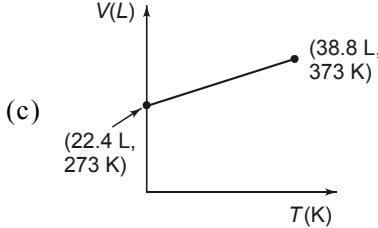
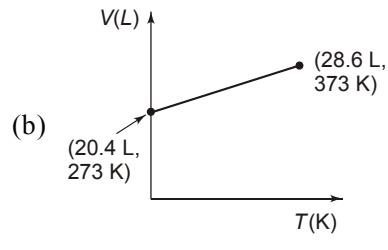
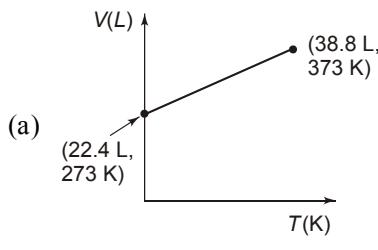
25. At 100 °C and 1 atm, if the density of liquid water is  $1.0 \text{ g cm}^{-3}$  and that of water vapour is  $0.0006 \text{ g cm}^{-3}$ , then the volume occupied by water molecules in 1 litre of steam at this temperature is

- |                      |                       |                        |                         |
|----------------------|-----------------------|------------------------|-------------------------|
| (a) $6 \text{ cm}^3$ | (b) $60 \text{ cm}^3$ | (c) $0.6 \text{ cm}^3$ | (d) $0.06 \text{ cm}^3$ |
|----------------------|-----------------------|------------------------|-------------------------|
- (2000)

26. The root mean square speed of an ideal gas at constant pressure varies with density ( $d$ ) as

- |           |         |                |                  |
|-----------|---------|----------------|------------------|
| (a) $d^2$ | (b) $d$ | (c) $\sqrt{d}$ | (d) $1/\sqrt{d}$ |
|-----------|---------|----------------|------------------|
- (2001)

27. Which of the following volume ( $V$ )–temperature ( $T$ ) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?



28. Negative deviation from ideal behaviour is due to the fact that

- |  |
|--|
| (a) there exists molecular interactions and $pV/nRT > 1$ |
| (b) there exists molecular interactions and $pV/nRT < 1$ |
| (c) atoms have finite size and $pV/nRT > 1$              |
| (d) atoms have finite size and $pV/nRT < 1$              |
- (2003)

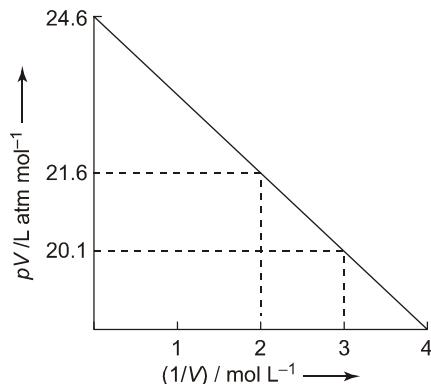
29. The root mean square speed of gaseous molecules (molar mass :  $M$ ) in terms of their molar kinetic energy ( $E$ ) is

- |                                     |                                     |
|-------------------------------------|-------------------------------------|
| (a) $u_{\text{rms}} = \sqrt{3E/2M}$ | (b) $u_{\text{rms}} = \sqrt{3E/2M}$ |
| (c) $u_{\text{rms}} = \sqrt{2E/M}$  | (d) $u_{\text{rms}} = \sqrt{E/3M}$  |
- (2004)

30. If methane and helium are allowed to diffuse out of a container under identical conditions of temperature and pressure, the ratio of rate of diffusion of methane to helium is  
 (a) 4.0                    (b) 2.0                    (c) 1.0                    (d) 0.5                    (2005)

31. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is  
 (a)  $nb$                     (b)  $n^2a/V^2$                     (c)  $-n^2a/V^2$                     (d)  $-nb$                     (2009)

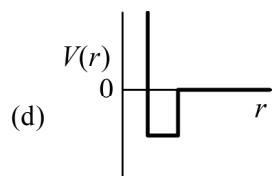
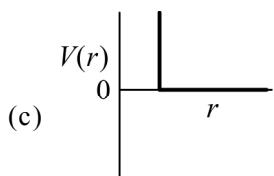
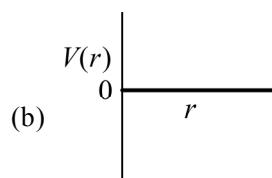
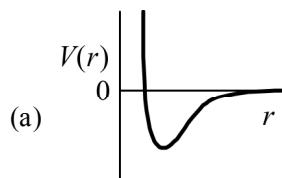
32. For one mole of a van der Waals gas when  $b = 0$  and  $T = 300$  K, the plot of  $pV$  versus  $1/V$  is shown below.



The value of the van der Waals constant  $a$  is

- (a)  $1.0 \text{ L}^2 \text{ atm mol}^{-2}$       (b)  $4.5 \text{ L}^2 \text{ atm mol}^{-2}$   
 (c)  $1.5 \text{ L}^2 \text{ atm mol}^{-2}$       (d)  $3.0 \text{ L}^2 \text{ atm mol}^{-2}$       (2012)

33. One mole of a monoatomic real gas satisfies the equation  $p(V - b) = RT$  where  $b$  is a constant. The relationship of interatomic potential  $V(r)$  and interatomic distance  $r$  for the gas is given by



(2015)

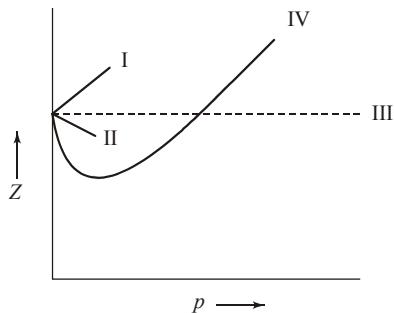
## **Multiple Correct-Choice Type**

1. If a gas is expanded at constant temperature

  - (a) the pressure decreases
  - (b) the kinetic energy of the molecules remains the same
  - (c) the kinetic energy of the molecules decreases
  - (d) the number of molecules of the gas increases

(1986)

2. Figure 1 displays the plot of the compression factor  $Z$  versus  $p$  for a few gases.



**Fig. 1**

Which of the following statements is/are correct for a van der Waals gas?

- (a) The plot I is applicable provided the van der Waals constant  $a$  is negligible
- (b) The plot II is applicable provided the van der Waals constant  $b$  is negligible
- (c) The plot III is applicable provided both the van der Waals constants  $a$  and  $b$  are negligible
- (d) The plot IV is applicable provided the temperature of the gas is much higher than its critical temperature. (2006)

3. A gas described by van der Waals equation

- (a) behaves similar to an ideal gas in the limit of large molar volumes
- (b) behaves similar to an ideal gas in the limit of large pressures
- (c) is characterised by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature
- (d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally. (2008)

4. According to the kinetic theory of gases

- (a) collisions are always elastic
- (b) heavier molecules transform more momentum to the wall of the container
- (c) only a small number of molecules have very high velocity
- (d) between collisions, the molecules move in straight lines with constant velocity (2011)

### Fill-in-the-Blanks Type

1. The total energy of one mole of an ideal monoatomic gas at 27 °C is \_\_\_\_\_ calories. (1984)
2.  $C_p - C_V$  for one mole of an ideal gas is \_\_\_\_\_. (1984)
3. Eight grams each of oxygen and hydrogen at 27 °C will have the total kinetic energy in the ratio of \_\_\_\_\_. (1989)
4. The value of  $pV$  for 5.6 L of an ideal gas is \_\_\_\_\_  $RT$  at STP. (1987)
5. The absolute temperature of an ideal gas is \_\_\_\_\_ to/than the average kinetic energy of the gas molecules. (1997)
6. A liquid which is permanently supercooled is frequently called a \_\_\_\_\_. (1997)

### Integer Answer Type

1. At 400 K, the root mean square (rms) speed of a gas X (relative molar mass = 40) is equal to the most probable speed of gas Y at 60 K. The relative molar mass of the gas Y is \_\_\_\_\_. (2009)

2. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm at 0 °C) are introduced. Considering the ideal gas behaviour, the total volume (in litres) of the gases at 0 °C is close to \_\_\_\_\_. (2011)

### True/False Type

- Nitrogen diffuses faster than oxygen through an orifice. (1978)
- Kinetic energy of a molecule is zero at 0 °C. (1985)
- A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. (1985)
- Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985)
- In the van der Waals equation,

$$\left( p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

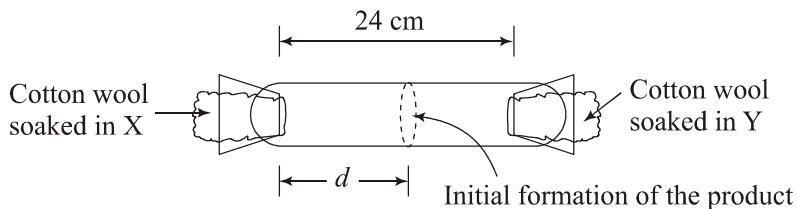
the constant ‘a’ reflects the actual volume of the gas molecules. (1993)

6. A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution. Is this statement true or false? Justify your answer in not more than two lines. (1996)

### Linked Comprehension Type

#### Passage-1

X and Y are two volatile liquids with molar mass of 10 g mol<sup>-1</sup> and 40 g mol<sup>-1</sup> respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneous placed at the ends of a tube of length L = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atm pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance d from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



- The value of d in cm (shown in the figure), as estimated from Graham's law, is
  - 8
  - 12
  - 16
  - 20
- The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to
  - larger mean free path for X as compared to that of Y
  - larger mean free path for Y as compared to that of X
  - increased collision frequency of Y with the inert gas as compared to that of X with the inert gas.
  - increased collision frequency of X with the inert gas as compared to that of Y with the inert gas. (2014)

### Reasoning Type

The questions below (1 and 2) consist of an ‘Assertion’ in column 1 and the ‘Reason’ in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.  
 (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.  
 (c) If *assertion* is CORRECT, but *reason* is INCORRECT.  
 (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

*Assertion* (column 1)

1. The value of van der Waals' constant ' $a$ ' is larger for ammonia than for nitrogen.
2. The pressure of fixed amount of an ideal gas is proportional to its temperature.

*Reason* (column 2)

- Hydrogen bonding is present in ammonia. (1998)  
 Frequency of collisions and their impact both increase in proportion to the square root of temperature. (2000)

**Matching Type**

- |                           |                   |
|---------------------------|-------------------|
| 1. (a) Neutrons           | (p) Kohlrausch    |
| (b) Molecular speed       | (q) van der Waals |
| (c) Intermolecular forces | (r) Maxwell       |
| (d) Conductance of ions   | (s) Chadwick      |
- (1982)

**Matrix Match Type**

1. Match gases under specified conditions listed in **Column I** with their properties/laws in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the following.

	p	q	r	s
a	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
b	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
c	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>

**Column I****Column II**

- |  |                                    |
|--|------------------------------------|
| (a) hydrogen gas ( $P = 200$ atm, $T = 273$ K) | (p) compression factor $\neq 1$    |
| (b) hydrogen gas ( $P \sim 0$ , $T = 273$ K)   | (q) attractive forces are dominant |
| (c) $\text{CO}_2$ ( $P = 1$ atm, $T = 273$ K)  | (r) $PV = nRT$                     |
| (d) real gas with very large molar volume      | (s) $P(V - nb) = nRT$              |
- (2007)

**Short Answer Type**

1. One way of writing the equation of state for real gases is

$$P\bar{V} = RT \left[ 1 + \frac{B}{\bar{V}} + \dots \right]$$

where  $B$  is a constant. Derive an approximate expression for  $B$  in terms of the van der Waals constants  $a$  and  $b$ . (1997)

2.  $C_V$  value of Ne is always  $3R/2$  but  $C_V$  value of  $H_2$  is  $3R/2$  at low temperature and  $5R/2$  at moderate temperature and more than  $5R/2$  at higher temperature. Explain. (2003)

### Subjective Type

- Calculate the density of ammonia at  $30^\circ C$  and 5 atm pressure. (1978)
  - 3.7 g of a gas at  $25^\circ C$  occupied the same volume as 0.184 g of hydrogen at  $17^\circ C$ , at the same pressure. What is the molar mass of the gas? (1979)
  - The vapour density (relative atomic mass of hydrogen = 1) of a mixture consisting of  $NO_2$  and  $N_2O_4$  is 38.3 at  $26.7^\circ C$ . Calculate the amount of  $NO_2$  in 100 g of the mixture. (1979)
  - 4.215 g of a metallic carbonate was heated in a hard glass tube and the  $CO_2$  evolved was found to measure 1336 mL at  $27^\circ C$ , and 700 mmHg pressure. What is the equivalent mass of the metal? (1979)
  - A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and  $NH_3$  gas through inlet Y are allowed to enter the tube at the same time. White fumes appear at a point P inside the tube. Find this distance of P from X. (1980)
  - The pressure in a bulb dropped from 2000 to 1500 mmHg in 47 min, when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molar mass  $79\text{ g mol}^{-1}$  in the molar ratio 1:1 at a total pressure of 4000 mmHg, was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min. (1981)
  - Calculate the average kinetic energy, in joules, of the molecules in 8.0 g of methane at  $27^\circ C$ . (1982)
  - The density of mercury is  $13.6\text{ g cm}^{-3}$ . Calculate approximately the diameter of an atom of mercury assuming that each atom occupying a cube of edge length equal to the diameter of the mercury atom. (1983)
  - Oxygen is present in 1-litre flask at a pressure of  $7.6 \times 10^{-10}\text{ mmHg}$ . Calculate the number of oxygen molecules in the flask at  $0^\circ C$ . (1983)
  - When 2 g of a gas A is introduced into an evacuated flask kept at  $25^\circ C$ , the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molar masses  $M_A : M_B$ . (1983)
  - Calculate the root mean square speed of ozone kept in a closed vessel at  $20^\circ C$  and 82 cmHg pressure. (1985)
  - A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm at  $27^\circ C$ . If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up. (1987)
  - The average speed at  $T_1$  (in kelvin) and the most probable speed at  $T_2$  (in kelvin) of  $CO_2$  gas is  $9.0 \times 10^4\text{ cm s}^{-1}$ . Determine  $I_1$  and  $I_2$ . (1990)
  - At room temperature the following reactions proceed nearly to completion:
- $$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$$
- The dimer  $N_2O_4$  solidified at 262 K. A 250 mL flask and a 100 mL flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled at 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally.) (1992)
- A gas bulb of 1 litre capacity contains  $2.0 \times 10^{21}$  molecules of nitrogen exerting a pressure of  $7.57 \times 10^3\text{ N m}^{-2}$ . Calculate the root mean square (rms) speed and the temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.84, calculate the most probable speed for these molecules at this temperature. (1993)
  - An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weights 29.0 kg and shows a pressure of 2.5 atm. In the course of use at  $27^\circ C$ , the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of  $0^\circ C$ . (1994)

17. The composition of the equilibrium mixture ( $\text{Cl}_2 \rightleftharpoons 2 \text{ Cl}$ ), which is attained at  $1200^\circ\text{C}$ , is determined by measuring the rate of effusion through a pinhole. It is observed that at  $1.80 \text{ mmHg}$  pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Relative atomic mass of Kr = 84.) (1995)
18. A mixture of ethane ( $\text{C}_2\text{H}_6$ ) and ethene ( $\text{C}_2\text{H}_4$ ) occupies 40 litres at  $1.00 \text{ atm}$  and  $400 \text{ K}$ . The mixture reacts completely with  $130 \text{ g}$  of  $\text{O}_2$  to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Assuming ideal gas behaviour, calculate the mole fractions of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  in the mixture. (1995)
19. A  $4 : 1$  molar mixture of He and  $\text{CH}_4$  is contained in a vessel at  $20 \text{ bar}$  pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (1994)
20. An evacuated glass vessel weighs  $50.0 \text{ g}$  when empty,  $148.0 \text{ g}$  when filled with a liquid of density  $0.98 \text{ g mL}^{-1}$  and  $50.5 \text{ g}$  when filled with an ideal gas at  $760 \text{ mmHg}$  at  $300 \text{ K}$ . Determine the molar mass of the gas. (1998)
21. Using van der Waals equation, calculate the constant  $a$  when two moles of a gas confined in a four-litre flask exerts a pressure of  $11.0 \text{ atm}$  at a temperature of  $300 \text{ K}$ . The value of  $b$  is  $0.05 \text{ L mol}^{-1}$ . (1998)
22. The degree of dissociation is 0.4 at  $400 \text{ K}$  and  $1.0 \text{ atm}$  for the gaseous reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at  $400 \text{ K}$  and  $1 \text{ atm}$ . (Relative atomic mass of P = 31.0 and that of Cl = 35.5.) (1998)
23. One mole of nitrogen gas at  $0.8 \text{ atm}$  takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at  $1.6 \text{ atm}$  takes 57 s to diffuse through the same hole. Determine the molecular formula of the compound. (1999)
24. The pressure exerted by  $12 \text{ g}$  of an ideal gas at temperature  $t$  (expressed in  $^\circ\text{C}$ ) in a vessel of volume  $V$  (expressed in litre) is one atm. When the temperature is increased by 10 degree Celsius at the same volume, the pressure increases by 10%. Calculate the temperature  $t$  and volume  $V$ . (Relative molar mass of the gas = 120.) (1999)
25. At room temperature, ammonia gas at  $1 \text{ atm}$  pressure and hydrogen chloride gas at the pressure  $p$  are allowed to effuse through identical pin holes from opposite ends of a glass tubes of  $1 \text{ m}$  length and of uniform cross-section. Ammonia chloride is first formed at a distance  $60 \text{ cm}$  from the end through which HCl gas is sent in. What is the value of pressure  $p$ ? (1982)
26. Calculate the volume occupied by  $5.0 \text{ g}$  of acetylene gas at  $50^\circ\text{C}$  and  $740 \text{ mmHg}$  pressure. (1991)
27. At  $27^\circ\text{C}$ , hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of  $\text{H}_2$  is leaked through the same hole for 20 minutes. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molar mass of the unknown gas? (1992)
28. Calculate the pressure exerted by one mole of  $\text{CO}_2$  gas at  $273 \text{ K}$  if the van der Waals constant  $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$ . Assume that the volume occupied by  $\text{CO}_2$  molecules is negligible. (2000)
29. The compression factor (compressibility factor) for one mole of a van der Waals gas at  $0^\circ\text{C}$  and  $100 \text{ atm}$  pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant  $a$ . (2001)
30. The density of the vapour of a substance at  $1 \text{ atm}$  pressure and  $500 \text{ K}$  is  $0.36 \text{ kg m}^{-3}$ . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.
- Determine (i) molecular weight, (ii) molar volume, (iii) compression factor ( $Z$ ) of the vapour and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive?
  - If the vapour behaves ideally at  $1000 \text{ K}$ , determine the average translational kinetic energy of a molecule. (2002)
31. The root mean square speed of molecules of gas is  $434 \text{ m s}^{-1}$ . What will be their average speed? (2003)

**ANSWERS****Straight Objective Type**

- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (b)  | 3. (a)  | 4. (b)  | 5. (b)  | 6. (d)  |
| 7. (a)  | 8. (b)  | 9. (b)  | 10. (c) | 11. (b) | 12. (a) |
| 13. (d) | 14. (a) | 15. (d) | 16. (c) | 17. (b) | 18. (b) |
| 19. (d) | 20. (c) | 21. (c) | 22. (c) | 23. (b) | 24. (b) |
| 25. (c) | 26. (d) | 27. (c) | 28. (b) | 29. (c) | 30. (d) |
| 31. (b) | 32. (c) | 33. (c) |         |         |         |

**Multiple Correct-Choice Type**

- |                  |                  |
|------------------|------------------|
| 1. (a), (b)      | 2. (a), (b), (c) |
| 3. (a), (c), (d) | 4. (a), (c), (d) |

**Fill-in-the-Blanks Type**

1.  $E = (3/2) (RT) = (3/2) (1.987 \text{ cal K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \approx 900 \text{ cal mol}^{-1}$
2. Gas constant  $R (= 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$
3. 1:16
4.  $5.6 \text{ L}/(22.4 \text{ L mol}^{-1}) = 0.25 \text{ mol}$
5. greater
6. glass

**Integer Answer Type**

1. 4      2. 7

**True/False Type**

1. True      2. False      3. False      4. True      5. False      6. False

**Linked Comprehension Type**

1. (c)      2. (d)

**Reasoning Type**

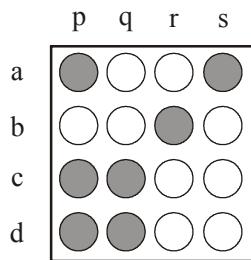
1. (a)      2. (b)

**Matching Type**

1. (a) – (s); (b) – (r); (c) – (q); (d) – (p)

**Matrix Match Type**

1. The correct-bubbled diagram is as follows.



### Short Answer Type

1. For one mole of a van der Waal gas, we have

$$\begin{aligned}
 \left( p + \frac{a}{V^2} \right) (V - b) &= RT \\
 \left( p + \frac{a}{V^2} \right) &= \frac{RT}{V - b} \\
 &= RT(V - b)^{-1} = \frac{RT}{V} \left( 1 - \frac{b}{V} \right)^{-1} \\
 &= \frac{RT}{V} \left[ 1 + \frac{b}{V} + \left( \frac{b}{V} \right)^2 + \dots \right] \\
 \text{or } pV &= RT \left[ 1 + \left( b - \frac{a}{RT} \right) \frac{1}{V} + \left( \frac{b}{V} \right)^2 + \dots \right]
 \end{aligned}$$

Thus, the expression for  $B$  is

$$B = b - \frac{a}{RT}$$

2. Helium is monatomic. If heat is given to helium gas, it is used only to increase its kinetic energy ( $= 3RT/2$ ). Hence,  $C_V = 3R/2$ . Hydrogen is diatomic. Heat given to hydrogen gas is used in increasing its kinetic energy, rotational energy and vibrational energy.

At low temperature, only kinetic energy is increased ( $= 3RT/2$ ). Hence,  $C_V = 3R/2$ .

At moderate temperature, both kinetic and rotational energies are increased ( $= 3RT/2 + RT$ ). Hence,  $C_V = 5R/2$ .

At high temperature, all the three energies, namely, kinetic, rotational and vibrational, are increased. Hence,  $C_V > 5R/2$ .

### Subjective Type

1.  $0.00342 \text{ g mL}^{-1}$
2.  $41.33 \text{ g mol}^{-1}$
3.  $0.434 \text{ mol}$
4.  $12.15 \text{ g mol}^{-1}$
5.  $81.1 \text{ cm}$
6.  $1.236 : 1$
7.  $3743 \text{ J mol}^{-1}$
8.  $2.90 \times 10^{-8} \text{ cm}$
9.  $2.686 \times 10^{10}$
10.  $1 : 3$
11.  $390.3 \text{ m s}^{-1}$
12. 10
13.  $T_1 = 1682.5 \text{ K}; T_2 = 2143.4 \text{ K}$
14.  $0.221 \text{ atm}$
15.  $415.14 \text{ m s}^{-1}$
16.  $V = 2.463 \text{ m}^3; p = 2.5 \text{ atm}$
17. 0.1374
18.  $x(\text{C}_2\text{H}_6) = 0.274; x(\text{C}_2\text{H}_4) = 0.726$
19.  $\text{He} : \text{CH}_4 :: 8 : 1$
20.  $123 \text{ g mol}^{-1}$

21.  $6.46 \text{ L}^2 \text{ atm mol}^{-2}$
22.  $4.54 \text{ g dm}^{-3}$
23.  $\text{XeF}_6$
24.  $t = -173^\circ\text{C}; V = 0.82 \text{ L}$
25.  $p = 2.20 \text{ atm}$
26.  $5.23 \text{ dm}^3$
27.  $1033 \text{ g mol}^{-1}$
28.  $100.601 \text{ kPa}$
29.  $1.2528 \text{ L}^2 \text{ atm mol}^{-2}$
30. (a) (i)  $18.09 \text{ g mol}^{-1}$  (ii)  $50.25 \text{ dm}^3 \text{ mol}^{-1}$   
 (iii) 1.22 (iv) Repulsive forces  
 (b)  $2.07 \times 10^{-20} \text{ J}$
31.  $399.8 \text{ m s}^{-1}$

## HINTS AND SOLUTIONS

### Straight Objective Type

1.  $n(\text{CH}_4) = m/(16 \text{ g mol}^{-1}); n(\text{O}_2) = m/(32 \text{ g mol}^{-1})$

$$\frac{P_{\text{O}_2}}{P} = \frac{(m/32 \text{ g mol}^{-1})}{(m/16 \text{ g mol}^{-1}) + (m/32 \text{ g mol}^{-1})} = \frac{(1/32)}{(1/16) + (1/32)} = \frac{16}{32+16} = \frac{1}{3}$$

2. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is known as Boyle temperature.

3.  $c_{\text{rms}} = \sqrt{3RT/M}$  and  $c_{\text{av}} = \sqrt{8RT/\pi M}$ . Hence

$$\frac{c_{\text{rms}}}{c_{\text{av}}} = \sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3 \times 3.14}{8}} = \sqrt{\frac{9.42}{8}} = \sqrt{1.165} = 1.086$$

4. The average molar kinetic energy of a gas is given by  $(3/2)RT$ . It is independent of the molar mass of the gas.

5. The molecules of an ideal gas do not exert force of attraction on each other.

6. Rate of diffusion of a gas is inversely proportional to the square root of its molar mass.

7. The expression of average speed is  $c_{\text{av}} = \sqrt{8RT/\pi M}$ . For two temperatures, we have

$$\frac{c_2}{c_1} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{927 + 273}{27 + 273}} = \sqrt{\frac{1200}{300}} = 2$$

$$c_2 = 2c_1 = 2(0.3 \text{ m s}^{-1}) = 0.6 \text{ m s}^{-1}$$

8. The intermolecular force between gaseous molecules is taken care by the van der Waals constant  $a$ .

9. Since  $c_{\text{rms}} = \sqrt{3RT/M}$ , larger the molar mass, lesser the speed and hence lesser the distance covered. Since  $M(\text{HCl}) < M(\text{NH}_3)$ , the ammonium chloride ring will be formed near the hydrogen chloride bottle.

10. Larger the value of van der Waals constant  $a$ , more easily the liquefaction of gas occurs.

11. For an ideal gas  $pV = nRT = (m/M)RT \Rightarrow psM = \rho RT$ , i.e.  $\rho = pM/RT$ .

Hence  $\rho_{(A)} = (M/R)(1 \text{ atm}/273 \text{ K}); \rho_{(B)} = (M/R)(2 \text{ atm}/273 \text{ K});$

$\rho_{(C)} = (M/R)(1 \text{ atm}/546 \text{ K})$

$\rho_{(D)} = (M/R)(2 \text{ atm}/546 \text{ K})$

The density will be highest for the choice b.

12.  $\frac{r(\text{CH}_4)}{r(\text{X})} = 2 = \sqrt{\frac{M(\text{X})}{M(\text{CH}_4)}}$ . Hence,  $M(\text{X}) = 4 M(\text{CH}_4) = 4 \times 16 \text{ g mol}^{-1} = 64 \text{ g mol}^{-1}$ .

13. The mean kinetic energy of the molecules is proportional to the kelvin temperature.

14. The pressure of a gas increases with increase in temperature. This is due to increase in molecular speeds of gaseous molecules, as this results into increase in molecular collisions with sides of the vessel.

15.  $n(\text{C}_2\text{H}_6) = m/(30 \text{ g mol}^{-1})$ ;  $n(\text{H}_2) = m/(2 \text{ g mol}^{-1})$

$$\frac{p(\text{H}_2)}{p(\text{H}_2) + p(\text{C}_2\text{H}_6)} = \frac{n(\text{H}_2)}{n(\text{H}_2) + n(\text{C}_2\text{H}_6)} = \frac{m/2}{(m/2) + (m/30)} = \left(\frac{1}{2}\right) \left(\frac{60}{32}\right) = \frac{30}{32} = \frac{15}{16}$$

16.  $\frac{u_{\text{rms}}(\text{H}_2)}{u_{\text{rms}}(\text{O}_2)} = \left[ \frac{T(\text{H}_2)}{M(\text{H}_2)} \frac{M(\text{O}_2)}{T(\text{O}_2)} \right]^{1/2} = \left[ \left(\frac{50}{2}\right) \left(\frac{32}{800}\right) \right]^{1/2} = 1$

17.  $\frac{t_2}{t_1} = \left(\frac{M_2}{M_1}\right)^{1/2}$ . For the choice a,  $t_2/t_1 = \sqrt{2}$ , for the choice b,  $t_2/t_1 = 4$ . For the choice c,  $t_2/t_1 = \sqrt{14}$ . For

the choice d,  $t_2/t_1 = \sqrt{22}$ .

18. For an ideal gas, the compression factor is equal to one.

19. Water has dipole moment. Because of hydrogen bonding, its  $T_c$  is larger.

20.  $\frac{r_A}{r_B} = \left(\frac{P_A}{P_B}\right) \left(\frac{M_B}{M_A}\right)^{1/2}$ . The first term is measure of its concentration and the second term is due to Graham's law of diffusion.

21.  $\frac{u_{\text{rms}}(\text{H}_2)}{u_{\text{rms}}(\text{N}_2)} = \sqrt{7} \Rightarrow \left[ \frac{T(\text{H}_2)}{M(\text{H}_2)} \frac{M(\text{N}_2)}{T(\text{N}_2)} \right]^{1/2} = \sqrt{7}$ .

Hence,  $\frac{T(\text{H}_2)}{T(\text{N}_2)} = 7 \frac{M(\text{H}_2)}{M(\text{N}_2)} = 7 \left(\frac{2}{28}\right) = \frac{1}{2}$

22. High temperature and low pressure conditions favour a gas to behave ideally.

23. The compression factor of a real gas is defined as  $Z = V_{\text{m, real}}/V_{\text{m, ideal}}$ . Hence,  
 $V_{\text{m, real}} < V_{\text{m, ideal}} (= 22.4 \text{ L})$

24.  $n(\text{CH}_4) = m/(16 \text{ g mol}^{-1})$ ;  $n(\text{H}_2) = m/(2 \text{ g mol}^{-1})$

$$\frac{p(\text{H}_2)}{p(\text{H}_2) + p(\text{CH}_4)} = \frac{n(\text{H}_2)}{n(\text{H}_2) + n(\text{CH}_4)} = \frac{m/2}{(m/2) + (m/16)} = \left(\frac{1}{2}\right) \left(\frac{16}{9}\right) = \frac{8}{9}$$

25. By definition,  $\rho = m/V$ . For the same mass of the substance, we have

$$\frac{\rho_1}{\rho_v} = \frac{V_v}{V_1}$$

or  $V_1 = \left(\frac{\rho_v}{\rho_1}\right) V_v = \left(\frac{0.0006}{1}\right) (10^3 \text{ cm}^3) = 0.6 \text{ cm}^3$

26. The expression of root mean square speed is

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV_m}{M}} = \sqrt{\frac{3p}{MV_m}} = \sqrt{\frac{3p}{\rho}}$$

27.  $V_2 = \left(\frac{V_1}{T_1}\right) T_2 = \left(\frac{22.4 \text{ L}}{273 \text{ K}}\right) (373 \text{ K}) = 30.6 \text{ L}$

28. Negative deviation means  $pV/nRT < 1$ . This is possible when the term  $nb$  is negligible in comparison to the volume of the gas. In this situation, van der Waals gas is reduced to

$$\left(p + \frac{n^2 a}{V^2}\right)(V) = nRT \quad \text{or} \quad \frac{pV}{nRT} = 1 - \frac{na}{VRT}$$

Hence, it is the constant  $a$  (which measures the attraction between molecules) responsible for making  $pV/nRT < 1$ .

29. The expression are

$$u_{\text{rms}} = \sqrt{3RT/M} \quad \text{and} \quad E = 3/2 RT$$

Hence,  $u_{\text{rms}} = \left[\left(\frac{3RT}{2}\right) \left(\frac{2}{M}\right)\right]^{1/2} = \sqrt{\frac{2E}{M}}$

30. The relative molar masses of methane and helium are 16 and 4, respectively. Hence

$$\frac{r_{\text{CH}_4}}{r_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_{\text{CH}_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

31. The van der Waals constants  $a$  and  $b$  accounts for the forces of attraction amongst gaseous molecules and volume occupied by 1 mol of gaseous molecules, respectively. The van der Waals equation is

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

The term  $n^2 a/V^2$  accounts for the pressure effects due to molecular attractions.

32. For one mole of a gas, the van der Waals equation is  $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

When  $b = 0$ , we have  $\left(p + \frac{a}{V^2}\right)V = RT$  i.e.  $pV = RT - \frac{a}{V}$

The plot of  $pV$  versus  $1/V$  will be a straight line with slope equal to  $-a$ . Hence

Slope of the given straight line is  $\frac{(20.1 - 21.6) \text{ L atm mol}^{-1}}{(3.0 - 2.0) \text{ mol L}^{-1}} = -1.5 \text{ L}^2 \text{ atm mol}^{-2}$

Equating this to  $-a$ , we get  $a = 1.5 \text{ L}^2 \text{ atm mol}^{-2}$

33. From the given equation of state, it follows that there exists no interatomic attractions. Thus, the potential energy remains zero till the two atoms touch each other, thereafter the potential energy will increase steeply as the distance between the two atoms cannot be decreased further.

### Multiple Correct-Choice Type

1. The pressure of a gas decreases with increase in volume at constant temperature. The average kinetic energy of the molecules also remains constant at a constant temperature.
2. The van der Waals equation of state is

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

When  $a$  is negligible, then

$$Z = \frac{pV_m}{RT} = 1 + \frac{b}{RT} p$$

that is,  $Z$  increases with increase in  $p$ .

When  $b$  is negligible, then

$$Z = \frac{pV_m}{RT} = 1 - \frac{b}{VRT}$$

Increase in  $p$  implies decrease in  $V$ , which in turn, implies increase in the value of  $a/VRT$  and hence decrease in the value of  $Z$ .

The curve IV is applicable provided temperature of the gas is near but larger than its critical temperature.

3. At larger molar volume, molecules will be far apart with negligible intermolecular interactions. Moreover, the volume occupied by molecules will be negligible in comparison to the molar volume. These facts leads to ideal-gas behaviour (choice a).

The van der Waals constants characterize a real gas and are independent of temperature (choice b). In the equation  $(p + a/V^2)(V - b) = RT$ , the term  $p + a/V^2$  corresponds to ideal-gas pressure. Hence,  $p_{\text{real}} < p_{\text{ideal}}$  (choice d).

4. The three statements (a), (c) and (d) hold good in the kinetic theory of gases.

For momentum, we have

$$p = mv = m\sqrt{3kT/m} = \sqrt{3mkT}$$

Though momentum depends on  $m$ , but the rate of change of momentum will be independent of  $m$ .

## Fill-in-the-Blanks Type

### Integer Answer Type

1. Root mean square speed =  $\sqrt{\frac{3RT}{M}}$

Most probable speed =  $\sqrt{\frac{2RT}{M}}$

Hence,  $\left(\frac{3R(400\text{ K})}{40\text{ g mol}^{-1}}\right)^{1/2} = \left(\frac{2R(60\text{ K})}{M}\right)^{1/2}$

This gives  $M = \frac{2(60)(40)}{3(400)} \text{ g mol}^{-1} = 4 \text{ g mol}^{-1}$

Therefore, the correct answer is 4.

2. For the piston to be at equilibrium position, the pressure in the vessel must be equal to the external pressure, i.e. 1 atm. The partial pressure of unknown compound will be equal to its vapour pressure. Hence, the partial pressure of helium will be

$$p_{\text{He}} = 1 \text{ atm} - 0.68 \text{ atm} = 0.32 \text{ atm}$$

The volume of the vessel for  $n = 0.1$  mol of helium at  $0^\circ\text{C}$  and 0.32 atm would be

$$\begin{aligned}
 V &= \frac{nRT}{p} \\
 &= \frac{(0.1 \text{ mol})(0.082 \text{ L atm K}^{-1}\text{mol}^{-1})(273 \text{ K})}{(0.32 \text{ atm})} \\
 &\approx 7 \text{ L}
 \end{aligned}$$

### True/False Type

2. Kinetic energy is  $(3/2) kT$  where  $T$  at  $0^\circ\text{C}$  is 273.15 K.
5. The constant  $a$  reflects the intermolecular attractions between gaseous molecules. The constant  $b$  reflects the actual volume of one mole of gaseous molecules.
6. An ideal gas cannot be liquefied as there exists no intermolecular attractions.

### Linked Comprehension Type

1. According to Graham's law, the rates of diffusion of the two gases is related to each other through the expression

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow \frac{d/t}{(24 \text{ cm} - d)/t} = \sqrt{\frac{40}{10}}$$

or  $\frac{d}{24 \text{ cm} - d} = 2$ . This gives  $d = 16 \text{ cm}$ .

2. The expression of collision frequency between the molecules of Gas 1 and Gas 2 is

$$Z_{12} = \pi \sigma_{12}^2 \bar{u} N_1^* N_2^* = \pi \sigma_{12}^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2} N_1^* N_2^*$$

where  $\sigma_{12} (= (\sigma_1 + \sigma_2)/2)$  is the molecular collision diameter,  $N_1^*$  and  $N_2^*$  are the respective number of molecules per unit volume and  $\mu$  is the reduced mass. The latter is given as

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{M_1 M_2}{(M_1 + M_2)} \frac{1}{N_A}$$

For the gases X and inert gas (molar mass  $M$ ), the reduced mass is

$$\mu_X = \frac{M_X M}{(M_X + M)} \frac{1}{N_A}$$

For the gases Y and inert gas, we have

$$\mu_Y = \frac{M_Y M}{(M_Y + M)} \frac{1}{N_A}$$

It can be shown that  $\mu_X < \mu_Y$ . Thus the collision frequency of X with inert gas will be larger than that between Y and inert gas.

The mean free path is

$$\lambda = \frac{1}{\pi \sigma_{12}^2 N_1^* N_2^*}$$

It follows that the mean free path is independent of molar masses.

### Matrix Match Type

1. (a) Hydrogen gas at  $P = 200 \text{ atm}$  and  $T = 273 \text{ K}$  has compression factor greater than 1 (choice p) and in van der Waals equation, the term  $n^2 a/V^2$  is negligible in comparison to high pressure (choice s).

- (b) Hydrogen gas at  $P \rightarrow 0$  and  $T = 273$  K behaves as an ideal gas (choice r).
- (c)  $\text{CO}_2$  at  $P = 1$  atm and  $T = 273$  K has compression factor lesser than 1 (choice p) and attractive forces are dominant (choice q), since the gas can be easily liquefiable.
- (d) Real gas with very large volume will have compression factor not equal to 1 (choice p). In van der Waals equation, the factor  $nb$  will be negligible in comparison to  $V$  but not the factor  $n^2 a/V^2$  in comparison to  $p$ . Hence, attractive forces will be dominant (choice q).

## Subjective Type

1. We have

$$pV = nRT \Rightarrow pV = (m/M) RT \Rightarrow pM = (m/V) RT = \rho RT$$

Hence

$$\begin{aligned}\rho &= \frac{pM}{RT} = \frac{(5 \text{ atm})(17 \text{ g mol}^{-1})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})} = 3.42 \text{ g L}^{-1} \\ &= 0.00342 \text{ g mL}^{-1}\end{aligned}$$

2. For the same values of  $p$  and  $V$ , we have

$$n_1 T_1 = n_2 T_2 \quad \text{i.e.} \quad n_1 = n_2 (T_2/T_1)$$

$$\text{This gives} \quad n_1 = \left( \frac{0.184 \text{ g}}{2 \text{ g mol}^{-1}} \right) \left( \frac{290.15 \text{ K}}{298.15 \text{ K}} \right) = 0.08953 \text{ mol}$$

$$M_1 = \frac{m_1}{n_1} = \frac{3.7 \text{ g}}{0.08953 \text{ mol}} = 41.33 \text{ g mol}^{-1}$$

3. Molar mass of the mixture is

$$\begin{aligned}M_{\text{mix}} &= (\text{vapour density}) (2 \text{ g mol}^{-1}) \\ &= (38.3) (2 \text{ g mol}^{-1}) = 76.6 \text{ g mol}^{-1}\end{aligned}$$

Let  $x$  be the mass of  $\text{NO}_2$  in the mixture. Then

$$\text{Amount of } \text{NO}_2 = \frac{x}{46 \text{ g mol}^{-1}}$$

$$\text{Amount of } \text{N}_2\text{O}_4 = \frac{100 \text{ g} - x}{92 \text{ g mol}^{-1}}$$

$$\text{Amount fraction of } \text{NO}_2, x_1 = \frac{x/46}{(x/46)+(100 \text{ g} - x)/92} = \frac{2x}{100 \text{ g} + x}$$

$$\text{Amount fraction of } \text{N}_2\text{O}_4, x_2 = \frac{100 \text{ g} - x}{100 \text{ g} + x}$$

The average molar mass of the mixture is given by

$$x_1 M_1 + x_2 M_2 = M_{\text{av}}$$

$$\text{i.e.} \quad \left( \frac{2x}{100 \text{ g} + x} \right) (46 \text{ g mol}^{-1}) + \left( \frac{100 \text{ g} - x}{100 \text{ g} + x} \right) (92 \text{ g mol}^{-1}) = 76.6 \text{ g mol}^{-1}$$

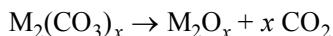
$$\text{Solving for } x, \text{ we get} \quad x = \frac{100 \times 92}{76.69} \text{ g} = 19.96 \text{ g}$$

$$\text{Amount of } \text{NO}_2 \text{ in the mixture} = \frac{19.96 \text{ g}}{46 \text{ g mol}^{-1}} = 0.434 \text{ mol}$$

4. The amount of  $\text{CO}_2$  gas evolved is

$$n = \frac{pV}{RT} = \frac{\{(700/760)\text{ atm}\}(1.336 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 0.05 \text{ mol}$$

The decomposition reaction may be represented as



$$\text{Mass of } \text{CO}_2 \text{ evolved} = (0.05 \text{ mol}) (44 \text{ g mol}^{-1}) = 2.2 \text{ g}$$

$$\begin{aligned} \text{Mass of } \text{M}_2\text{O}_x &= \text{Mass of } \text{M}_2(\text{CO}_3)_x - \text{Mass of } \text{CO}_2 \text{ evolved} \\ &= 4.215 \text{ g} - 2.2 \text{ g} = 2.015 \text{ g} \end{aligned}$$

From the decomposition reaction, this mass will be given by the expression

$$[2M + x(16 \text{ g mol}^{-1})] \left[ \frac{0.05 \text{ mol}}{x} \right] = 2.015 \text{ g}$$

$$\text{This gives } \frac{M}{x} = 12.15 \text{ g mol}^{-1}$$

which is the equivalent mass of the metal M.

5. Let the distance  $PX = x$ . The distance  $PY = 200 \text{ cm} - x$ . Since the rate of diffusion is inversely proportional to the square root of molar mass, we will get

$$\frac{x}{200 \text{ cm} - x} = \sqrt{\frac{17}{36.5}} = 0.6825$$

$$\text{Solving for } x, \text{ we get } x = \frac{(200 \text{ cm})(0.6825)}{1+0.6825} = 81.1 \text{ cm}$$

6. Since the mixture contains 1:1 molar ratio of oxygen and another gas, partial pressures of oxygen and the second gas would be 2000 mmHg and 2000 mmHg, respectively. Now in 74 min, the decrease in partial pressure of oxygen would be

$$-\Delta p_{\text{O}_2} = \frac{(2000 - 1500) \text{ mmHg}}{47 \text{ min}} \times 74 \text{ min} = 787.2 \text{ mmHg}$$

Hence, Partial pressure of oxygen at the end of 74 min =  $(2000 - 787.2)$  mmHg = 1212.8 mmHg

$$\text{Now, the ratio of rate of diffusion would be } \frac{r_2}{r_1} = \sqrt{\frac{32}{79}} = 0.6364$$

$$\text{Thus } -\Delta p_{\text{unknown gas}} = (0.6364)(787.2 \text{ mmHg}) = 501 \text{ mmHg}$$

Partial pressure of unknown gas at the end of 74 min =  $(2000 - 501)$  mmHg = 1499 mmHg

Now since the amount of the gas remaining will be directly proportional to its partial pressure, we would have

$$\frac{n_2}{n_1} = \frac{1499}{1212.8} = \frac{1.236}{1}$$

7. We have

$$\text{Average kinetic energy of the gas} = \frac{3}{2} RT = \left(\frac{3}{2}\right) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300.15 \text{ K}) = 3743 \text{ J mol}^{-1}.$$

8. Volume of one atom of Hg is

$$v = \frac{\text{mass of one atom}}{\text{density}} = \frac{(200 \text{ g mol}^{-1}) / (6.023 \times 10^{23} \text{ mol}^{-1})}{13.6 \text{ g cm}^{-3}} = 2.44 \times 10^{-23} \text{ cm}^3$$

As each atom occupies a cube of edge length equal to the diameter of the Hg atom, we will have

$$d^3 = 2.44 \times 10^{-23} \text{ cm}^3$$

$$\text{or } d = (2.44 \times 10^{-23} \text{ cm}^3)^{1/3} = 2.90 \times 10^{-8} \text{ cm.}$$

9. Using the expression  $pV = nRT$ , we have

$$n = \frac{pV}{RT} = \frac{\{(7.6 \times 10^{-10} / 760) \text{ atm}\} (1 \text{ L})}{(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})} = 4.459 \times 10^{-14} \text{ mol}$$

$$N = nN_A = (4.459 \times 10^{-14} \text{ mol}) (6.023 \times 10^{23} \text{ mol}^{-1}) = 2.686 \times 10^{10}.$$

10. Since  $pV = nRT$ , we have

$$pV = RT \quad \text{or} \quad M = \frac{mRT}{pV}$$

$$\text{Hence, } M_A = \frac{(2 \text{ g})RT}{(1 \text{ atm})V} \quad \text{and} \quad M_B = \frac{(3 \text{ g})RT}{(0.5 \text{ atm})V}$$

$$\text{Thus, } \frac{M_A}{M_B} = \left(\frac{2}{1}\right)\left(\frac{0.5}{3}\right) = \frac{1}{3}.$$

11. We have

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}{(0.048 \text{ kg mol}^{-1})}}^{1/2} = 390.3 \text{ m s}^{-1}.$$

12. We have,

$$\text{Volume of balloon} = \frac{4}{3} \pi r^3 = \left(\frac{4}{3}\right) \left(\frac{22}{7}\right) \left(\frac{21 \text{ cm}}{2}\right)^3 = 4851 \text{ cm}^3$$

Total volume of the gas available at STP conditions is

$$V = \frac{p_1 V_1}{T_1} \frac{T_0}{p_0} = \frac{(20 \text{ atm})(2.82 \text{ L})}{(300 \text{ K})} \left(\frac{273 \text{ K}}{1 \text{ atm}}\right) = 51.324 \text{ L} = 51324 \text{ cm}^3$$

When the balloons are being filled, the pressure in the cylinder will decrease. We can continue filling from the cylinder till the pressure within the cylinder is also 1 atm. At this stage, the volume of  $2820 \text{ cm}^3$  of the gas will remain within the cylinder.

$$\begin{aligned} \text{Hence, } & \text{Volume of the gas which can be transferred to balloons will be} \\ & = 51324 \text{ cm}^3 - 2820 \text{ cm}^3 = 48504 \text{ cm}^3 \end{aligned}$$

$$\text{Number of balloons that can be filled up} = \frac{48504 \text{ cm}^3}{4851 \text{ cm}^3/\text{balloon}} = 10 \text{ balloons.}$$

13. We have  $u_{av} = \sqrt{\frac{8RT}{\pi M}}$

Hence,  $\sqrt{\frac{8RT_1}{\pi M}} = 9.0 \times 10^4 \text{ cm s}^{-1}$

or  $T_1 = (9.0 \times 10^2 \text{ m s}^{-1})^2 \left( \frac{\pi M}{8R} \right)$

$$= (9.0 \times 10^2 \text{ m s}^{-1})^2 \left[ \frac{(3.14)(44 \times 10^{-3} \text{ kg mol}^{-1})}{(8)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \right] = 1682.5 \text{ K}$$

For most probable speed, we have

$$\sqrt{\frac{2RT_2}{\pi M}} = 9.0 \times 10^2 \text{ m s}^{-1}$$

Hence,  $T_2 = (9.0 \times 10^2 \text{ m s}^{-1})^2 \left( \frac{M}{2R} \right)$

$$= (9.0 \times 10^2 \text{ m s}^{-1})^2 \left[ \frac{44 \times 10^{-3} \text{ kg mol}^{-1}}{(2)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \right] = 2143.4 \text{ K}$$

14. To start with, we have

$$\text{Amount of nitric oxide} = \frac{pV}{RT} = \frac{(1.053 \text{ atm})(0.250 \text{ L})}{(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 0.01069 \text{ mol}$$

$$\text{Amount of oxygen} = \frac{pV}{RT} = \frac{(0.789 \text{ atm})(0.100 \text{ L})}{(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 3.203 \times 10^{-3} \text{ mol}$$

According to the reaction  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ , 1 mol of  $\text{O}_2$  reacts with 2 mol of NO. Thus, after the reaction, we will have

$$\text{Amount of oxygen} = 0$$

$$\text{Amount of nitric oxide} = (0.01069 - 2 \times 0.0032) \text{ mol} = 4.283 \times 10^{-3} \text{ mol}$$

$$\text{Amount of N}_2\text{O}_4 \text{ formed} = 3.203 \times 10^{-3} \text{ mol}$$

Now on cooling,  $\text{N}_2\text{O}_4(\text{g})$  is condensed. Thus, only nitric oxide will be present in the entire volume of 0.350 L. Hence,

$$\begin{aligned} \text{Pressure of the gas} &= \frac{nRT}{V} = \frac{(4.283 \times 10^{-3} \text{ mol})(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1})(220 \text{ K})}{(0.350 \text{ L})} \\ &= 0.221 \text{ atm.} \end{aligned}$$

15. We are given that

$$V = 1 \text{ L} \equiv 1 \text{ dm}^3 \equiv 10^{-3} \text{ m}^3; \quad N = 2.0 \times 10^{21}$$

$$p = 7.57 \times 10^3 \text{ N m}^{-2}$$

$$T = ?; \quad c_{\text{rms}} = ?; \quad c_{\text{mp}}/c_{\text{rms}} = 0.84; \quad c_{\text{mp}} = ?$$

Now Amount of gas =  $\frac{2.0 \times 10^{21}}{6.023 \times 10^{23} \text{ mol}^{-1}}$

Using ideal gas equation, we get

$$T = \frac{pV}{nR} = \frac{(7.57 \times 10^3 \text{ N m}^{-2})(10^{-3} \text{ m}^3)}{(2.0 \times 10^{21}/6.023 \times 10^{23} \text{ mol}^{-1})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} = 274.2 \text{ K}$$

Now  $c_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \left[ \frac{3(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(274.2 \text{ K})}{28 \times 10^{-3} \text{ kg mol}^{-1}} \right]^{1/2} = 494.22 \text{ m s}^{-1}$   
 $c_{\text{mp}} = (0.84)(494.22 \text{ ms}^{-1}) = 415.14 \text{ m s}^{-1}$ .

16. Mass of gas used up =  $(29.0 - 23.2) \text{ kg} = 5.8 \text{ kg}$

Molar mass of *n*-butane ( $\text{C}_4\text{H}_{10}$ ) =  $58 \text{ g mol}^{-1}$

$$\text{Amount of gas used up} = \frac{5.8 \times 10^3 \text{ g}}{58 \text{ g mol}^{-1}} = 10^2 \text{ mol}$$

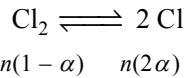
Using ideal gas equation,  $V = nRT/p$ , we get

$$V = \frac{(10^2 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{1 \text{ atm}} \quad (\text{For normal usage, } p = 1 \text{ atm})$$

$$= 2463 \text{ L} = 2463 \text{ dm}^3 = 2.463 \text{ m}^3.$$

*Final Pressure Inside the Cylinder* The cylinder contains liquefied petroleum gas in equilibrium with its vapours. So long liquid remains present, the pressure inside the cylinder remains constant. Since the cylinder contains 8.4 kg (= 23.2 kg – 14.8 kg) of the remaining LPG, the pressure inside the cylinder would be 2.5 atm.

17. Let the initial amount of  $\text{Cl}_2$  be  $n$ . If  $\alpha$  is the fraction of  $\text{Cl}_2$  dissociated at equilibrium, we will have



Total amount of species at equilibrium,  $n_{\text{total}} = n_{\text{Cl}_2} + n_{\text{Cl}} = n(1 - \alpha) + n(2\alpha) = n(1 + \alpha)$

$$\text{Average molar mass of the mixture at equilibrium, } (M_{\text{av}})_{\text{mix}} = \frac{n M_{\text{Cl}_2}}{n(1 + \alpha)} = \frac{M_{\text{Cl}_2}}{1 + \alpha}$$

According to Graham's law of diffusion, we get

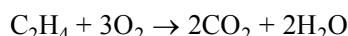
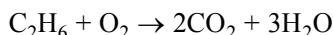
$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \left[ \frac{M_{\text{Kr}}}{(M_{\text{av}})_{\text{mix}}} \right]^{1/2} = \left[ \frac{M_{\text{Kr}} (1 + \alpha)}{M_{\text{Cl}_2}} \right]^{1/2}$$

$$\text{or } \alpha = \left( \frac{M_{\text{Cl}_2}}{M_{\text{Kr}}} \right) \left( \frac{r_{\text{mix}}}{r_{\text{Kr}}} \right)^2 - 1 = \left( \frac{71}{84} \right) (1.16)^2 - 1 = 1.1374 - 1 = 0.1374.$$

18. Total amount of the mixture,

$$n = \frac{pV}{RT} = \frac{(1.00 \text{ atm})(4.0 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})} = 1.295 \text{ mol}$$

The combustion reactions are



Let  $x$  be the amount of  $\text{C}_2\text{H}_6$  in the mixture. As per the above equations, the amount of oxygen consumed would be

$$n(\text{O}_2) = \frac{7}{2}x + 3(1.295 \text{ mol} - x)$$

This will be equal to the given amount which is  $130 \text{ g}/32 \text{ g mol}^{-1}$ , i.e.  $(130/32) \text{ mol}$ . Hence

$$\frac{7}{2}x + 3(1.295 \text{ mol} - x) = \frac{130}{32} \text{ mol}$$

$$\text{or } \frac{7}{2}x - 3x = \left(\frac{130}{32} - 3 \times 1.295\right) \text{ mol}$$

$$\text{or } x = 2(4.0625 - 3.885) \text{ mol} = 0.355 \text{ mol}$$

$$\text{Mole fraction of C}_2\text{H}_6 = \frac{0.355}{1.295} = 0.274$$

$$\text{Mole fraction of C}_2\text{H}_4 = 1.0 - 0.274 = 0.726$$

$$19. \text{ Partial pressure of He} = \frac{4 \text{ mol}}{(4+1) \text{ mol}} \times 20 \text{ bar} = 16 \text{ bar}$$

$$\text{Partial pressure of CH}_4 = 20 \text{ bar} - 16 \text{ bar} = 4 \text{ bar}$$

If  $r_{\text{He}}$  and  $r_{\text{CH}_4}$  are the rates of effusion of He and  $\text{CH}_4$ , respectively, then

$$\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \left(\frac{p_{\text{He}}}{p_{\text{CH}_4}}\right) \left(\frac{M_{\text{CH}_4}}{M_{\text{He}}}\right)^{1/2} = \left(\frac{16}{4}\right) \left(\frac{16}{4}\right)^{1/2} = 8$$

Since the rate of effusion of He is eight times more than that of  $\text{CH}_4$ , the initial mixture issuing out will contain He and  $\text{CH}_4$  in the molar ratio of 8 : 1.

$$20. \text{ Mass of water filled in the glass vessel, } m_1 = (148.0 - 50.0) \text{ g} = 98.0 \text{ g}$$

$$\text{Volume of glass vessel, } V = \frac{m_1}{\rho} = \frac{98.0 \text{ g}}{0.98 \text{ g mol}^{-1}} = 100 \text{ mL} = 0.1 \text{ dm}^3$$

$$\text{Mass of gas filled in the vessel, } m = (50.5 - 50.0) \text{ g} = 0.5 \text{ g}$$

If  $M$  is the molar mass of the gas, we will have

$$pV = nRT = \frac{m}{M} RT$$

$$\text{or } M = \frac{mRT}{pV} = \frac{(0.5 \text{ g})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{(101.325 \text{ kPa})(0.1 \text{ dm}^3)} = 123 \text{ g mol}^{-1}$$

$$21. \text{ Substituting the given data in the van der Waals equation of state}$$

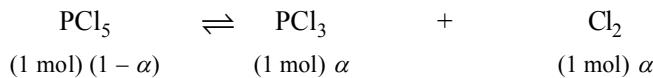
$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\text{we get } \left[11 \text{ atm} + \frac{(2 \text{ mol})^2 a}{(4 \text{ L})^2}\right] [4 \text{ L} - (2 \text{ mol})(0.05 \text{ L mol}^{-1})] \\ = (2 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})$$

$$\text{or } \left(11 \text{ atm} + \frac{a}{4} \text{ mol}^2 \text{ L}^{-2}\right)(4 \text{ L} - 0.1 \text{ L}) = 49.2 \text{ L atm}$$

$$\text{or } a = 4 \left( \frac{49.2}{3.9} \text{ atm} - 11 \text{ atm} \right) \text{ L}^2 \text{ mol}^{-2} = 4(12.615 - 11) \text{ L}^2 \text{ atm mol}^{-2} \\ = 6.46 \text{ L}^2 \text{ atm mol}^{-2}$$

**22.** If we start with 1 mol of  $\text{PCl}_5$ , we will have



$$\text{Total amount of gases} = (1 \text{ mol}) (1 + \alpha) = 1.4 \text{ mol} \quad (\text{since } \alpha = 0.4)$$

Volume of gaseous mixture would be

$$V = \frac{nRT}{p} = \frac{(1.4 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{(101.325 \text{ kPa})} = 45.95 \text{ dm}^3$$

$$\text{Molar mass of } \text{PCl}_5 = (31.0 + 5 \times 35.5) \text{ g} = 208.5 \text{ g}$$

$$\text{Density of equilibrium mixture} = \frac{208.5 \text{ g}}{45.95 \text{ dm}^3} = 4.54 \text{ g dm}^{-3}$$

**23.** The rate of diffusion depends on the following factors.

$$r \propto p \quad \text{and} \quad r \propto \sqrt{1/M}$$

Taking these together, we get

$$\frac{r_2}{r_1} = \frac{p_2}{p_1} \left( \frac{M_1}{M_2} \right)^{1/2}$$

Since  $r \propto 1/t$ , we can write

$$\frac{t_1}{t_2} = \left( \frac{p_2}{p_1} \right) \left( \frac{M_1}{M_2} \right)^{1/2} \quad \text{or} \quad M_2 = \left( \frac{p_2}{p_1} \frac{t_2}{t_1} \right)^2 M_1$$

Identifying the script 1 with nitrogen and 2 with unknown gas, we get

$$M_2 = \left( \frac{1.6}{0.8} \times \frac{57}{38} \right)^2 (28 \text{ g mol}^{-1}) = 252 \text{ g mol}^{-1}$$

Let the molecular formula of the unknown compound be  $\text{XeF}_n$ . We will have

$$M_{\text{Xe}} + nM_{\text{F}} = 252 \text{ g mol}^{-1} \quad \text{i.e.} \quad [131 + n(19)] \text{ g mol}^{-1} = 252 \text{ g mol}^{-1}$$

$$n = \frac{252 - 131}{19} = 6.36 \approx 6$$

Hence, the molecular formula of the gas is  $\text{XeF}_6$ .

**24.** From the expression  $pV = nRT$ , we can write

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \quad (\text{since } V \text{ and } n \text{ are constant})$$

From the given data, we get

$$\frac{1 \text{ atm}}{1.1 \text{ atm}} = \frac{(273 + t/\text{ }^\circ\text{C}) \text{ K}}{(273 + t/\text{ }^\circ\text{C} + 10) \text{ K}} \quad \text{or} \quad 283 + t/\text{ }^\circ\text{C} = 1.1 (273 + t/\text{ }^\circ\text{C})$$

$$\text{or} \quad t/\text{ }^\circ\text{C} = \frac{283 - 1.1 \times 273}{0.1} = -173 \quad \text{or} \quad t = -173 \text{ }^\circ\text{C}$$

For the given system,

$$n = \frac{12 \text{ g}}{120 \text{ g mol}^{-1}} = 0.1 \text{ mol} \quad \text{and} \quad T = (273 - 173) \text{ K} = 100 \text{ K}$$

$$\text{Hence, } V = \frac{nRT}{p} = \frac{(0.1 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(100 \text{ K})}{1 \text{ atm}} = 0.82 \text{ L}$$

**25.** We have

Distance travelled by the gas  $\propto$  rate of effusion of the gas  $\propto p/\sqrt{M}$ .  
Hence,

$$\begin{aligned} \frac{l_{\text{HCl}}}{l_{\text{NH}_3}} &= \frac{p_{\text{HCl}}/\sqrt{M_{\text{HCl}}}}{p_{\text{NH}_3}/\sqrt{M_{\text{NH}_3}}} \Rightarrow p_{\text{HCl}} = \frac{l_{\text{HCl}}}{l_{\text{NH}_3}} \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} p_{\text{NH}_3} \\ &= \left( \frac{60 \text{ cm}}{40 \text{ cm}} \right) \left[ \frac{36.5 \text{ mol}^{-1}}{17 \text{ g mol}^{-1}} \right]^{1/2} (1 \text{ atm}) = 2.20 \text{ atm.} \end{aligned}$$

**26.** We have

Molar mass of acetylene = 26 g mol<sup>-1</sup>

$$\text{Amount of acetylene, } n = \frac{5.0 \text{ g}}{26 \text{ g mol}^{-1}}$$

Temperature,  $T = (50 + 273) \text{ K} = 323 \text{ K}$

$$\text{Pressure, } p = 740 \text{ mmHg} = \frac{740}{760} \times 101.325 \text{ kPa}$$

Now, using the ideal gas equation, we get

$$\begin{aligned} V &= \frac{nRT}{p} = \frac{(5.0 \text{ mol}/26)(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(323 \text{ K})}{(740 \times 101.325 \text{ kPa})/760} \\ &= 5.23 \text{ dm}^3 \end{aligned}$$

**27.** We have

Total amount of gases in the mixture

$$\begin{aligned} &= \frac{pV}{RT} = \frac{(6 \text{ atm})(3 \text{ L})}{(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \\ &= 0.7308 \text{ mol} \end{aligned}$$

Thus

Amount of unknown gas = 0.7308 mol - 0.7 mol = 0.0308 mol

$$\text{Now } \frac{r_1}{r_2} = \frac{\text{Amount of hydrogen gas}}{\text{Amount of unknown gas}} = \frac{0.7}{0.0308}$$

$$\text{Moreover, } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } M_2 = \left( \frac{r_1}{r_2} \right)^2 M_1 = \left( \frac{0.7}{0.0308} \right)^2 (2 \text{ g mol}^{-1}) \\ = 1033 \text{ g mol}^{-1}$$

**28.** The given problem is incomplete as the volume of CO<sub>2</sub> gas is not provided.

The van der Waals equation for one mole of a gas is

$$\left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

It is given that the volume occupied by CO<sub>2</sub> molecules is negligible. Hence, the equation of state becomes

$$\left( p + \frac{a}{V_m^2} \right) (V_m) = RT \quad \text{or} \quad p = \frac{RT}{V_m} - \frac{a}{V_m^2}$$

Assuming V<sub>m</sub> = 22.414 dm<sup>3</sup> mol<sup>-1</sup>, we will get

$$\begin{aligned} p &= \frac{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(273 \text{ K})}{(22.414 \text{ dm}^3 \text{ mol}^{-1})} - \frac{3.592 \text{ dm}^6 \text{ atm mol}^{-2}}{(22.414 \text{ dm}^3 \text{ mol}^{-1})^2} \\ &= 101.246 \text{ kPa} - 7.15 \times 10^{-3} \text{ atm} \\ &= 101.246 \text{ kPa} - (7.15 \times 10^{-3} \text{ atm}) (101.325 \text{ kPa/1 atm}) \\ &= 101.264 \text{ kPa} - 0.724 \text{ kPa} \\ &= 100.601 \text{ kPa} \end{aligned}$$

**29.** For one mole of a gas, the van der Waals equation is

$$\left( p + \frac{a}{V_m^2} \right) (V_m - b) = RT$$

Ignoring b, we get

$$\left( p + \frac{a}{V_m^2} \right) V_m = RT \quad \text{or} \quad pV_m + \frac{a}{V_m} = RT$$

$$\text{or } \frac{pV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$\text{or } Z = \frac{pV_m}{RT} = 1 - \frac{a}{V_m RT} \tag{1}$$

It is given that

$$Z = \frac{pV_m}{RT} = 0.5 \Rightarrow V_m = \frac{0.5RT}{p}$$

With this, Eq. (1) becomes

$$0.5 = 1 - \frac{a}{(0.5RT/p)RT}$$

$$\text{or } a = (0.5) \left( \frac{0.5RT}{p} \right) RT = 0.25 \frac{R^2 T^2}{p}$$

Substituting the given values, we get

$$\begin{aligned} a &= (0.25) \left[ \frac{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})^2 (273 \text{ K})^2}{(100 \text{ atm})} \right] \\ &= 1.2528 \text{ L}^2 \text{ atm mol}^{-2} \end{aligned}$$

**30.** (a) (i) Using Graham's law of diffusion,  $r_1/r_2 = \sqrt{M_2/M_1}$ , we get

$$\frac{1.33}{1} = \left( \frac{32 \text{ g mol}^{-1}}{M_1} \right)^{1/2}$$

or  $M_1 = \frac{32 \text{ g mol}^{-1}}{(1.33)^2} = 18.09 \text{ g mol}^{-1}$

(ii) The molar volume of the vapour is

$$V_m = \frac{M_1}{\rho} = \frac{18.09 \text{ g mol}^{-1}}{0.36 \text{ kg m}^{-3}} = \frac{18.09 \text{ g mol}^{-1}}{0.36 \text{ g dm}^{-3}} = 50.25 \text{ dm}^3 \text{ mol}^{-1}$$

(iii) The compression factor is

$$\begin{aligned} Z &= \frac{V_{m,\text{real}}}{V_{m,\text{ideal}}} = \frac{V_{m,\text{real}}}{RT/p} = \frac{pV_{m,\text{real}}}{RT} \\ &= \frac{(101.325 \text{ kPa})(50.25 \text{ dm}^3 \text{ mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(500 \text{ K})} \\ &= 1.22 \end{aligned}$$

(iv) Since  $Z > 1$ , the repulsive forces dominate among the gaseous molecules.

(b) The average translational kinetic energy of molecule is

$$\overline{\text{KE}} = \frac{3}{2} kT = \left( \frac{3}{2} \right) (1.38 \times 10^{-23} \text{ J K}^{-1}) (1000 \text{ K}) = 2.07 \times 10^{-20} \text{ J}$$

**31.** By definitions, we have,

$$c_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{and} \quad c_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$$

Hence,  $\frac{c_{\text{av}}}{c_{\text{rms}}} = \sqrt{\frac{8RT/\pi M}{3RT/M}} = \sqrt{\frac{8}{3\pi}}$

i.e.  $c_{\text{av}} = \left( \sqrt{\frac{8}{3\pi}} \right) c_{\text{rms}} = \sqrt{\frac{8}{3(22/7)}} (434 \text{ m s}^{-1}) = 399.8 \text{ m s}^{-1}$

## SECTION - II LIQUID STATE

### Straight Objective Type

1. When the temperature is increased, surface tension of water
 

(a) increases	(b) decreases
(c) remains constant	(d) shows irregular behaviour

### ANSWERS

### Straight Objective Type

1. (b)

## HINTS AND SOLUTIONS

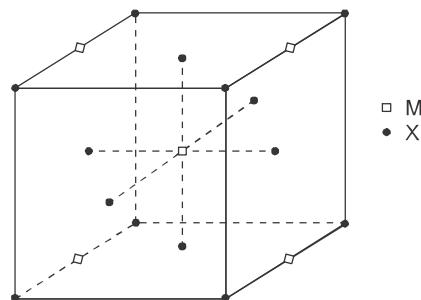
## **Straight Objective Type**

1. Increase in temperature decreases the effects of intermolecular forces and hence surface tension.

## **SECTION-III SOLID STATE**

## **Straight Objective Type**

8. A compound  $M_pX_q$  has cubic close packing (CCP) arrangement of X. Its unit cell structure is shown below.

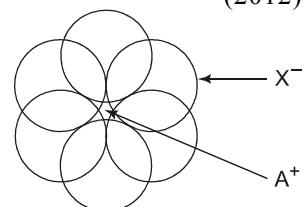


The empirical formula of the compound is



10. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with  $m$  fraction of octahedral holes occupied by aluminium ions and  $n$  fraction of tetrahedral holes occupied by magnesium ions,  $m$  and  $n$ , respectively, are

- (a)  $\frac{1}{2}, \frac{1}{8}$       (b)  $1, \frac{1}{4}$       (c)  $\frac{1}{2}, \frac{1}{2}$       (d)  $\frac{1}{4}, \frac{1}{8}$       (2015)



## **Multiple Correct-Choice Type**

1. Which of the following statements is (are) correct?

  - (a) The coordination number of each type of ion in CsCl is 8.
  - (b) A metal that crystallises in bcc structure has a coordination number of 12.
  - (c) A unit cell of an ionic crystal shares some of its ions with other unit cells.
  - (d) The length of the unit cell in NaCl is 552 pm. ( $r_{\text{Na}^+} = 95$  pm,  $r_{\text{Cl}^-} = 181$  pm) (1998)

2. The correct statement(s) regarding defects in solids is (are)

  - (a) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
  - (b) Frenkel defect is a dislocation defect
  - (c) Trapping of an electron in the lattice leads to the formation of F-center
  - (d) Schottky defects have no effect on the physical properties of solids. (2009)

## **Fill-in-the-Blanks Type**

1. In the sodium chloride structure, each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions nearest neighbours and \_\_\_\_\_  $\text{Na}^+$  ion next nearest neighbours.

## **Integer Answer Type**

1. The number of hexagonal faces that are present in a truncated octahedron is \_\_\_\_\_ . (2011)

## **Reasoning Type**

The question below (1) consist of an '*Assertion*' in column 1 and the '*Reason*' in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.
  - (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
  - (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
  - (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

<i>Assertion</i> (column 1)	<i>Reason</i> (column 2)
1. In any ionic solid [MX] with Schottky defects, the number of positive and negative ions are same.	Equal number of cation and anion vacancies are present. (2001)

## **Linked Comprehension Type**

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in between them. A space-filling model of this structure, called hexagonal close-packed (HCP), is constituted of a sphere on a flat surface surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Each one of these three spheres touches three spheres of the bottom layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be ' $r$ '.



## **Matrix Match Type**

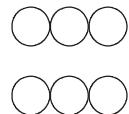
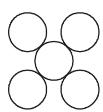
- 1.** Match the crystal system/unit cells mentioned in Column I with their characteristic features mentioned in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the following.

	p	q	r	s
a	○	○	○	○
b	○	○	○	○
c	○	○	○	○
d	○	○	○	○

- | Column I                                | Column II   |
|---|---|
| (a) simple cubic and face-centred cubic | (p) have these cell parameters<br>$a = b = c$ and $\alpha = \beta = \gamma$ |
| (b) cubic and rhombohedral              | (q) are two crystal systems   |
| (c) cubic and tetragonal                | (r) have only two crystallographic angles of $90^\circ$                     |
| (d) hexagonal and monoclinic            | (s) belong to same crystal system (2007)                                    |

### Short Answer Type

1. The figures given below show the location of atoms in three crystallographic planes in a FCC lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.



(2000)

### Subjective Type

- Sodium metal crystallises in body-centred cubic lattice with the cell edge,  $a = 4.29 \text{ \AA}$ . What is the radius of sodium atom? (1994)
- The composition of a sample of wustite is  $\text{Fe}_{0.93}\text{O}_{1.00}$ . What percentage of the ion is present in the form of  $\text{Fe(III)}$ ? (1995)
- A metallic element crystallises into a lattice containing a sequence of layers of ABABAB... Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (1996)
- A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride? (1997)
- Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in  $\text{g/cm}^3$ ? (1997)
- A metal crystallizes into two cubic phases, face centred cubic (FCC) and body centred cubic (BCC), whose unit cell length are 3.5 and 3.0  $\text{\AA}$ , respectively. Calculate the ratio of densities of FCC and BCC. (1999)
- Marbles of diameter 8 mm are available. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of marbles per unit area. (2003)
- AB crystallizes in a rock-salt structure. The nearest distance between A and B is  $Y^{1/3} \text{ nm}$ , where Y is a constant. The molecular mass of AB is  $6.023 \times 10^{-23} \text{ Y amu}$ . Determine the density in  $\text{kg m}^{-3}$ . (2003)
- An element (molar mass:  $75 \text{ g mol}^{-1}$ ) crystallizes in a cubic lattice. The edge-length of its unit cell is 500 pm. If the density of the crystals is  $2 \text{ g cm}^{-3}$ , determine the radius of atoms. Use:  $N_A = 6 \times 10^{23} \text{ mol}^{-1}$ . (2006)

### ANSWERS

#### Straight Objective Type

- |        |        |         |        |        |        |        |
|--------|--------|---------|--------|--------|--------|--------|
| 1. (e) | 2. (a) | 3. (d)  | 4. (a) | 5. (c) | 6. (b) | 7. (d) |
| 8. (b) | 9. (a) | 10. (a) |        |        |        |        |

**Multiple Correct-Choice Type**

1. (a), (c), (d)      2. (b), (c)

**Fill-in-the-Blanks Type**

1. twelve

**Integer Answer Type**

1. 8

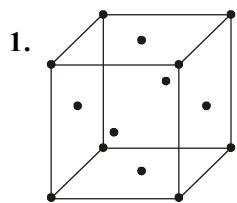
**Linked Comprehension Type**

1. (b)      2. (a)      3. (d)

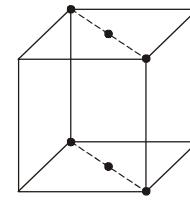
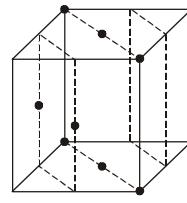
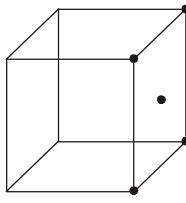
**Matrix Match Type**

1. The correct-bubbled diagram is as follows.

	p	q	r	s
a	●	○	○	●
b	●	●	○	○
c	○	●	○	○
d	○	●	●	○

**Short Answer Type**

Unit cell of FCC

**Subjective Type**

- |                                   |                             |                        |
|-----------------------------------|-----------------------------|------------------------|
| 1. $1.86 \text{ \AA}$             | 2. $15.05\%$                | 3. $26\%$              |
| 4. $2.166 \text{ g cm}^{-3}$      | 5. $7.30 \text{ g cm}^{-3}$ | 6. 1.26                |
| 7. $1.56 \text{ marbles cm}^{-3}$ | 8. $0.50 \text{ kg m}^{-3}$ | 9. $216.5 \text{ pm.}$ |

**HINTS AND SOLUTIONS****Straight Objective Type**

3. The structure of AB is shown in Fig. 2-1

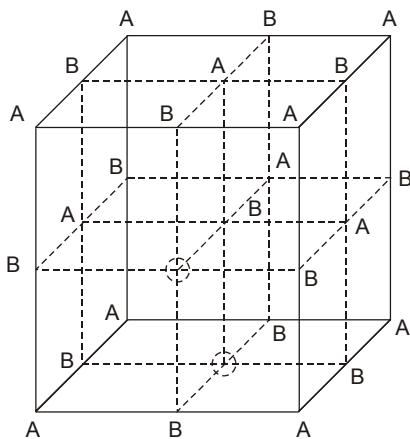


Fig. 2-1

Number of A atoms per unit cell

$$= 8(1/8) \quad + \quad 4(1/2) \quad = 3 \\ \text{from corners} \qquad \qquad \qquad \text{from face-centre}$$

Number of B atoms per unit cell

$$= 12 (1/3) \quad + \quad 1 \quad = 4 \\ \text{from edges} \qquad \qquad \qquad \text{from body-centre.}$$

Hence, the stoichiometry of the solid is  $A_3B_4$ .

4. Each atom at the corner is shared amongst eight unit cells. Hence, number of atoms A per unit cell is

$$n_A = (\text{Number of corners}) (\text{Contribution from each corner}) \\ = 8 \left( \frac{1}{8} \right) = 1$$

Each atom at the centre of each face is shared between two unit cells. Hence, number of atoms B per unit cell is

$$n_B = (\text{Number of faces}) (\text{Contribution from each face}) \\ = 6 \left( \frac{1}{2} \right) = 3$$

The structure of the given substance is  $AB_3$ .

5. We will have

$$f = \frac{(M/\rho_1) - (M/\rho_2)}{(M/\rho_2)} = \frac{(1/\rho_1) - (1/\rho_2)}{(1/\rho_2)} = \frac{(\rho_2 - \rho_1)}{\rho_1} = \frac{\rho_2}{\rho_1} - 1 \\ = \frac{2.178}{2.165} - 1 = 1.006 - 1 = 0.006$$

6.  $Na_2O$  has an anti-fluorite structure in which anions form a cubical-closest packing and cations occupy tetrahedral voids.

$ZnS$  has a zinc-blende structure in which anions form a cubical-closest packing and cations are present in half of the alternate tetrahedral voids.

$CaF_2$  has a fluorite structure in which cations form cubical-closest packing and anions occupy tetrahedral voids.

$CaO$  has a rock-salt structure in which anions form a face-centred cubic unit cell and cations occupy octahedral voids.

7. Since the circles touch each other along the diagonal, we will have

$$4r = \sqrt{2}a \Rightarrow r = \sqrt{2}a/4.$$

The area occupied by circles =  $2(\pi r^2) = 2\pi(2a^2/16) = \pi a^2/4$ .

The area of square unit cell =  $a^2$

$$\text{The per cent packing efficiency} = \frac{(\pi a^2 / 4)}{a^2} \times 100\%$$

$$= 25\pi\% = 25(3.14)\% = 78.5\%$$

8. The atom at the corner of the cube is shared amongst 8 unit cells; the atom at the centre of a face is shared between 2 unit cells, the atom at the centre of edges is shared amongst 4 unit cells and that at the centre of the cube belongs wholly to the unit cell.

There are eight X atoms at the corners and six X atoms at the centre of faces. Thus, the number of X atoms per unit cell is

$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 1 + 3 = 4$$

There are four M atoms at the centre of edges and one M atom at the centre of the cube.

Thus, the number of M atoms per unit cell is

$$4\left(\frac{1}{4}\right) + 1(1) = 1 + 1 = 2$$

The formula of the compound will be  $M_2X_4$  and the empirical formula will be  $MX_2$ .

Therefore, the **choice (b)** is correct.

9. The cation  $A^+$  occupy the octahedral void created by six  $X^-$  anions.

The size of  $A^+$  that can be fitted in the void is related to those of  $X^-$  by the relation

$$\frac{r_{A^+}}{r_{X^-}} = 0.414 \quad \text{Thus } r_{A^+} = 0.414 \quad r_{X^-} = (0.414)(250 \text{ pm}) = 103.5 \text{ pm}$$

Therefore, the **choice (a)** is correct.

10. Let there be  $x$  ions of  $Al^{3+}$  and  $y$  ions of  $Mg^{2+}$ . Since there are 4 oxide ions per unit cell of cubical-closest packed structure, the balancing of positive and negative charges gives

$$x(+3) + y(+2) = -4(-2)$$

This equation is satisfied if  $x = 2$  and  $y = 1$ . Since there are 4 octahedral holes per unit cell, the fraction of holes occupied by  $Al^{3+}$  ions is  $2/4$  i.e.  $1/2$ .

Since there are 8 tetrahedral holes per unit cell, the fraction of holes occupied by  $Mg^{2+}$  ions is  $1/8$ .

Therefore, the choice (a) is correct.

## Multiple Correct-Choice Type

1. The crystals of  $CsCl$  has body-centred cubic unit cell. Hence, each ion in this structure has coordination number of eight.

The crystals of  $NaCl$  has two interpenetrating face-centred cubic lattices, one composed entirely of  $Na^+$  ions and the other of  $Cl^-$  ions. Each  $Na^+$  ion is located halfway between two  $Cl^-$  ions and vice versa. A unit cell of  $NaCl$  crystal has  $Cl^-$  ions at the corners as well as at the face-centres and  $Na^+$  ions are located in octahedral voids. On each edge of cubic unit cell, there are two  $Cl^-$  ions and one  $Na^+$  ion. Hence.

$$\begin{aligned} a &= 2(r_{Na^+} + r_{Cl^-}) \\ &= 2(95 \text{ pm} + 181 \text{ pm}) = 552 \text{ pm} \end{aligned}$$

2. In Frenkel defect, the ion, instead of being in its expected location, is found in one of the interstices. This defect is favoured by a large difference in size between the positive and negative ions.

Schottky defect involves the absence of cation or anion from the position which it is expected to occupy in the periodic arrangement of ions. This affects the physical properties of solids.

### Integer Answer Type

- In a truncated octahedron, there are 14 faces in which there are eight regular hexagon and six square.  
Hence, the correct answer is **8**.

### Matrix Match Type

- The crystallographic parameters of the given crystal systems are as follows.

Cubic system  $a = b = c; \alpha = \beta = \gamma = 90^\circ$

Rhombohedral system  $a = b = c; \alpha = \beta = \gamma \neq 90^\circ$

Tetragonal  $a = b \neq c; \alpha = \beta = \gamma = 90^\circ$

Hexagonal  $a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ$

Monoclinic  $a \neq b \neq c; \alpha = \beta = 90^\circ; \gamma \neq 120^\circ$

- Simple cubic and face-centred cubic (i) have the cell parameters  $a = b = c$  and  $\alpha = \beta = \gamma$  (choice p) and belong to same crystal system (choice s).
- Cubic and rhombohedral (i) have the cell parameters  $a = b = c$  and  $\alpha = \beta = \gamma$  (choice p), and (ii) are two crystal systems (choice q).
- Cubic and tetragonal are two crystal systems (choice q).
- Hexagonal and monoclinic (i) are two crystal systems (choice q) and (ii) have only two crystallographic angles of  $90^\circ$  (choice r).

Hence, the correct-bubled diagram is as follows

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
b	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
c	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>

### Linked Comprehension Type

- There are 6 atoms per unit cell of HCP. Three atoms are inside the cell, one atom comes from the corners of each of top and bottom of the cell (making a total of two atoms) and half of atom comes from each of the central atom at the top and bottom of unit cell (making a total of one atom).
- The hexagonal base consists of six equilateral triangles, each with side  $2r$  and altitude  $2r \sin 60^\circ$ . Hence,

$$\text{Area of base} = 6 \left[ \frac{1}{2} (2r) (2r \sin 60^\circ) \right] = 6\sqrt{3} r^2$$

The height of hexagonal is twice the distance between closest-packed layers. This can be determined with reference to the cubical-closest packing. There are three closest-packed layers in its body diagonal, and thus the distance between two closest-packed layers is  $\sqrt{3} a/3 = a/\sqrt{3}$ . The edge length is related to the radius atom by the relation  $4r = \sqrt{2}a$  since atoms touch each other along the face diagonal of the cube. Hence, height of HCP unit cell is  $2(a/\sqrt{3})$  where  $a = 2\sqrt{2}r$ . Hence

$$\text{Height of unit cell} = 2(2\sqrt{2}r/\sqrt{3}) = 4\sqrt{2}r/\sqrt{3}$$

$$\text{Volume of unit cell} = (\text{area of base})(\text{height}) = (6\sqrt{3}r^2)(4\sqrt{2}r/\sqrt{3}) = 24\sqrt{2}r^3$$

3. Since there are six atoms per unit cell, percentage of volume occupied by atom is

$$\frac{6\left(\frac{4}{3}\pi r^3\right)}{24\sqrt{2}r^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = \frac{3.14}{3 \times 1.414} \times 100 = 74\%$$

Percentage of empty space =  $100 - 74 = 26\%$

### Subjective Type

1. In a body centred cubic lattice, atoms touch along the body diagonal of the cube. Thus,

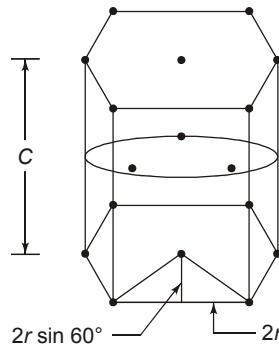
$$4r = \sqrt{3}a$$

$$\text{or } r = \left(\frac{\sqrt{3}}{4}\right)a = \left(\frac{\sqrt{3}}{4}\right)(4.29 \text{ \AA}) = 1.86 \text{ \AA}$$

2. The compound  $\text{Fe}_{0.93}\text{O}_{1.00}$  is a non-stoichiometric where electrical neutrality is achieved by converting appropriate  $\text{Fe}^{2+}$  ions into  $\text{Fe}^{3+}$  ions. There are 7  $\text{Fe}^{2+}$  ions missing out of the expected 100  $\text{Fe}^{2+}$  ions. The missing  $2 \times 7$  positive charge is compensated by the presence of  $\text{Fe}^{3+}$  ions. Replacement of one  $\text{Fe}^{2+}$  ions by  $\text{Fe}^{3+}$  ion increases one positive charge. Thus, 14 positive charges is compensated by the presence of 14  $\text{Fe}^{3+}$  ions out of a total of 93 iron ions.

$$\text{Hence, Percent of } \text{Fe}^{3+} \text{ ions present} = \frac{14}{93} \times 100 = 15.05$$

3. The unit cell of ABABAB . . . packing is as shown in the following.



The hexagonal base consists of six equilateral triangles, each with side  $2r$  and altitude  $2r \sin 60^\circ$ . Hence,

$$\text{Area of base} = 6\left[\frac{1}{2}(2r)(2r \sin 60^\circ)\right]6\sqrt{3}r^2$$

The height of hexagonal is twice the distance between closest-packed layers. The latter can be determined by reference to a face-centred cubic lattice with unit cell length  $a$ . In such a lattice, the distance between closest-packed layers is one third the body diagonal, i.e.  $\sqrt{3}a/3$ . Hence

$$C = 2\left(\frac{\sqrt{3}a}{3}\right) = \frac{2a}{\sqrt{3}}$$

Now in the face-centred lattice, atoms touch one another along the face diagonal. Thus

$$4r = \sqrt{2}a$$

With this, the height of the hexagonal becomes

$$C = \frac{2}{\sqrt{3}} \left( \frac{4r}{\sqrt{2}} \right) = \left( \frac{4\sqrt{2}}{\sqrt{3}} r \right)$$

Volume of hexagonal unit is

$$V = (\text{base area}) (\text{height}) = (6\sqrt{3} r^2) \left( \frac{4\sqrt{2}}{\sqrt{3}} r \right) = 24\sqrt{2} r^3$$

In one hexagonal unit cell, there are 6 atoms as shown in the following.

- (a) 3 atoms in the central layer which exclusively belong to the unit cell.
- (b) 1 atom from the centre of the base. There are two atoms of this type and each is shared between two hexagonal unit cells.
- (c) 2 atoms from the corners. There are twelve such atoms and each is shared amongst six hexagonal unit cells.

$$\text{The volume occupied by atoms} = 6 \left( \frac{4}{3} \pi r^3 \right)$$

Fraction of volume occupied by atoms

$$= \frac{\text{Volume occupied by atoms}}{\text{Volume of hexagonal unit cell}} = \frac{6 \left( \frac{4}{3} \pi r^3 \right)}{24\sqrt{2} r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

$$\text{Fraction of empty space} = 1 - 0.74 = 0.26$$

$$\text{Percentage of empty space} = 26\%$$

**4.** We have

$$\begin{aligned} \rho &= \frac{N}{a^3} \frac{M}{N_A} \\ &= \frac{4}{(0.564 \times 10^{-7} \text{ cm})^3} \left( \frac{58.5 \text{ g mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} \right) = 7.30 \text{ g cm}^{-3} \end{aligned}$$

**5.** In a body-centred cubic lattice, atoms touch each other along the body-diagonal of the cube. Hence

$$4r = \sqrt{3} a$$

$$\text{or } r = \frac{\sqrt{3} a}{4} = \frac{(1.732)(287 \text{ pm})}{4} = 124.27 \text{ pm}$$

The expression of density is

$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

Substituting the values, we get

$$\rho = \frac{2}{(287 \times 10^{-10} \text{ cm})^3} \left( \frac{51.99 \text{ g mol}^{-1}}{9.023 \times 10^{23} \text{ g mol}^{-1}} \right) = 7.30 \text{ g cm}^{-3}$$

**6.** The expression of density is

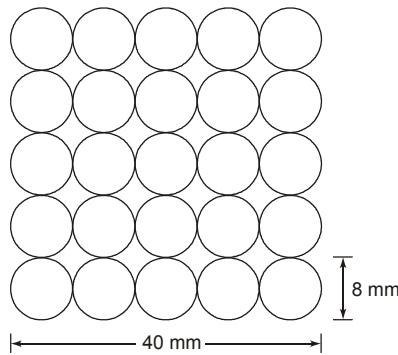
$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

For face-centred cubic unit cell,  $N = 4$

For body-centred cubic unit cell,  $N = 2$

$$\text{Hence, } \frac{\rho_{\text{FCC}}}{\rho_{\text{BCC}}} = \frac{N_{\text{FCC}}}{N_{\text{BCC}}} \frac{a_{\text{BCC}}^3}{a_{\text{FCC}}^3} = \frac{4}{2} \frac{(3.0 \text{ \AA})^3}{(3.5 \text{ \AA})^3} = 1.26$$

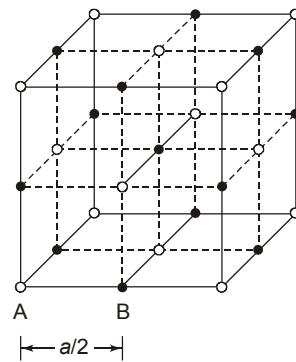
7. The arrangement showing maximum number of marbles within the square of edge length 40 mm is displayed in the following.



Number of marbles per unit area

$$= \frac{25 \text{ marbles}}{(40 \text{ mm})^2} = 0.0156 \text{ marbles mm}^{-2} = 1.56 \text{ marbles cm}^{-2}$$

8. The rock-salt structure is shown in Fig. 2-2. From Fig. C-1, it is obvious that the edge length of unit cell is twice the nearest distance between A and B.



**Fig. 2-2** Unit cell of rock-salt

The volume of unit cell is  $V = a^3 = (2Y^{1/3} \text{ nm})^3 = 8Y \text{ nm}^3$

There are four A and four B in one unit cell, i.e. there are four molecules of AB in one unit cell. The density of crystal AB is

$$\rho = \frac{m}{V} = \frac{4(6.023Y \text{ amu})}{8Y \text{ nm}^3} = \frac{(4)(6.023Y)(10^{-3} \text{ kg}/6.023 \times 10^{23})}{8Y(10^{-9} \text{ m})^3} = 5.0 \text{ kg m}^{-3}$$

9. The density of element crystallises in cubic lattice is given by

$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

**2.38**

IIT Chemistry: Topic-wise Solved Questions

Hence, the number  $N$  of atoms per unit cell is

$$N = (\rho a^3) \left( \frac{N_A}{M} \right) = (2 \text{ g cm}^{-3}) (500 \times 10^{-10} \text{ cm})^3 \left[ \frac{(6 \times 10^{23} \text{ mol}^{-1})}{75 \text{ g mol}^{-1}} \right] \\ = 2$$

This implies that the unit cell is body-centred for which

$$\sqrt{3} a = 4r$$

$$\text{This gives } r = \frac{\sqrt{3}}{4} a = \left( \frac{\sqrt{3}}{4} \right) (500 \text{ pm}) \\ = 216.5 \text{ pm}$$

# ATOMIC STRUCTURE

3

## **Straight Objective Type**

**10.** Which one of the following sets of quantum numbers represents an impossible arrangement?

- |                                 |                                 |
|---------------------------------|---------------------------------|
| $n \quad l \quad m_l \quad m_s$ | $n \quad l \quad m_l \quad m_s$ |
| (a) 3 2 -2 1/2                  | (b) 4 0 0 1/2                   |
| (c) 3 2 -3 1/2                  | (d) 5 3 0 -1/2                  |
- (1986)

**11.** The ratio of the energy of a photon of 200 nm wavelength radiation to that of 400 nm radiation is

- (a) 1/4 (b) 4 (c) 1/2 (d) 2 (1986)

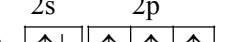
**12.** The triad of nuclei that is isotonic is

- |   |   |
|---|---|
| (a) $^{14}_6\text{C}$ , $^{15}_7\text{N}$ , $^{17}_9\text{F}$ | (b) $^{12}_6\text{C}$ , $^{14}_7\text{N}$ , $^{19}_9\text{F}$ |
| (c) $^{14}_6\text{C}$ , $^{14}_7\text{N}$ , $^{17}_9\text{F}$ | (d) $^{14}_6\text{C}$ , $^{14}_7\text{N}$ , $^{19}_9\text{F}$ |
- (1988)

**13.** The wavelength of a spectral line for an electronic transition is inversely related to

- (a) the number of electrons undergoing the transition
  - (b) the nuclear charge of the atom
  - (c) the difference in the energy of the energy levels involved in the transition
  - (d) the velocity of electron undergoing the transition
- (1988)

**14.** The orbital diagram in which the aufbau principle is violated is

- |  |   |
|--|---|
| 2s      2p<br>(a)   | 2s      2p<br>(b)   |
| 2s      2p<br>(c)  | 2s      2p<br>(d)  |
- (1988)

**15.** The outermost electronic configuration of the most electronegative element is

- (a)  $(ns)^2(np)^3$  (b)  $(ns)^2(np)^4$  (c)  $(ns)^2(np)^5$  (d)  $(ns)^2(np)^6$  (1988)

**16.** The correct ground state electronic configuration of chromium atom is

- |   |   |
|---|---|
| (a) [Ar](3d) <sup>5</sup> (4s) <sup>1</sup> | (b) [Ar](3d) <sup>4</sup> (4s) <sup>2</sup> |
| (c) [Ar](3d) <sup>6</sup> (4s) <sup>0</sup> | (d) [Ar](4d) <sup>5</sup> (4s) <sup>1</sup> |
- (1989)

**17.** Which one of the following is the smallest in size?

- (a)  $\text{N}^{3-}$  (b)  $\text{O}^{2-}$  (c)  $\text{F}^-$  (d)  $\text{Na}^+$  (1989)

**18.** The correct set of quantum numbers for the unpaired electron of chlorine atom is

- |                                    |                                    |
|------------------------------------|------------------------------------|
| $n \quad l \quad m_l$<br>(a) 2 1 0 | $n \quad l \quad m_l$<br>(b) 2 1 1 |
| (c) 3 1 1                          | (d) 3 0 0                          |
- (1989)

**19.** Which of the following does not characterise X-rays?

- (a) The radiation can ionise gases.
  - (b) It causes ZnS to fluoresce.
  - (c) Deflected by electric and magnetic fields.
  - (d) Have wavelengths shorter than ultraviolet rays.
- (1992)

**20.** Which of the following relates to photon both as wave motion and as a stream of particles?

- (a) Interference (b)  $E = mc^2$  (c) Diffraction (d)  $E = h\nu$  (1992)

**21.** The orbital angular momentum of an electron in 2s orbital is:

- (a)  $+\frac{1}{2}\frac{\hbar}{2\pi}$  (b) Zero (c)  $\frac{\hbar}{2\pi}$  (d)  $\sqrt{2}\frac{\hbar}{2\pi}$  (1996)

**22.** The first use of quantum theory to explain the structure of atom was made by

- (a) Heisenberg (b) Bohr (c) Planck (d) Einstein (1997)

23. For a d-electron, the orbital angular momentum is

- (a)  $\sqrt{6} (h/2\pi)$       (b)  $\sqrt{2} (h/2\pi)$       (c)  $(h/2\pi)$       (d)  $2(h/2\pi)$       (1997)

24. The energy of an electron in the first Bohr orbit of H atom is  $-13.6 \text{ eV}$ . The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is (are)

- (a)  $-3.4 \text{ eV}$       (b)  $-4.2 \text{ eV}$       (c)  $-6.8 \text{ eV}$       (d)  $+6.8 \text{ eV}$       (1998)

25. The electrons, identified by quantum numbers  $n$  and  $l$  (i)  $n = 4, l = 1$ , (ii)  $n = 4, l = 0$ , (iii)  $n = 3, l = 2$  and (iv)  $n = 3, l = 1$  can be placed in order of increasing energy, from the lowest to highest, as

- (a) (iv) < (ii) < (iii) < (i)      (b) (ii) < (iv) < (i) < (iii)  
 (c) (i) < (iii) < (ii) < (iv)      (d) (iii) < (i) < (iv) < (ii)      (1999)

26. Ground state electronic configuration of nitrogen atom can be represented by

- |   |  |
|---|--|
| (a)  | (b)  |
| (c)  | (d)  |

27. Correct set of four quantum numbers for the valence (outer most) electron of rubidium ( $Z = 37$ ) is

- (a)  $5, 0, 0, +1/2$       (b)  $5, 1, 0, +1/2$       (c)  $5, 1, 1, +1/2$       (d)  $6, 0, 0, +1/2$       (1984)

28. Which electronic level would allow the hydrogen atom to absorb a photon but not emit a photon?

- (a) 3s      (b) 2p      (c) 3p      (d) 1s

29. The electronic configuration of an element is  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^5(4s)^1$ . This represents its

- (a) excited state      (b) ground state  
 (c) catonic form      (d) anionic form      (2000)

30. The number of nodal planes in a  $p_x$  orbital is

- (a) one      (b) two      (c) three      (d) zero      (2000)

31. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order

- (a)  $10^{-10} \text{ m}$       (b)  $10^{-20} \text{ m}$       (c)  $10^{-30} \text{ m}$       (d)  $10^{-40} \text{ m}$

32. The quantum numbers  $+1/2$  and  $-1/2$  for the electron spin represent

- (a) rotation of the electron in clockwise and anticlockwise direction respectively  
 (b) rotation of the electron in anticlockwise and clockwise direction respectively  
 (c) magnetic moment of the electron pointing up and down respectively  
 (d) two quantum mechanical spin states which have no classical analogue      (2001)

33. Rutherford's experiment, which established the nuclear model of the atom, used a beam of

- (a)  $\beta$ -particles, which impinged on a metal foil and got absorbed  
 (b)  $\gamma$ -rays, which impinged on a metal foil and ejected electrons  
 (c) helium atoms, which impinged on a metal foil and got scattered  
 (d) helium nuclei, which impinged on a metal foil and got scattered      (2002)

34. If the nitrogen atom had electronic configuration  $1s^7$ , it would have energy lower than that of the normal ground state configuration  $(1s)^2(2s)^2(2p)^3$ , because the electrons would be closer to the nucleus. yet,  $1s^7$  is not observed because it violates

- (a) Heisenberg uncertainty principle      (b) Hund's rule  
 (c) Pauli exclusion principle      (d) Bohr postulate of stationary orbits      (2002)

## **Multiple Correct-Choice Type**



## **Fill-in-the-Blanks Type**

1. The total number of electrons present in 18 mL of water is \_\_\_\_\_. (1980)
  2. The mass of a hydrogen atom is \_\_\_\_\_ kg. (1982)
  3. When there are two electrons in the same orbital, they have \_\_\_\_\_ spins. (1982)
  4. Isotopes of an element differ in the number of \_\_\_\_\_ in their nuclei. (1982)
  5. An element  ${}_{Z}^{A}M$  undergoes an  $\alpha$ -emission followed by two successive  $\beta$ -emissions. The element formed is \_\_\_\_\_. (1982)
  6. Elements of the same mass number but different atomic numbers are known as \_\_\_\_\_. (1983)
  7. The number of neutrons in the parent nucleus which gives  ${}^{14}N$  on beta emission is \_\_\_\_\_. (1985)

8. The uncertainty principle and the concept of wave nature of matter were proposed by \_\_\_\_\_ and \_\_\_\_\_, respectively. (Heisenberg, Schrödinger, Maxwell, de Broglie) (1988)
9. A radioactive nucleus decays emitting one alpha and two beta particles, the daughter nucleus is \_\_\_\_\_ of the parent.
10. The light radiations with discrete quantities of energy are called \_\_\_\_\_. (1993)
11. Wave functions of electrons in atoms and molecules are called \_\_\_\_\_. (1993)
12. The  $2p_x$ ,  $2p_y$  and  $2p_z$  orbitals of atom have identical shapes but differ in their \_\_\_\_\_. (1993)
13. The outermost electronic configuration of Cr is \_\_\_\_\_. (1994)

### Integer Answer Type

1. The maximum number of electrons that can have principal quantum number,  $n = 3$ , and spin quantum number,  $m_s = -1/2$  is \_\_\_\_\_. (2011)
2. The work function ( $\phi$ ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wavelength falls on the metals is \_\_\_\_\_. (2011)
 

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
$\phi/\text{eV}$	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(Given:  $h = 6.626 \times 10^{-34} \text{ J s}$ ; 1 eV =  $1.602 \times 10^{-19} \text{ J}$ ;  $c = 3 \times 10^8 \text{ m s}^{-1}$ .)
3. The atomic masses of He and Ne are 4 and 20 amu, respectively. The value of the de Broglie wavelength of He gas at  $-73^\circ\text{C}$  is "M" times that of the de Broglie wavelength of Ne at  $727^\circ\text{C}$ . The value of "M" is \_\_\_\_\_. (2013)
4. In an atom, the total number of electrons having quantum number  $n = 4$ ,  $|m_l| = 1$  and  $m_s = -1/2$  is \_\_\_\_\_. (2014)
5. Not considering the electronic spin, the degeneracy of the second excited state ( $n = 3$ ) of H atom is 9, while the degeneracy of the second excited state of  $\text{H}^-$  is \_\_\_\_\_. (2015)

### True/False Type

1. The outer electronic configuration of the ground state chromium atom is  $(3d)^4(4s)^2$ . (1982)
2. Gamma rays are electromagnetic radiations of wavelengths of  $10^{-6} \text{ cm}$  to  $10^{-5} \text{ cm}$ . (1983)
3. The energy of the electron in the  $3d$ -orbital is less than that in the  $4s$ -orbital of a hydrogen atom. (1983)
4. The electron density in the  $xy$  plane in  $3d_{x^2-y^2}$  orbital is zero. (1986)
5. Dipoles zinc exhibits paramagnetism due to loss of two electrons from a  $3d$ -orbital of neutral atom. (1987)
6. In  $\beta$ -emission from a nucleus the atomic number of the daughter element decreases by one. (1990)

### Linked Comprehension Type

#### Paragraph for questions 1 to 3

The hydrogen-like species  $\text{Li}^{2+}$  is in a spherically symmetric state  $S_1$  with one radial node. Upon absorbing light the ion undergoes transition to a state  $S_2$ . The state  $S_2$  has one radial node and its energy is equal to the ground state energy of the hydrogen atom

1. The state  $S_1$  is
 

(a) 1s	(b) 2s	(c) 2p	(d) 3s
--------	--------	--------	--------
2. Energy of the state  $S_1$  in units of the hydrogen atom ground state energy is
 

(a) 0.75	(b) 1.50	(c) 2.25	(d) 4.50
----------	----------	----------	----------

## **Matching Type**

- 1.** Match the following

(a) J.J. Thomson	(p) Cathode rays
(b) Henry Becquerel	(q) Mass spectrograph
(c) Moseley	(r) X-ray spectra
(d) Aston	(s) Laws of electrolysis
	(t) Nuclear model of atom
	(u) Radioactivity
	(v) Discovery of Neutrons

(1978)

**2.** In the following,  $V_n$ ,  $K_n$  and  $E_n$  represent potential energy, kinetic energy and total energy of an electron in the  $n$ th Bohr orbit (radius:  $r$ ) of hydrogen like species (nuclear charge:  $Z$ ). Match the entries on the left with those given on right.

(a) $V_n/K_n = ?$	(p) - 1
(b) $V_n/E_n = ?$	(q) - 2
(c) $K_n/E_n = ?$	(r) 1
(d) $1/r \propto (Z)^x : x = ?$	(s) 2

(2006)

## **Matrix Match Type**

1. Match the entries in **Column I** with the correctly related quantum number(s) in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the following.

	p	q	r	s
a	○	○	○	○
b	○	○	○	○
c	○	○	○	○
d	○	○	○	○

### **Column I**

## Column II

- (a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital      (p) Principal quantum number  
(b) A hydrogen-like one-electron wave function obeying Pauli principle      (q) Azimuthal quantum number  
(c) Shape, size and orientation of hydrogen like atomic orbitals      (r) Magnetic quantum number  
(d) Probability density of electron at the nucleus in hydrogen-like atom      (s) Electron spin quantum number

(2008)

## **Short Answer Type**

1. The ground state outermost electronic configuration of Si is   and not   (1985)

2. What is the maximum number of electrons that may be present in all the atomic orbitals with principal quantum number 3 and azimuthal quantum number 2. (1985)

### Subjective Type

- Find (i) the total number of neutrons and (ii) the total mass of neutrons in 7 mg of  $^{14}\text{C}$ . (Assume that mass of neutron = mass of a hydrogen atom.) (1980)
- The energy of the electron in the second and third Bohr orbits of the hydrogen atom is  $-5.42 \times 10^{-19}$  J and  $-2.41 \times 10^{-19}$  J, respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit. (1981)
- Calculate the wavelength of the photon that is emitted when an electron in Bohr orbit  $n = 2$  returns to the orbit  $n = 1$  in the hydrogen atom. The ionization potential of the ground state of hydrogen atom is  $2.17 \times 10^{-18}$  J per atom. (1982)
- The energy of an electron in hydrogen atom is given by  $E_n = (-21.7 \times 10^{-19} \text{ J})/n^2$ . Calculate the energy required to remove an electron completely from the  $n = 2$  orbit. What is the longest wavelength of radiation that can be used to cause this transition? (1984)
- According to Bohr's theory, the electronic energy of hydrogen atom in the  $n$ th Bohr's orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19} \text{ J}}{n^2}$$

Calculate the longest wavelength of radiation that will be needed to remove an electron from the third orbit of the  $\text{He}^+$  ion. (1990)

- Estimate the difference in energy between the 1<sup>st</sup> and 2<sup>nd</sup> Bohr orbit for a hydrogen atom. At what minimum atomic number, would a transition from  $n = 2$  to  $n = 1$  energy level result in the emission of X-rays with  $\lambda = 3.0 \times 10^{-8}$  m? Which hydrogen atom-like species does this atomic number correspond to? (1993)
- What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition,  $n = 4$ , to  $n = 2$  of  $\text{He}^+$  spectrum? (1993)
- Consider the hydrogen atom to be a proton embedded in a cavity of radius  $a_0$  (Bohr radius) whose charge is neutralised by the addition of an electron to the cavity in vacuum, infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralisation process. Also, if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy. (1996)
- An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. (1998)
- Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol<sup>-1</sup>. (2000)
- Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996)
- Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit. (1994)
- Calculate the wave number for the shortest wavelength transition in the Balmer series of atomic hydrogen. (1996)
- With what velocity should an  $\alpha$ -particle travel towards the nucleus of a copper atom so as to arrive at a distance  $10^{-13}$  metre from the nucleus of the copper atom? (1997)
- An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å. (1997)
- Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H—H bond is 436 kJ mol<sup>-1</sup>. (2000)

17. The wavelength of electronic transition in hydrogen atom is 92.0 nm, what will be the wavelength of the corresponding transition in helium ion ( $\text{He}^+$ )?  
 (2003)
18. (a) The wave function of 3s electron is given by

$$\psi_{3s} = \frac{1}{81\sqrt{3}\pi} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$$

It has a node at  $r = r_0$ . Find the relation between  $r_0$  and  $a_0$ .

(b) Determine the wavelength of 100 g particle moving with a velocity of 200 m s<sup>-1</sup>.

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (d)  | 2. (c)  | 3. (d)  | 4. (a)  | 5. (a)  | 6. (b)  |
| 7. (b)  | 8. (b)  | 9. (b)  | 10. (c) | 11. (d) | 12. (a) |
| 13. (c) | 14. (b) | 15. (c) | 16. (a) | 17. (d) | 18. (c) |
| 19. (c) | 20. (c) | 21. (b) | 22. (b) | 23. (a) | 24. (a) |
| 25. (a) | 26. (a) | 27. (a) | 28. (d) | 29. (b) | 30. (a) |
| 31. (c) | 32. (d) | 33. (d) | 34. (c) | 35. (d) | 36. (a) |
| 37. (c) |         |         |         |         |         |

### Multiple Correct-Choice Type

- |                  |             |             |
|------------------|-------------|-------------|
| 1. (a), (c)      | 2. (b), (d) | 3. (a), (c) |
| 4. (a), (b), (c) | 5. (c), (d) |             |

### Fill-in-the-Blanks Type

- |                                   |                               |                 |                           |
|-----------------------------------|-------------------------------|-----------------|---------------------------|
| 1. $6.022 \times 10^{24}$         | 2. $1.667 \times 10^{-27}$ kg | 3. Antiparallel | 4. neutrons               |
| 5. ${}_{Z}^{A-4}\text{M}$         | 6. isobars                    | 7. eight        | 8. Heisenberg, de Broglie |
| 9. isobars                        | 10. photons                   | 11. orbitals    | 12. orientations          |
| 13. $(3\text{d})^5 (4\text{s})^1$ |                               |                 |                           |

### Integer Answer Type

- |       |      |       |      |
|-------|------|-------|------|
| 1. 9. | 2. 4 | 3. 5. | 4. 6 |
| 5. 3  |      |       |      |

### True/False Type

- |          |          |         |          |
|----------|----------|---------|----------|
| 1. False | 2. False | 3. True | 4. False |
| 5. False | 6. False |         |          |

### Linked Comprehension Type

1. (b)                  2. (c)                  3. (b)

### Matching Type

1. (a)–(p); (b)–(u); (c)–(r); m(d)–(q)                  2. (a)–(q); (b)–(s); (c)–(p); (d)–(r)

### Matrix Match Type

1. The correct-bubbled diagram is as follows.

	p	q	r	s
a	(p)	(q)	(r)	(s)
b	(p)	(q)	(r)	(s)
c	(p)	(q)	(r)	(s)
d	(p)	(q)	(r)	(s)

### Short Answer Type

1. The configuration should satisfy Hund's rule.  
2. Ten electrons as there are five 3d orbitals.

### Subjective Type

19. 9                  20. 4

### HINTS AND SOLUTIONS

### Straight Objective Type

- Number of neutrons = mass number – atomic number =  $70 - 30 = 40$
- $\alpha$ -particles originate from nucleus of an atom.
- A single p orbital can accommodate two electrons.
- The principal quantum number can be correlated with size of an orbital.
- Rutherford's experiment involves the scattering of  $\alpha$ -particles by nucleus of an atom.
- Bohr model was successful in explaining the spectrum of one-electron species only.
- The radius of atomic nucleus is of the order of  $10^{-13}$  cm.
- Radio waves have maximum wavelength as compared to ultraviolet, infrared and X-ray.
- Rutherford's experiment led to the conclusion that electrons occupy space around the nucleus.
- The choice c is not correct as the value of  $m_l$  cannot be greater than  $l$ .
- Since  $E = hc/\lambda$ , the ratio  $E_{200\text{nm}}/E_{400\text{nm}}$  will be equal to 2.
- Isotones have the same number of neutrons. The choice a contains 8 neutrons in all the three species.
- The wavelength of spectral line is inversely related to the energy difference between two energy levels.
- The choice b violates aufbau principle as 2s orbital contains one electron. It should be filled completely before filling 2p orbitals.

15. One electron short of stable configuration is the most electronegative element. Thus, configuration is  $(ns)^2(np)^5$ .
16. The electronic configuration of Cr is  $[Ar](3d)^5(4s)^1$ .
17. Amongst the given species,  $Na^+$  will have the smallest size.
18. The electronic configuration of  $^{17}Cl$  is  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^5$ . The quantum numbers of 3p orbital are  $n = 3$ ,  $l = 1$  and  $m$  may be equal to 1.
19. X-rays are not deflected by electric and magnetic fields.
20. The expression  $E = h\nu$  relates photon as wave motion and particle nature.
21. The orbital angular momentum is given by  $L = \sqrt{l(l+1)}(h/2\pi)$ . For s orbital,  $l = 0$ . Hence  $L = 0$ .
22. Bohr theory was the first theory.
23. For d-electron,  $l = 2$ . hence  $L = \sqrt{l(l+1)}(h/2\pi) = \sqrt{6}(h/2\pi)$ .
24. The energy of excited state of hydrogen is given by  $E_n = E_1/n^2$ . For  $n = 2$ ,  $E_2 = -13.6 \text{ eV}/4 = -3/4 \text{ eV}$ .
25. Larger the value of  $n + l$ , larger the energy of electron. For the same value of  $n + l$ , the larger value of  $n$  has larger energy.
26. The ground state electronic configuration of nitrogen atom is  $(1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$
27. The electronic configuration of rubidium ( $z = 37$ ) is  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^10(4s)^2(4p)^6(5s)^1$
28. The element is chromium atom in the ground state.
29. The de-Broglie wavelength is  $\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ J s})}{(0.200 \text{ kg})\{5 \text{ m}/60 \times 60 \text{ s}\}} = 2.4 \times 10^{-30} \text{ m}$
30. The expression of radius is  $r = n^2 \left[ \frac{h^2}{4\pi^2 m (Ze^2 / 4\pi\epsilon_0)} \right]$  that is  $r \propto \frac{n^2}{Z}$
31. For  $Be^{3+}$ ,  $Z = 4$ . Hence, when  $n = 2$   $r \propto \frac{2^2}{4} = 1$
32. For H,  $Z = 1$ . Hence, when  $n = 1$   $r \propto \frac{1^2}{1} = 1$
33. Number of radial nodes in an orbital is equal to  $n - l - 1$ , where  $n$  and  $l$  are the principal and azimuthal quantum numbers, respectively. For 3p and 4s orbitals, we have  
 $3p \quad n = 3, l = 1 \text{ radial nodes} = 3 - 1 - 1 = 1$   
 $4s \quad n = 4, l = 0 \text{ radial nodes} = 4 - 0 - 1 = 3$
34. Bohr model of an atom satisfies the following two requirements.

$$\frac{(Ze)(e)}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r}$$

- Quantization of angular momentum, i.e.

$$mvr = n \left( \frac{h}{2\pi} \right)$$

Eliminating  $v$  in these two expressions, we get

$$r = n^2 \left[ \frac{h^2}{4\pi^2 m (Ze^2 / 4\pi\epsilon_0)} \right] = \left( \frac{h}{2\pi} \right)$$

where  $a_0$  is the Bohr radius. The kinetic energy of the electron in Bohr orbit of an atom is

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m\left[\frac{n}{mr}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{1}{2}m\left[\frac{n}{m(n^2a_0/Z)}\left(\frac{h}{2\pi}\right)\right]^2 = \frac{Z^2}{n^2}\left(\frac{h^2}{8\pi^2ma_0^2}\right)$$

For the second Bohr orbit of hydrogen atom,  $Z = 1$ , and  $n = 2$ . Hence

$$\text{KE} = \frac{1}{32}\left(\frac{h^2}{\pi^2 ma_0^2}\right)$$

### Multiple Correct-Choice Type

- The penetration of  $\alpha$ -particles in Rutherford's experiment is due to empty space in atom. Also  $\alpha$ -particles are much heavier than electrons, thus, these are not reflected much while passing through empty spaces.
- Isotones involve the same number neutrons, which in the present case, is 44.
- Non-integral atomic mass is due to isotopes which have different masses.
- The choices a, b and c are correct. The choice d is incorrect as the oxidation state of N in  $\text{HN}_3$  is  $-1/3$  and not  $-3$ .

### Integer Answer Type

- In the principal quantum number,  $n = 3$ , the completely occupied orbitals are

3s	3p	3d
$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

There are nine electrons with  $m_s = -1/2$ .

- Energy of 1 photon of wave length 300 nm is

$$\begin{aligned} E &= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(3.0 \times 10^8 \text{ m s}^{-1})}{(300 \times 10^{-9} \text{ m})} \\ &= 6.626 \times 10^{-19} \text{ J} \\ &\equiv (6.626 \times 10^{-19}/1.602 \times 10^{-19}) \text{ eV} \\ &= 4.13 \text{ eV} \end{aligned}$$

For the emission of electrons, the work function of the metal should be smaller than the energy of a photon. Hence, there will be emission of electrons by Li, Na, K and Mg only.

- We have de Broglie relation  $\lambda = h/mv$

$$\text{Average kinetic energy } \frac{1}{2}mv^2 = \frac{3}{2}kT$$

$$\text{Hence } \lambda = \frac{h}{mv} = \frac{h}{m} \sqrt{\frac{m}{3kT}} = \frac{h}{\sqrt{3m k T}}$$

Thus  $\lambda \propto 1/(mT)^{1/2}$ . Hence

$$\frac{\lambda_{\text{He}}}{\lambda_{\text{Ne}}} = \left[ \frac{(20 \text{ amu})(1000 \text{ K})}{(4 \text{ amu})(200 \text{ K})} \right]^{1/2} = 5$$

Therefore, the value of M is 5.

4. For  $n = 4$ , we will have

$$l = 0, 1, 2, 3$$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The number of orbitals with  $n = 4$  and  $|m_l| = 1$  will be

1.  $l = 1, m_l = \pm 1$       2.  $l = 2, m_l = \pm 1$  and      3.  $l = 3, m_l = \pm 1$

Hence, there will be 6 orbitals. Each orbital can accommodate one electron with  $m_s = -1/2$ .

Thus, the answer is **six**.

5. For one-electron species, the energy of electron is governed by the principal quantum number  $n$  while for the multi-electron species, the energy is governed by the sum of principal and azimuthal quantum numbers (i.e.  $n + l$ )

In H atom, for  $n = 3$ , the degeneracy is 9 involving 3s, three 3p orbitals and five 3d orbitals.

In  $\text{H}^-$  ion, the second excited state is 2p orbitals and their degeneracy is **three**.

### True/False Type

1. The configuration is  $(3\text{d})^5 (4\text{s})^1$ .
2. The wavelength of gamma rays is of the order of  $10^{-11}$  m.
3. In hydrogen atom, the energy of an electron depends only on the principal quantum number of the orbital which it occupies.
4. In  $xz$ -plane, there is no electron density if an electron occupies  $3\text{d}_{x^2-y^2}$  orbital.
5. The electronic configuration of  $\text{Zn}^{2+}$  (atomic number 30) is  $(1\text{s})^2 (2\text{s})^2 (2\text{p})^6 (3\text{s})^2 (3\text{p})^6 (3\text{d})^{10}$ . There is no unpaired electrons, hence, it is diamagnetic.
6. In  $\beta$ -emission, the atomic number of daughter element is increased by one, due to the basic conversion of neutron into proton in the nucleus.

### Linked Comprehension Type

1. Since the state  $S_1$  is spherical symmetrical, it must represent s orbital. Since the number of radial node of an orbital is equal to  $n - l - 1$ , the state  $S_1$  has principal quantum number equal to 2. Thus, the state  $S_1$  is 2s orbital.
2. The energy expression for the hydrogen-like species is

$$E = - \frac{Z^2 R_{\text{H}} hc}{n^2} = \frac{Z^2}{n^2} E_{\text{H}} \text{ where } E_{\text{H}} = - R_{\text{H}} hc$$

For  $\text{Li}^{2+}$ ,  $Z = 3$ . Thus, for  $S_1$  state we have

$$E = \frac{3^2}{2^2} E_{\text{H}} = \frac{9}{4} E_{\text{H}} = + 2.25 E_{\text{H}}$$

3. The state  $S_2$  has energy equal to the ground state energy of hydrogen atom. Hence,

$$\frac{Z^2}{n^2} E_{\text{H}} = E_{\text{H}}. \text{ This gives } n = Z = 3.$$

Since the state  $S_2$  has one radial node, which is equal to  $n - l - 1$ , we must have  $l = 1$ . That is, the state  $S_2$  is 3p.

### Matrix Match Type

1. (a) Orbital angular moment of the electron in a hydrogen-like atomic orbital is governed by the azimuthal quantum number (choice q).

- (b) A hydrogen-like one electron wave function obeying Pauli principle is due to the electron spin quantum numbers. Two electrons in the same wave function have different values of spin quantum number (choice s).
- (c) Shape is governed by the azimuthal quantum number (choice q), size is governed by the principle quantum number (choice p) and orientation is governed by azimuthal as well as magnetic quantum numbers (choices q and r).
- (d) Probability density of electron at the nucleus in hydrogen-like atom is decided by the square wave function which, in turn, depends on the three quantum numbers,  $n$ ,  $l$  and  $m$ .

### Subjective Type

1. Number of C atoms in 7 mg of  $^{14}\text{C}$  =  $(6.022 \times 10^{23} \text{ mol}^{-1}) \left( \frac{7 \times 10^{-3} \text{ g}}{14 \text{ g mol}^{-1}} \right) = 3.011 \times 10^{20}$

Since there are 8 neutrons in one atom of  $^{14}\text{C}$ , the number of neutrons in 7 mg of  $^{14}\text{C}$  is

$$N = (8) (3.011 \times 10^{20}) = 2.41 \times 10^{21}$$

Mass of these neutrons is

$$m = (2.41 \times 10^{21}) \left( \frac{1 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} \right) = 4.09 \times 10^{-3} \text{ g.}$$

2. We have

$$|\Delta E_2 \leftarrow_3| = -2.41 \times 10^{-19} \text{ J} - (-5.42 \times 10^{-19} \text{ J}) = 3.01 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(3.01 \times 10^{-19} \text{ J})} = 6.604 \times 10^{-7} \text{ m.}$$

3. From the given data, it follows that

$$E_1 = -2.17 \times 10^{-18} \text{ J}$$

$$E_2 = \frac{E_1}{n^2} = -\frac{21.7 \times 10^{-18}}{4} \text{ J} = -5.425 \times 10^{-19} \text{ J}$$

Hence,  $|\Delta E_1 \leftarrow_2| = -5.425 \times 10^{-19} \text{ J} - (-2.17 \times 10^{-18} \text{ J}) = 1.6275 \times 10^{-18} \text{ J}$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J})(3 \times 10^8 \text{ m s}^{-1})}{(1.6275 \times 10^{-18} \text{ J})} = 1.221 \times 10^{-7} \text{ m.}$$

4. The energy of  $n = 2$  orbit is

$$E = -\frac{21.7 \times 10^{-19} \text{ J}}{4} = -5.425 \times 10^{-19} \text{ J}$$

To remove electron completely, we will require

$$E = 5.425 \times 10^{-19} \text{ J}$$

Hence,  $\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(5.425 \times 10^{-19} \text{ J})} = 3.664 \times 10^{-7} \text{ m.}$

5. In a one electron system, the expression of electronic energy is

$$E = -Z^2 E_H$$

where  $Z$  is the nuclear charge. Hence, for  $\text{He}^+$  ion, we have

$$E = \frac{4 \times 21.76 \times 10^{-19} \text{ J}}{n^2}$$

To remove the electron from third orbit of  $\text{He}^+$ , the energy needed would be

$$E = \frac{4 \times 21.76 \times 10^{-19} \text{ J}}{9}$$

$$\begin{aligned}\text{Hence, } \lambda &= \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \text{ m s}^{-1})}{(4 \times 21.76 \times 10^{-19} \text{ J})/9} \\ &= 2.055 \times 10^{-7} \text{ m} = 205.5 \text{ nm.}\end{aligned}$$

- 6.** For a hydrogen atom, the expression of energy difference between two electronic levels is

$$\Delta E = Rhc \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Hence,

$$\Delta E_2 \leftarrow 1 = (1.09677 \times 10^7 \text{ m}^{-1}) (6.626 \times 10^{-34} \text{ J s}) \times (3 \times 10^8 \text{ m s}^{-1}) \times \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 1.635 \times 10^{-8} \text{ J}$$

For hydrogen-like species, the expression is

$$\Delta E = Z^2 Rhc \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{or } \frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Thus } \frac{1}{3 \times 10^{-8} \text{ m}} = Z^2 (1.09677 \times 10^7 \text{ m}^{-1}) \left( \frac{3}{4} \right)$$

$$\text{or } Z^2 = \frac{1}{(3 \times 10^{-8} \text{ m})(1.09677 \times 10^7 \text{ m}^{-1})(3/4)} \approx 4.0$$

$$\text{or } Z = 2$$

The species is  $\text{He}^+$ .

- 7.** For  $\text{He}^+$  ion, we have

$$\frac{1}{\lambda} = Z^2 R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (2)^2 R \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = \frac{3}{4} R \quad (1)$$

Now for hydrogen atom

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2)$$

Equating Eqs (1) and (2), we get

$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

Obviously,  $n_1 = 1$  and  $n_2 = 2$ . Hence, the transition  $n = 2$  to  $n = 1$  in hydrogen atom will have the same wavelength as the transition,  $n = 4$  to  $n = 2$  in  $\text{He}^+$  species.

- 8.** Work obtained in the neutralisation process is

$$w = - \int_{\infty}^{a_0} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2} dr = \frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$$

This work will be obtained from the average total energy of electron.

$$\text{Hence, } \overline{\text{KE}} = -w = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$$

$$\text{It is given that } \overline{\text{KE}} = \frac{1}{2}|\overline{\text{PE}}|$$

$$\text{Hence, } \overline{\text{TE}} = \overline{\text{KE}} + \overline{\text{PE}} - \frac{e^2}{(4\pi\epsilon_0)a_0} = -\frac{1}{2}\overline{\text{PE}} + \overline{\text{PE}}$$

$$\text{or } \overline{\text{PE}} = -2\overline{\text{KE}} = -2\left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{a}\right)$$

- 9.** For 1.54 Å wavelength, the momentum of electron would be given by the expression

$$p = \frac{h}{\lambda} \Rightarrow v = \frac{h}{m\lambda}$$

The potential to which a beam of electrons be accelerated is given by the expression

$$eV = \frac{1}{2}mv^2$$

$$\text{i.e. } V = \frac{1}{2me} \left( \frac{h}{\lambda} \right)^2$$

Substituting the values, we get

$$\begin{aligned} V &= \frac{1}{(2)(9.1 \times 10^{-31} \text{ kg})(1.6 \times 10^{-19} \text{ C})} \left( \frac{6.6626 \times 10^{-34} \text{ J s}}{1.54 \times 10^{-10} \text{ m}} \right)^2 \\ &= 63.573 \text{ m s}^{-1} \end{aligned}$$

- 10.** Amount of hydrogen gas is

$$n_1 = \frac{PV}{RT} = \frac{(1 \text{ atm})(1 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.04092 \text{ mol}$$

Energy consumed in dissociating hydrogen molecule

$$E_1 = (0.04092 \text{ mol})(436 \text{ kJ mol}^{-1}) = 17.84 \text{ kJ}$$

Since each hydrogen molecule gives two hydrogen atoms, the amount of hydrogen atoms will be

$$n_2 = 2n_1 = 2 \times 0.04092 \text{ mol} = 0.08184 \text{ mol}$$

Energy required to excite one mole of hydrogen atoms from the ground electronic state to the first excited state is

$$\begin{aligned} \Delta E &= N_A R_H hc \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} N_A R_H hc \\ &= \left( \frac{3}{4} \right) (6.023 \times 10^{23} \text{ mol}^{-1}) (109679 \text{ cm}^{-1}) \times (6.626 \times 10^{-34} \text{ J}) \times (3 \times 10^8 \text{ cm s}^{-1}) \\ &= 9848.5 \text{ J mol}^{-1} \end{aligned}$$

For exciting 0.08184 mol of hydrogen atoms, we will have

$$E_2 = (0.08184 \text{ mol})(9.8485 \text{ kJ mol}^{-1}) = 0.806 \text{ kJ}$$

Hence, the total energy required will be

$$E = E_1 + E_2 = (17.84 + 0.81) \text{ kJ} = 18.65 \text{ kJ}$$

11. The shortest wavelength transition in the Balmer series corresponds to the transition  $n = 2 \rightarrow n = \infty$ . Hence,

$$\begin{aligned}\Delta\tilde{E} &= R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (109\ 677 \text{ cm}^{-1}) \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \\ &= 27\ 419.25 \text{ cm}^{-1}\end{aligned}$$

12. In general, the number of waves made by a Bohr electron in an orbit is equal to its quantum number.

$$\begin{array}{ll}\text{In the 3rd orbit } mvr = 3\left(\frac{h}{2\pi}\right) & (\text{Bohr's postulate of angular momentum}) \\ \lambda = \frac{h}{mv} & (\text{de Broglie expression})\end{array}$$

Substituting this in the first expression, we get

$$\left(\frac{h}{\lambda}\right)r = 3\left(\frac{h}{2\pi}\right)$$

$$\text{or } 3\lambda = 2\pi r$$

Thus, the circumference of the 3rd orbit is equal to three times the wavelength of electron, i.e. the electron makes three revolution around the 3rd orbit.

13. The shortest wavelength transition in the Balmer series corresponds to the transition  $n = 2 \rightarrow n = \infty$ . Hence,

$$\begin{aligned}\Delta\tilde{E} &= R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = (109677 \text{ cm}^{-1}) \left( \frac{1}{2^2} - \frac{1}{\infty^2} \right) \\ &= 27419.25 \text{ cm}^{-1}\end{aligned}$$

14. Potential energy of  $\alpha$ -particle at a distance  $10^{-13}\text{m}$  from the nucleus of a copper atom is

$$\begin{aligned}V &= -\frac{Z_1 Z_2 e^2}{(4\pi\epsilon_0)r} = -\frac{(29)(4)(1.6 \times 10^{-19}\text{C})^2}{(4)(3.14)(8.85 \times 10^{-12}\text{J}^{-1}\text{C}^2\text{m}^{-1})(10^{-13}\text{m})} \\ &= -2.67 \times 10^{-13}\text{ J}\end{aligned}$$

Velocity at which  $\alpha$ -particle should move is

$$\begin{aligned}v &= \sqrt{\frac{2|V|}{m}} = \sqrt{\frac{(2)(2.67 \times 10^{-13}\text{J})}{(4.0 \times 10^{-3}\text{kg mol}^{-1})/(6.023 \times 10^{23}\text{mol}^{-1})}} \\ &= 8.97 \times 10^6 \text{ m s}^{-1}\end{aligned}$$

15. For  $1.54\text{ nm}$  wavelength, the momentum of electron would be given by expression

$$p = \frac{h}{\lambda} \Rightarrow v = \frac{h}{m\lambda}$$

The potential to which a beam of electrons be accelerated is given by the expression

$$eV = \frac{1}{2}mv^2,$$

$$\text{i.e., } V = \frac{1}{2me} \left( \frac{h}{\lambda} \right)^2$$

Substituting the values, we get

$$\begin{aligned}V &= \frac{1}{(2)(9.1 \times 10^{-31}\text{kg})(1.6 \times 10^{-19}\text{C})} \left( \frac{6.626 \times 10^{-34}\text{ Js}}{1.54 \times 10^{-10}\text{m}} \right)^2 \\ &= 63.573 \text{ V}\end{aligned}$$

**16.** Amount of hydrogen gas is

$$\begin{aligned} n_1 &= \frac{PV}{RT} = \frac{(1 \text{ atm})(1 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})} \\ &= 0.04092 \text{ mol} \end{aligned}$$

Energy consumed in dissociating hydrogen molecule

$$\begin{aligned} E_1 &= (0.04092 \text{ mol}) (436 \text{ kJ mol}^{-1}) \\ &= 17.84 \text{ kJ} \end{aligned}$$

Since each hydrogen molecule gives two hydrogen atoms, the amount of hydrogen atoms will be

$$n_2 = 2n_1 = 2 \times 0.04092 \text{ mol} = 0.08184 \text{ mol.}$$

Energy required to excite one mole of hydrogen atoms from the ground electronic state to the first excited state is

$$\begin{aligned} \Delta E &= N_A R_H hc \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} N_A R_H hc \\ &= \left( \frac{3}{4} \right) (6.023 \times 10^{23} \text{ mol}^{-1}) (109 679 \text{ cm}^{-1}) (6.626 \times 10^{-34} \text{ J}) \times (3 \times 10^8 \text{ cm s}^{-1}) \\ &= 9848.5 \text{ J mol}^{-1} \end{aligned}$$

For exciting 0.08184 mol of hydrogen atoms, we will have

$$E_2 = (0.08184 \text{ mol}) (9.8485 \text{ kJ mol}^{-1}) = 0.81 \text{ kJ}$$

Hence, the total energy required will be

$$E = E_1 + E_2 = (17.84 + 0.81) \text{ kJ} = 18.65 \text{ kJ}$$

**17.** The electronic transitions in hydrogen-like species follow the expression

$$\Delta \tilde{E} = Z^2 R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\text{Hence, } \frac{(\Delta \tilde{E})_{\text{He}^+}}{(\Delta \tilde{E})_{\text{H}}} = Z^2 \text{ or } \frac{\lambda_{\text{H}}}{\lambda_{\text{He}^+}} = 4 \text{ or } \lambda_{\text{He}^+} = \frac{\lambda_{\text{H}}}{4} = \frac{92.0 \text{ nm}}{4} = 23.0 \text{ nm}$$

**18.** (a) At nodeal point  $\psi = 0$ . From the given wave function we find that  $\psi = 0$  at the following values of  $r$ .

$$2(r_0/a_0)^2 - 18(r_0/a_0) + 27 = 0$$

Solving for  $r/a_0$ , we get

$$\frac{r_0}{a_0} = \frac{18 \pm \sqrt{18^2 - 216}}{4} = \frac{18 \pm 10.4}{2} = 14.2 \text{ and } 3.9$$

Hence,  $r_0 = 14.2 a_0$  and  $r_0 = 3.9 a_0$

Besides these, there is a node at  $r = \infty$ .

(b) Using de-Broglie relation, we get

$$\lambda = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ J s})}{(0.1 \text{ kg})(200 \text{ m s}^{-1})} = 3.313 \times 10^{-35} \text{ m}$$



# PERIODICITY OF PROPERTIES OF ELEMENTS

4

## Straight Objective Type

1. The first ionization potentials in electron volts of nitrogen and oxygen atoms are respectively given by  
(a) 14.6, 13.6      (b) 13.6, 14.6      (c) 13.6, 13.6      (d) 14.6, 14.6      (1987)
2. Atomic radii of fluorine and neon in Angstrom units are respectively given by  
(a) 0.72, 1.60      (b) 1.60, 1.60      (c) 0.72, 0.72      (d) none of these values      (1987)
3. The electronegativity of the following elements increases in the order  
(a) C, N, Si, P      (b) N, Si, C, P      (c) Si, P, C, N      (d) P, Si, N, C      (1987)
4. The first ionization potential of Na, Mg, Al and Si are in the order  
(a)  $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$       (b)  $\text{Na} > \text{Mg} > \text{Al} > \text{Si}$   
(c)  $\text{Na} < \text{Mg} < \text{Al} > \text{Si}$       (d)  $\text{Na} > \text{Mg} > \text{Al} < \text{Si}$       (1988)
5. Which one of the following is the smallest in size?  
(a)  $\text{N}^{3-}$       (b)  $\text{O}^{2-}$       (c)  $\text{F}^-$       (d)  $\text{Na}^+$       (1989)
6. Amongst the following elements (whose electronic configurations are given below), the one having the highest ionization energy is  
(a)  $[\text{Ne}] (3s)^2 (3p)^1$       (b)  $[\text{Ne}] (3s)^2 (3p)^3$   
(c)  $[\text{Ne}] (3s)^2 (3p)^2$       (d)  $[\text{Ar}] (3d)^{10} (4s)^2 (4p)^3$       (1990)
7. The statement that is not correct for the periodic classification of elements is  
(a) The properties of elements are the periodic function of their atomic numbers.  
(b) Non-metallic elements are lesser in number than metallic elements.  
(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.  
(d) For transition elements the d subshells are filled with electrons monotonically with increase in atomic number.      (1992)
8. The correct order of the second ionization energy of C, N, O and F is  
(a)  $\text{C} > \text{N} > \text{O} > \text{F}$       (b)  $\text{O} > \text{N} > \text{F} > \text{C}$   
(c)  $\text{O} > \text{F} > \text{N} > \text{C}$       (d)  $\text{F} > \text{O} > \text{N} > \text{C}$       (1981)
9. The incorrect statement among the following is  
(a) the first ionization potential of Al is less than the first ionization potential of Mg.  
(b) the second ionization potential of Mg is greater than the second ionization potential of Na.  
(c) the first ionization potential of Na is less than the first ionization potential of Mg.  
(d) the third ionization potential of Mg is greater than the third ionization potential of Al.      (1997)

10. Property of the alkaline earth metals that increases with their atomic number is  
 (a) ionisation energy; (b) solubility of their hydroxides;  
 (c) solubility of their sulphates; (d) electronegativity. (1997)
11. Ionic radii of  
 (a)  $Ti^{4+} < Mn^{7+}$  (b)  $^{35}Cl^- < ^{37}Cl^-$  (c)  $K^+ > Cl^-$  (d)  $P^{3+} > P^{5+}$  (1999)
12. The correct order of radii is  
 (a)  $N < Be < B$  (b)  $F^- < O^{2-} < N^{3-}$  (c)  $Na < Li < K$  (d)  $Fe^{3+} < Fe^{2+} < Fe^{4+}$  (2000)
13. The set representing the correct order of first ionization potential is  
 (a)  $K > Na > Li$  (b)  $Be > Mg > Ca$  (c)  $B > C > N$  (d)  $Ge > Si > C$  (2001)
14. Identify the least stable ion amongst the following:  
 (a)  $Li^-$  (b)  $Be^-$  (c)  $B^-$  (d)  $C^-$  (2002)

### Multiple Correct-Choice Type

1. The statements that are true for the long form of the periodic table are  
 (a) It reflects the sequence of filling the electrons in the order of sub energy levels s, p, d and f.  
 (b) It helps predict the stable valency states of the elements.  
 (c) It reflects trends in physical and chemical properties of the elements.  
 (d) It helps predict the relative ionicity of the bond between any two elements. (1988)

### Fill-in-the-Blanks Type

1. The energy released when an electron is added to a neutral gaseous atom is called \_\_\_\_\_ of the atom. (1982)
2.  $Ca^{2+}$  has a smaller ionic radius than  $K^+$  because it has \_\_\_\_\_. (1993)

### Integer Answer Type

1. The total number of lone pairs of electrons in  $N_2O_3$  is \_\_\_\_\_. (2015)

### True/False Type

1. The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. (1993)
2. The softness of group IA metals increases down the group with increasing atomic number. (1986)
3. In Group IA of alkali metals, the ionization potential decreases down the group. Therefore, lithium is a poor reducing agent. (1987)
4. The basic nature of the hydroxides of Group 13 (Gr. III B) decreases progressively down the group. (1993)

### Reasoning Type

The question below (1 and 2) consist of an '*Assertion*' in column 1 and the '*Reason*' in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.  
 (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.  
 (c) If *assertion* is CORRECT, but *reason* is INCORRECT.  
 (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

**Assertion (column 1)**

1. F atom has a less negative electron affinity than Cl atom.
2. The first ionisation energy of Be is greater than that of B.

**Reason (column 2)**

Additional electrons are repelled more effectively by 3p electrons in Cl atom than by 2p electrons in F atom.  
 2p orbital is lower in energy than 2s.

(1998)  
 (2000)

**Short Answer Type**

1. Explain the following:

The first ionization energy of carbon atom is greater than that of boron atom, whereas the reverse is true for the second ionization energy.

(1989)

2. Bond dissociation energy of  $F_2$  is less than that of  $Cl_2$ .
3. Compare qualitatively the first and second ionisation potentials of copper and zinc. Explain the observation.
4. The crystalline salts of alkaline earth metals contain more water of crystallisation than the corresponding alkali metal salts. Why?
5. Arrange the following ions in order of their increasing radii:  $Li^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Al^{3+}$ .
6. Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability:  $BeSO_4$ ,  $MgSO_4$ ,  $CaSO_4$ ,  $SrSO_4$ .

**ANSWERS****Straight Objective Type**

- |        |        |         |         |         |         |         |
|--------|--------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (a) | 3. (c)  | 4. (a)  | 5. (d)  | 6. (b)  | 7. (c)  |
| 8. (c) | 9. (b) | 10. (b) | 11. (d) | 12. (b) | 13. (b) | 14. (b) |

**Multiple Correct-Choice Type**

1. (a), (b), (c), (d)

**Fill-in-the-Blanks Type**

1. electron affinity
2. larger positive charge in the nucleus or larger effective nuclear charge.

**Integer Answer Type**

1. 8

**True/False Type**

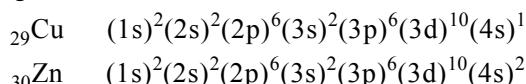
1. False
2. True
3. True
4. False,

**Reasoning Type**

1. (c)
2. (c)

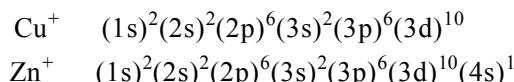
## Short Answer Type

- From the electronic configurations of  $_6\text{C}$  ( $1s^2, 2s^2, 2p^2$ ) and  $_5\text{B}$  ( $1s^2, 2s^2, 2p^1$ ), we find that the  $2p$  electron in carbon will experience more nuclear attraction due to more positive charge on it. Hence, the first ionization energy of carbon atom is greater than that of boron atom. After the removal of one electron, the electronic configuration of  $\text{B}^+$  corresponds to the fully-filled orbital from which it is comparatively difficult to remove an electron. Hence, the second ionization energy of B is greater than that of C.
- The dissociation energy of  $\text{Cl}_2$  being higher than  $\text{F}_2$  is due to the presence of an additional  $\pi$ -bond. This is created via donor-acceptor mechanism in which an unshared electron pair of one atom overlap with a free  $3d$  orbital of the other atom.
- The electronic configurations of Cu and Zn are



The first ionization of Cu requires lesser energy than Zn as the removal of  $4s$  electron in Cu leads to the stable fully-filled  $3d^{10}$  configuration.

The electronic configuration of  $\text{Cu}^+$  and  $\text{Zn}^+$  are



In this case,  $\text{Zn}^+$  has lower ionization energy as it leads to the formation of  $3d^{10}$  configuration. The removal of electron in  $\text{Cu}^+$  will require very high energy as it is difficult to remove the electron from the stable  $3d^{10}$  configuration.

- This is due to the smaller size and increased positive charge on the Group II ions as compared to those of the Group I ions.
- $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Li}^+ < \text{K}^+$
- $\text{SrSO}_4 > \text{CaSO}_4 > \text{MgSO}_4 > \text{BeSO}_4$

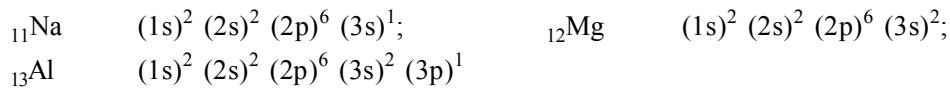
## HINTS AND SOLUTIONS

### Straight Objective Type

- The electronic configurations are  
 ${}_7\text{N}$  ( $1s)^2(2s)^2(2p_x)^1(2p_y)^1(2p_z)^1$  and  ${}_8\text{O}$  ( $1s)^2(2s)^2(2p_x)^2(2p_y)^1(2p_z)^1$ )  
 Nitrogen is expected to have higher ionization energy because it has stable half-filled electronic configuration.
- Atomic radius of neon will be larger than fluorine.
- Electronegativity increases along a period and decreases down the group. Nitrogen is expected to have maximum electronegativity.
- The electronic configurations are  ${}_{11}\text{Na}$  ( $3s$ ) $^1$ ;  ${}_{12}\text{Mg}$  ( $3s$ ) $^2$ ;  ${}_{13}\text{Al}$  ( $3s$ ) $^2$ ( $3p$ ) $^1$ ;  ${}_{14}\text{Si}$  ( $3s$ ) $^2$ ( $3p$ ) $^2$ ;  
 The ionization energy of Mg will be larger than that of Na due to fully-filled configuration  $3s^2$ .  
 The ionization of Al will be smaller than that of Mg due to one electron extra than the stable configuration.  
 The ionization of Al will be smaller than that of Si due to increase in effective nuclear charge of Si. Hence, the trend will follow the order  $\text{Na} < \text{Mg} > \text{Al} < \text{Si}$ .
- All the four species are isoelectronic. The cation  $\text{Na}^+$  will have smallest size because of more electrostatic attraction between nucleus and electrons.
- The configuration  $[\text{Ne}]$ ( $3s$ ) $^2$ ( $3p$ ) $^3$  will have highest ionization energy due to the stable half-filled electronic configuration.  $[\text{Ar}]$ ( $3d$ ) $^{10}$ ( $4s$ ) $^2$ ( $4p$ ) $^3$  is expected to have lesser value due to the larger distance of valence electrons from the nucleus.

7. The first ionization energy tends to increase along the period.

9. The electronic configurations of  $_{11}\text{Na}$ ,  $_{12}\text{Mg}$  and  $_{13}\text{Al}$  are



The first ionization potential of Al is lesser than that of Mg because in magnesium the electron to be removed belongs to stable fully-filled s orbital. Thus, the statement a is correct.

The second ionization potential of Mg is smaller than that of Na because in Na the electron to be removed is from the stable inert gas configuration. Thus, the statement b is incorrect.

Proceeding similarly, the correctness of statements c and d can be explained.

10. Lattice energy controls the solubility which decreases on descending the group causing increase in solubility.

11.  $_{22}\text{Ti}^{4+}$  and  $_{25}\text{Mn}^{7+}$  are isoelectronic, the larger nuclear charge in Mn causes more electronic attraction and hence the size of  $\text{Mn}^{7+}$  will be smaller than that of  $\text{Ti}^{4+}$ .

The sizes of  $^{35}\text{Cl}^-$  and  $^{37}\text{Cl}^-$  would be more or less identical.

$\text{K}^+$  and  $\text{Cl}^-$  are isoelectronic, the cation  $\text{K}^+$  will have the smaller size than the anion  $\text{Cl}^-$ .

The larger the charge number of cation, the smaller the size.

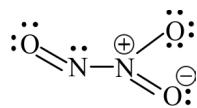
12. As we go from F to O to N, the positive charge in the nucleus decreases. This causes decrease in nucleus-electron attraction causing the electron cloud to spread more in space. Also, larger negative charge involves larger electron-electron repulsion causing spreading of electron cloud in space.

### Multiple Correct-Choice Type

14. Beryllium loses its fully-filled electronic configuration  $2s^2$  and thus  $\text{Be}^-$  will be least stable.

### Integer Answer Type

1. The structure of  $\text{N}_2\text{O}_3$  is



There are 8 pairs of lone electrons in  $\text{N}_2\text{O}_3$ .

### True/False Type

1. The correct order is  $\text{Cl} > \text{F} > \text{Br}$ . The larger electronic repulsion in F atom due to its small size is responsible for lesser electron affinity in F atom than in Cl atom.
4. The basic nature increases as the element becomes more electropositive (or acquires more metallic characteristics).

### Reasoning Type

2. Boron atom contains one extra electron in p orbital as compared to beryllium atom. The removal of p electron requires less energy as compared to the removal of electron from the more stable fully-filled 2s orbitals.



# BONDING AND MOLECULAR STRUCTURE

5

## Straight Objective Type

1. The octet rule is not valid for the molecule  
(a)  $\text{CO}_2$       (b)  $\text{H}_2\text{O}$       (c)  $\text{O}_2$       (d)  $\text{CO}$       (1979)
2. The compound which contains both ionic and covalent bonds is  
(a)  $\text{CH}_4$       (b)  $\text{H}_2$       (c)  $\text{KCN}$       (d)  $\text{KCl}$       (1979)
3. The total number of electrons in one molecule of carbon dioxide is  
(a) 22      (b) 44      (c) 66      (d) 88      (1979)
4. Which of the following compounds is covalent?  
(a)  $\text{H}_2$       (b)  $\text{CaO}$       (c)  $\text{KCl}$       (d)  $\text{Na}_2\text{S}$       (1980)
5. Element X is strongly electropositive and element Y is strongly electronegative. Both are univalent. The compound formed will be  
(a)  $\text{X}^+\text{Y}^-$       (b)  $\text{X}^-\text{Y}^+$       (c)  $\text{X}-\text{Y}$       (d)  $\text{X} \rightarrow \text{Y}$       (1980)
6. The total number of electrons that take part in forming the bond in  $\text{N}_2$  is  
(a) 2      (b) 4      (c) 6      (d) 8      (e) 10      (1980)
7. If a molecule  $\text{MX}_3$  has zero dipole moment, the sigma bonding molecular orbitals used by M (atomic number < 4) are  
(a) pure p      (b) sp hybrid      (c)  $\text{sp}^2$  hybrid      (d)  $\text{sp}^3$  hybrid      (1981)
8. The bond order of individual carbon-carbon bonds in benzene is  
(a) one      (b) two  
(c) between one and two      (d) one and two alternatively      (1981)
9. The compound with no dipole moment is  
(A) methyl chloride      (B) carbon tetrachloride  
(C) methylene chloride      (D) chloroform      (1982)
10. Carbon tetrachloride has no net dipole moment because of  
(A) its planar structure  
(B) its regular tetrahedral structure  
(C) similar sizes of carbon and chlorine atoms  
(D) similar electron affinities of carbon and chlorine      (1983)
11. Which one among the following does not have the hydrogen bond?  
(A) Phenol      (B) Liquid  $\text{NH}_3$       (C) Water      (D) Liquid  $\text{HCl}$       (1983)

- 12.** The types of bonds present in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are only  
 (A) electrovalent and covalent  
 (B) electrovalent and coordinate covalent  
 (C) electrovalent, covalent and coordinate covalent  
 (D) covalent and coordinate covalent (1983)
- 13.** The molecule having one unpaired electron is  
 (A)  $\text{NO}$       (B)  $\text{CO}$       (C)  $\text{CN}^-$       (D)  $\text{O}_2$  (1985)
- 14.** The bond between two identical nonmetal atoms has a pair of electrons  
 (A) unequally shared between the two  
 (B) transferred fully from one atom to another  
 (C) with identical spins  
 (D) equally shared between them. (1986)
- 15.** The hydrogen bond is strongest in  
 (A)  $\text{O}-\text{H} \cdots \text{S}$       (B)  $\text{S}-\text{H} \cdots \text{O}$       (C)  $\text{F}-\text{H} \cdots \text{F}$       (D)  $\text{F}-\text{H} \cdots \text{O}$  (1986)
- 16.** The hybridisation in sulphur dioxide is  
 (A)  $\text{sp}$       (B)  $\text{sp}^2$       (C)  $\text{sp}^3$       (D)  $\text{dsp}^2$  (1986)
- 17.** The bonds present in  $\text{N}_2\text{O}_5$  are  
 (A) only ionic      (B) covalent and coordinate  
 (C) only covalent      (D) covalent and ionic (1986)
- 18.** The species in which the central atom uses  $\text{sp}^2$  hybrid orbitals in its bonding is  
 (A)  $\text{PH}_3$       (B)  $\text{NH}_3$       (C)  $\text{CH}_3^+$       (D)  $\text{SbH}_3$  (1988)
- 19.** The ion that is isoelectronic with  $\text{CO}$  is  
 (A)  $\text{CN}^-$       (B)  $\text{O}_2^+$       (C)  $\text{O}_2^-$       (D)  $\text{N}_2^+$  (1982)
- 20.** Among the following, the molecule that is linear is  
 (A)  $\text{CO}_2$       (B)  $\text{NO}_2$       (C)  $\text{SO}_2$       (D)  $\text{ClO}_2$  (1988)
- 21.** The molecule which has zero dipole moment is  
 (A)  $\text{CH}_2\text{Cl}_2$       (B)  $\text{BF}_3$       (C)  $\text{NF}_3$       (D)  $\text{ClO}_2$  (1989)
- 22.** Which of the following is paramagnetic?  
 (A)  $\text{O}_2^-$       (B)  $\text{CN}^-$       (C)  $\text{CO}$       (D)  $\text{NO}^+$  (1989)
- 23.** The molecule which has a pyramidal shape is  
 (A)  $\text{PCl}_3$       (B)  $\text{SO}_3$       (C)  $\text{CO}_3^{2-}$       (D)  $\text{NO}_3^-$  (1989)
- 24.** The linear structure is assumed by  
 (A)  $\text{SnCl}_2$       (B)  $\text{NCO}^-$       (C)  $\text{NO}_2^+$       (D)  $\text{SO}_2$  (1991)
- 25.** The type of hybrid orbitals used by chlorine atom in  $\text{ClO}_2^-$  is  
 (A)  $\text{sp}^3$       (B)  $\text{sp}^2$       (C)  $\text{sp}$       (D)  $\text{dsp}^2$  (1992)
- 26.** The maximum number of hydrogen bonds a water molecule can form is  
 (A) 2      (B) 4      (C) 3      (D) 1 (1992)
- 27.** Which of the following contains both polar and non-polar bonds?  
 (A)  $\text{NH}_4\text{Cl}$       (B)  $\text{HCN}$       (C)  $\text{H}_2\text{O}_2$       (D)  $\text{CH}_4$  (1997)
- 28.** Which of the following compounds has  $\text{sp}^2$  hybridisation?  
 (A)  $\text{CO}_2$       (B)  $\text{SO}_2$       (C)  $\text{N}_2\text{O}$       (D)  $\text{CO}$  (1997)

- 29.** Among the following compounds the one that is polar and has the central atom with  $sp^2$  hybridisation is  
 (A)  $H_2CO_3$       (B)  $SiF_4$       (C)  $BF_3$       (D)  $HClO_2$       (1997)
- 30.** Molecular shapes of  $SF_4$ ,  $CF_4$  and  $XeF_4$  are  
 (A) the same, with 2, 0 and 1 lone pair of electrons, respectively.  
 (B) the same, with 1, 1 and 1 lone pair of electrons, respectively  
 (C) different, with 0, 1 and 2 lone pair of electrons, respectively  
 (D) different with 1, 0 and 2 lone pair of electrons, respectively      (2000)
- 31.** The hybridisation of atomic orbitals of nitrogen in  $NO_2^+$ ,  $NO_3^-$  and  $NH_4^+$  are  
 (A)  $sp$ ,  $sp^3$  and  $sp^2$  respectively      (B)  $sp$ ,  $sp^2$  and  $sp^3$  respectively  
 (C)  $sp^2$ ,  $sp$  and  $sp^3$  respectively      (D)  $sp^2$ ,  $sp^3$  and  $sp$  respectively      (2000)
- 32.** On hybridization of one s and one p orbitals, we get  
 (a) two mutually perpendicular orbitals      (b) two orbitals at  $180^\circ$   
 (c) four orbitals directed tetrahedrally      (d) three orbitals in a plane.      (1984)
- 33.** The hydration energy of  $Mg^{2+}$  is larger than that of  
 (a)  $Al^{3+}$       (b)  $Na^+$       (c)  $Be^{2+}$       (d)  $Mg^{2+}$       (1984)
- 34.** The cyanide ion,  $CN^-$  and  $N_2$  are isoelectronic. But in contrast to  $CN^-$ ,  $N_2$  is chemically inert, because of  
 (a) low bond energy  
 (b) absence of bond polarity  
 (c) unsymmetrical electron distribution  
 (d) presence of more number of electrons in bonding orbitals.      (1992)
- 35.** Among the following species, identify the isostructural pairs.  
 $NF_3$ ,  $NO_3^-$ ,  $BF_3$ ,  $H_3O^+$ ,  $HN_3$   
 (a)  $[NF_3, NO_3^-]$  and  $[BF_3, H_3O^+]$       (b)  $[NF_3, HN_3]$  and  $[NO_3^-, BF_3]$   
 (c)  $[NF_3, H_3O^+]$  and  $[NO_3^-, BF_3]$       (d)  $[NF_3, H_3O^+]$  and  $[HN_3, BF_3]$       (1996)
- 36.** The number and type of bonds between two carbon atoms in  $CaC_2$  are:  
 (a) one sigma ( $\sigma$ ) and one pi ( $\pi$ ) bonds  
 (b) one sigma ( $\sigma$ ) and two pi ( $\pi$ ) bonds  
 (c) one sigma ( $\sigma$ ) and one and a half pi ( $\pi$ ) bonds  
 (d) one sigma ( $\sigma$ ) bond.      (1996)
- 37.** Which of the following statements is correct for  $CsBr_3$ ?  
 (a) It is a covalent compound.      (b) It contains  $Cs^{3+}$  and  $Br^-$  ions.  
 (c) It contains  $Cs^+$  and  $Br_3^-$  ions.      (d) It contains  $Cs^+$ ,  $Br^-$  and lattice  $Br_2$  molecule.      (1996)
- 38.** KF combines with HF to form  $KHF_2$ . The compound contains the species:  
 (a)  $K^+$ ,  $F^-$  and  $H^+$       (b)  $K^+$ ,  $F^-$  and HF  
 (c)  $K^+$  and  $[HF_2]^-$       (d)  $[KHF]^+$  and  $F^-$       (1996)
- 39.** Among  $KO_2$ ,  $AlO_2^-$ ,  $BaO_2$  and  $NO_2^+$ , unpaired electron is present in  
 (a)  $NO_2^+$  and  $BaO_2$       (b)  $KO_2$  and  $AlO_2^-$   
 (c)  $KO_2$  only      (d)  $BaO_2$  only      (1997)
- 40.** The geometry and the type of hybrid orbital present about the central atom in  $BF_3$  is  
 (a) linear,  $sp$       (b) trigonal planar,  $sp^2$   
 (c) tetrahedral,  $sp^3$       (d) pyramidal,  $sp^3$       (1998)

- 41.** The correct order of increasing C—O bond length of CO,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$  is  
 (a)  $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$       (b)  $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$   
 (c)  $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$       (d)  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$  (1999)
- 42.** The geometry of  $\text{H}_2\text{S}$  and its dipole moment are  
 (a) angular and nonzero      (b) angular and zero  
 (c) linear and nonzero      (d) linear and zero (1999)
- 43.** The common features among the species  $\text{CN}^-$ , CO and  $\text{NO}^+$  are  
 (a) bond order three and isoelectronic      (b) bond order three and weak field ligands  
 (c) bond order two and  $\pi$ -acceptors      (d) isoelectronic and weak field ligands (2001)
- 44.** The correct order of hybridisation of the central atom in the following species  $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is  
 (a)  $\text{dsp}^2$ ,  $\text{dsp}^3$ ,  $\text{sp}^2$  and  $\text{sp}^3$       (b)  $\text{sp}^3$ ,  $\text{dsp}^2$ ,  $\text{dsp}^3$ ,  $\text{sp}^2$   
 (c)  $\text{dsp}^2$ ,  $\text{sp}^2$ ,  $\text{sp}^3$ ,  $\text{dsp}^3$       (d)  $\text{dsp}^2$ ,  $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{dsp}^3$  (2001)
- 45.** Specify the coordination geometry around and hybridisation of N and B atoms in a 1 : 1 complex of  $\text{BF}_3$  and  $\text{NH}_3$   
 (a) N : tetrahedral,  $\text{sp}^3$ ; B : tetrahedral,  $\text{sp}^3$       (b) N : pyramidal,  $\text{sp}^3$ ; B : pyramidal,  $\text{sp}^3$   
 (c) N : pyramidal,  $\text{sp}^3$ ; B : planar,  $\text{sp}^2$       (d) N : pyramidal,  $\text{sp}^3$ ; B : tetrahedral,  $\text{sp}^3$  (2002)
- 46.** Which of the following molecular species has unpaired electron(s)?  
 (a)  $\text{N}_2$       (b)  $\text{F}_2$       (c)  $\text{O}_2^-$       (d)  $\text{O}_2^{2-}$  (2002)
- 47.** The nodal plane in the  $\pi$ -bond of ethene is located in  
 (a) the molecular plane  
 (b) a plane parallel to the molecular plane  
 (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon  $\sigma$ -bond at right angle  
 (d) a plane perpendicular to the molecular plane which contains the carbon-carbon  $\sigma$ -bond (2002)
- 48.** Total number of lone pair of electrons in  $\text{XeF}_4$  is  
 (a) 0      (b) 1      (c) 2      (d) 3 (2004)
- 49.** Which of the following statements regarding  $\text{O}_2^-$  is correct?  
 (a) paramagnetic, bond order greater than that of  $\text{O}_2$   
 (b) paramagnetic, bond order lesser than that of  $\text{O}_2$   
 (c) paramagnetic, bond order is equal to that of  $\text{O}_2$   
 (d) diamagnetic, bond order greater than that of  $\text{O}_2$  (2004)
- 50.** Which of the following contains maximum number of lone pairs of electrons on the central atom?  
 (a)  $\text{ClO}_3^-$       (b)  $\text{XeF}_4$       (c)  $\text{I}_3^-$       (d)  $\text{SF}_4$  (2005)
- 51.** Among the following, the paramagnetic compound is  
 (a)  $\text{Na}_2\text{O}_2$       (b)  $\text{O}_3$       (c)  $\text{N}_2\text{O}$       (d)  $\text{KO}_2$  (2007)
- 52.** The species having bond order different from that in CO is  
 (a)  $\text{NO}^-$       (b)  $\text{NO}^+$       (c)  $\text{CN}^-$       (d)  $\text{N}_2$  (2007)
- 53.** The percentage of p-character in the orbitals forming P—P bonds in  $\text{P}_4$  is  
 (a) 25      (b) 33      (c) 50      (d) 75 (2007)
- 54.** Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule  $\text{B}_2$  is  
 (a) 1 and diamagnetic      (b) 0 and diamagnetic  
 (c) 1 and paramagnetic      (d) 0 and paramagnetic (2010)

55. The species having pyramidal shape is

- (a)  $\text{SO}_3$       (b)  $\text{BrF}_3$       (c)  $\text{SiO}_3^{2-}$       (d)  $\text{OSF}_2$       (2010)

56. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is

- (a)  $\text{Be}_2$       (b)  $\text{B}_2$       (c)  $\text{C}_2$       (d)  $\text{N}_2$       (2014)

### Multiple Correct-Choice Type

1. Carbon dioxide is isostructural with

- (a)  $\text{HgCl}_2$       (b)  $\text{SnCl}_2$       (c)  $\text{C}_2\text{H}_2$       (d)  $\text{NO}_2$       (1986)

2. Which of the following have identical bond order?

- (a)  $\text{CN}^-$       (b)  $\text{O}_2^-$       (c)  $\text{NO}^+$       (d)  $\text{CN}^+$       (1992)

3. Pick out the isoelectronic structures from the following:

- I.  $\text{CH}_3^+$       II.  $\text{H}_3\text{O}^+$       III.  $\text{NH}_3$       IV.  $\text{CH}_3^-$   
 (a) I and II      (b) III and IV      (c) I and III      (d) II, III and IV      (1993)

4. Resonance structure of a molecule should have

- (a) identical arrangement of atoms      (b) nearly the same energy content  
 (c) the same number of paired electrons      (d) identical bonding      (1984)

### Fill-in-the-Blanks Type

1. The compound having both sp and  $\text{sp}^2$  hybridised carbon atom is \_\_\_\_\_. (propene, propane, propadiene)      (1981)

2. The angle between two covalent bonds is maximum in \_\_\_\_\_. ( $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ )      (1981)

3. Pair of molecules which forms strongest intermolecular hydrogen bonding is \_\_\_\_\_. ( $\text{SiH}_4$  and  $\text{SiF}_4$ ;  $\text{CH}_3\text{COCH}_3$  and  $\text{CHCl}_3$ ,  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$ ).      (1981)

4. There are \_\_\_\_  $\pi$  bonds in nitrogen molecule.      (1982)

5. \_\_\_\_ hybrid orbitals of nitrogen are involved in the formation of ammonium ions.      (1982)

6. On Mulliken scale, the average of ionization energy and electron affinity is known as \_\_\_\_\_.      (1985)

7. Sodium dissolved in liquid ammonia conducts electricity because of the presence of \_\_\_\_\_.      (1985)

8. When  $\text{N}_2$  goes to  $\text{N}_2^+$ , the N—N bond distance \_\_\_\_\_, and when  $\text{O}_2$  goes to  $\text{O}_2^+$ , the O—O bond distance \_\_\_\_\_.      (1996)

9. Among  $\text{N}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{I}_3^+$  and  $\text{I}_3^-$ , the linear species are \_\_\_\_ and \_\_\_\_\_.      (1997)

### Integer Answer Type

1. Based on VSEPR theory, the number of 90 degree F—Br—F angles in  $\text{BrF}_5$  is \_\_\_\_\_.      (2010)

2. Among the triatomic molecules/ions,  $\text{BeCl}_2$ ,  $\text{N}_3^-$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2^+$ ,  $\text{O}_3$ ,  $\text{SCl}_2$ ,  $\text{ICl}_2^-$ ,  $\text{I}_3^-$  and  $\text{XeF}_2$ , the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is \_\_\_\_\_.  
 [Atomic number: S = 16, Cl = 17, I = 53 and Xe = 54]      (2015)

### True/False Type

1. Solid sodium chloride is a good conductor of electricity because it consists of ions      (1978)

2. Linear overlap of two atomic p-orbitals leads to a sigma bond.      (1983)

3. The bond angle H—N—H in  $\text{NH}_3$  is greater than the bond angle H—As—H in  $\text{AsH}_3$ . (1984)
4. Anhydrous HCl is a bad conductor of electricity but aqueous HCl is a good conductor. (1985)
5. *o*-nitrophenol is steam volatile whereas *p*-nitrophenol is not. (1985)
6. All molecules with polar bonds have dipole moment. (1985),(1990)
7.  $\text{SnCl}_2$  is a nonlinear molecule. (1985)
8.  $\text{sp}^2$  hybrid orbitals have equal s and p character. (1987)
9. The presence of polar bonds in a polyatomic molecule suggests that the molecule has non-zero dipole moment. (1990)

### Reasoning Type

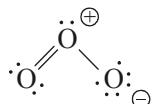
The questions below (1 and 2) consist of an ‘*Assertion*’ in column 1 and the ‘*Reason*’ in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.
- (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
- (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
- (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

*Assertion* (column I)

*Reason* (column II)

1. The electronic structure of  $\text{O}_3$  is



$\cdot\ddot{\text{O}}^{\oplus}\equiv\ddot{\text{O}}\cdots\ddot{\text{O}}^{\ominus}\cdot$  structure is not allowed

because octet around O cannot be expanded.

(1998)

2. LiCl is predominantly a covalent compound.

Electronegativity difference between Li and Cl is too small.

(1978)

3. STATEMENT-1: Band gap in germanium is small

because

STATEMENT-2: The energy spread of each germanium atomic energy level is infinitesimally small.

- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (c) Statement-1 is True, Statement-2 is False
- (d) Statement-1 is False, Statement-2 is True

(2007)

### Matrix Match Type

1. Match each of the diatomic molecule in **Column I** with its property/properties in **Column II**.

**Column I**

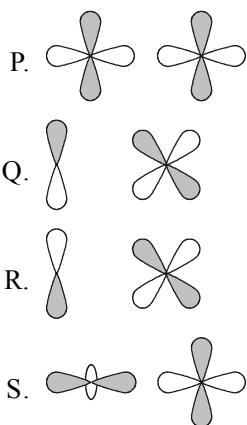
- (a)  $\text{B}_2$
- (b)  $\text{N}_2$
- (c)  $\text{O}_2^-$
- (d)  $\text{O}_2$

**Column II**

- (p) paramagnetic
- (q) undergoes oxidation
- (r) undergoes reduction
- (s) Bond order  $\geq 2$
- (t) Mixing of s and p orbitals

(2009)

2. Match the orbital overlap figures shown in **List-I** with the description given in **List-II** and select the correct answer using the code given below the lists.

**List-I****List-II**

1. p – d  $\pi$  antibonding
2. d – d  $\sigma$  bonding
3. p – d  $\pi$  bonding
4. d – d  $\sigma$  antibonding

**Code:**

	P	Q	R	S
(a)	2	1	3	4
(b)	4	3	1	2
(c)	2	3	1	4
(d)	4	1	3	2

(2014)

### Short Answer Type

1. Classify the following compounds as ionic or covalent.  
(i) MgF<sub>2</sub>, (ii) BrCl, (iii) CBr<sub>4</sub>, (iv) C<sub>2</sub>N<sub>2</sub>, (v) CuS, (vi) PH<sub>3</sub> (1978)
2. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case. (1978)
3. Give Lewis dot structures for the following.  
(i) IO<sub>3</sub><sup>-</sup>, (ii) N<sub>2</sub>O<sub>4</sub>, (iii) SO<sub>2</sub>Cl<sub>2</sub>, (iv) P<sub>2</sub>O<sub>7</sub><sup>4-</sup> (1978)
4. Give Lewis dot formulae for the following.  
(i) N<sub>2</sub>O<sub>5</sub>, (ii) S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, (iii) ClO<sub>3</sub><sup>-</sup>, (iv) CO, (v) SOCl<sub>2</sub> (1978)
5. How many sigma bonds and how many pi bonds are present in a benzene molecule? (1985)
6. Write down the resonance structure of nitrous oxide. (1985)
7. Write the Lewis dot structures of O<sub>3</sub> and COCl<sub>2</sub>. (1991), (1986)
8. Write the two resonance structures of N<sub>2</sub>O that satisfy the octet rule. (1990)
9. Using the VSEPR theory, identify the type of hybridisation and draw the structure of OF<sub>2</sub>. What are the oxidation states of O and F? (1994)
10. Explain the difference in the nature of bonding in LiF and LiI. (1996)
11. Anhydrous AlCl<sub>3</sub> is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137 kJ mol<sup>-1</sup>;  $\Delta_{\text{hyd}}H$  for Al<sup>3+</sup> = -4665 kJ mole<sup>-1</sup>;  $\Delta_{\text{hyd}}H$  for Cl<sup>-</sup> = -381 kJ mol<sup>-1</sup>). (1997)
12. Interpret the non-linear shape of H<sub>2</sub>S molecule and non-planar shape of PCl<sub>3</sub> using valence shell electron pair repulsion (VSEPR) theory. (Atomic numbers: H = 1; P = 15, S = 16; Cl = 17.) (1998)
13. Write the MO electron distribution of O<sub>2</sub>. Specify its bond order and magnetic property. (2000)
14. Using VSEPR theory, draw the shapes of PCl<sub>5</sub> and BrF<sub>5</sub>. What are the hybridisation of orbitals of P and Br in these molecules? (2003)

15. Using VSEPR theory, draw the molecular structures of  $\text{OSF}_4$  and  $\text{XeOF}_4$ , indicating the location of lone pair(s) of electrons and hybridisation of central atoms. (2004)
16. Arrange the following compounds in the increasing order of basicity on the bases of Brönsted-Lowry concept:  $\text{BaO}$ ,  $\text{CO}_2$ ,  $\text{SO}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Cl}_2\text{O}_7$ . (2004)
17. Arrange the following compounds in the increasing order of bond length of O—O bond.  
 $\text{O}_2$ ,  $\text{O}_2[\text{AsF}_6]$ ,  $\text{KO}_2$  (2004)

### Subjective Type

1. The dipole moment of  $\text{KCl}$  is  $3.336 \times 10^{-29}$  Coulomb metre which indicates that it is a highly polar molecule. The interatomic distance between  $\text{K}^+$  and  $\text{Cl}^-$  in this molecule is  $2.6 \times 10^{-10}$  m. Calculate the dipole moment of  $\text{KCl}$  molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of  $\text{KCl}$ . (1993)

## ANSWERS

### Straight Objective Types

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (d)  | 2. (c)  | 3. (a)  | 4. (a)  | 5. (a)  | 6. (c)  | 7. (c)  |
| 8. (c)  | 9. (b)  | 10. (b) | 11. (d) | 12. (c) | 13. (a) | 14. (d) |
| 15. (c) | 16. (b) | 17. (b) | 18. (c) | 19. (a) | 20. (a) | 21. (b) |
| 22. (a) | 23. (a) | 24. (b) | 25. (a) | 26. (b) | 27. (c) | 28. (b) |
| 29. (c) | 30. (d) | 31. (b) | 32. (b) | 33. (b) | 34. (b) | 35. (c) |
| 36. (b) | 37. (c) | 38. (c) | 39. (c) | 40. (b) | 41. (d) | 42. (a) |
| 43. (a) | 44. (b) | 45. (a) | 46. (c) | 47. (a) | 48. (c) | 49. (b) |
| 50. (c) | 51. (d) | 52. (a) | 53. (d) | 54. (a) | 55. (d) | 56. (c) |

### Multiple Correct-Choice Type

1. (a), (c)      2. (a), (c)      3. (b), (d)      4. (a), (b), (c)

### Fill-in-the-Blanks Type

- |                       |                       |  |
|-----------------------|-----------------------|--|
| 1. propadiene         | 2. $\text{CO}_2$      | 3. $\text{HCOOH}$ and $\text{CH}_3\text{COOH}$ |
| 4. 2                  | 5. $\text{sp}^3$      | 6. Electronegativity                           |
| 7. solvated electrons | 8. Increase, decrease | 9. $\text{N}_2\text{O}$ , $\text{I}_3^-$       |

### Integer Answer Type

1. 4      2. 4

**True/False Type**

- |          |         |          |          |         |
|----------|---------|----------|----------|---------|
| 1. False | 2. True | 3. True  | 4. True  | 5. True |
| 6. False | 7. True | 8. False | 9. False |         |

**Reasoning Type**

1. (a)                  2. (c)                  3. (c)

**Matrix Match Type**

1. The correct-bubbled diagram is as follows.

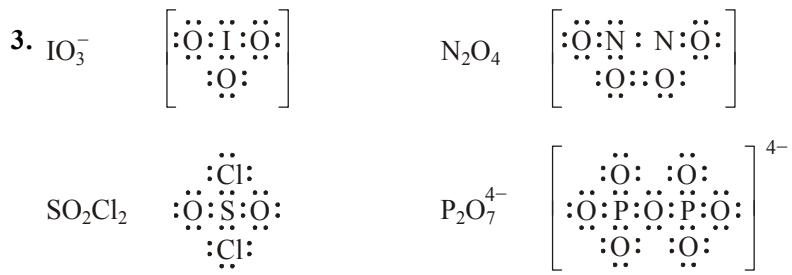
	p	q	r	s	t
a	●	○	●	○	●
b	○	○	○	●	●
c	●	●	○	○	○
d	●	●	○	●	○

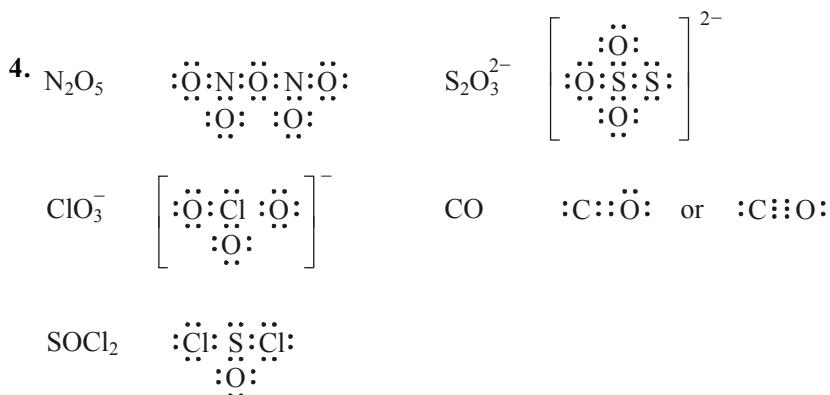
2. (c)

**Short Answer Type**

1. (i) ionic;                  (ii) covalent;                  (iii) covalent;                  (iv) covalent  
 (v) ionic;                  (vi) covalent

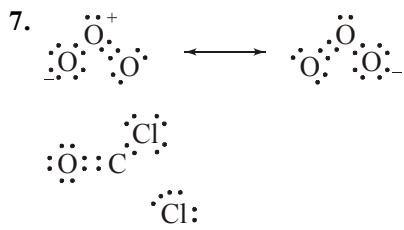
2. Property	Ionic	Covalent
(i) Boiling point	high	low
(ii) Melting point	high	low
(iii) Lattice energy	high	low
(iv) Volatility	nonvolatile	volatile





5. There are twelve sigma bonds (six C—C and six C—H) and three pi bonds (C=C).

6. The resonance structure of  $\text{N}_2\text{O}$  are



8. The two resonating structures of  $\text{N}_2\text{O}$  that satisfy the octet rule are given below.

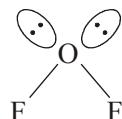


9. The Lewis structure of  $\text{OF}_2$  is



Since there are four pair of electrons (two lone pairs and two bonded pairs) around the central O atom, the arrangement of these electron pairs as per VSEPR theory must be tetrahedral.

Since the hybrid orbitals arranged tetrahedrally are obtained by  $\text{sp}^3$  hybridisation, the oxygen atom involves  $\text{sp}^3$  hybrid orbitals in bonding with fluorine. The structure of  $\text{OF}_2$  would be



The molecule of  $\text{OF}_2$  is V-shaped with F—O—F bond angle of  $103^\circ 18'$ . The normal tetrahedral angle of  $109^\circ 28'$  is decreased because of strong repulsion of bond pairs by the two lone pairs of electrons.

The oxidation number of F is always  $-1$ . Hence, in  $\text{OF}_2$ ,

Oxidation number of F =  $-1$  and Oxidation number of O =  $+2$

10. LiF has more of ionic character while LiI has more of covalent character. The latter is due the larger polarizability of larger sized iodide ion by the lithium ion.

11. The total hydration energy of  $\text{Al}^{3+}$  and  $3\text{Cl}^-$  ions is

$$\Delta_{\text{hyd}}H = \{-4665 + 3(-381)\} \text{ kJ mol}^{-1} = -5808 \text{ kJ mol}^{-1}$$

The energy released is more than that required for the ionization of Al to  $\text{Al}^{3+}$  (which is  $-4665 \text{ kJ mol}^{-1}$ ) causing ionization of  $\text{AlCl}_3$  in solution. Thus, the compound  $\text{AlCl}_3$  becomes ionic in aqueous solution.

### 12. Shape of $\text{H}_2\text{S}$ molecule

Electronic configuration of  ${}_{16}\text{S}$ :

$$(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^2(3\text{p})^4$$

Number of valence electrons of S = 6

Lewis structure of  $\text{H}_2\text{S}$



Since there are four pairs of electrons around sulphur, these will form a regular tetrahedron. The shape of  $\text{H}_2\text{S}$  will be non-linear with two lone pairs of electrons on sulphur. However, the bond angle H—S—H will be considerably less than  $109^\circ 28'$  due to the stronger repulsion between lone pair of electrons.

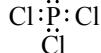
### Shape of $\text{PCl}_3$

Electronic configuration of  ${}_{15}\text{P}$ :

$$(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^2(3\text{p})^3$$

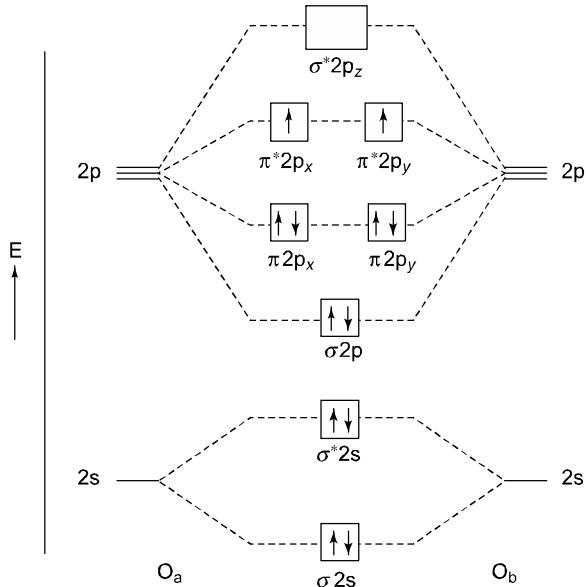
Number of valence electrons around P = 5

Lewis structure of  $\text{PCl}_3$



There are four pairs of electrons around phosphorus. These will form a regular tetrahedron. The structure of  $\text{PCl}_3$  will be a tetrahedral with a lone pair of electrons around phosphorus.

13. The total number of valence electrons in molecular oxygen is 12. These are allotted to the available molecular orbitals as shown in Fig. 5.1.



**Fig. 5.1**

The molecular electronic configuration is

$$\text{KK} (\sigma 2\text{s})^2 (\sigma^* 2\text{s})^2 (\sigma 2\text{p})^2 (\pi 2\text{p}_x)^2 (\pi 2\text{p}_y)^2 (\pi^* 2\text{p}_x) (\pi^* 2\text{p}_y)$$

Number of bonding electrons: 8

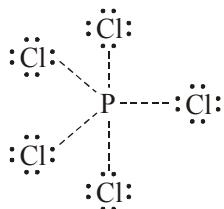
Number of antibonding electrons: 4

$$\text{Bond order} = \frac{1}{2} \text{ Number of (bonding-antibonding) electrons}$$

$$= \frac{1}{2} (8 - 4) = 2$$

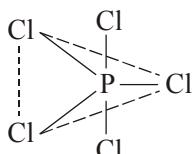
The molecular oxygen is paramagnetic as it contains two unpaired electrons.

14. The valence electrons in  $\text{PCl}_5 = 5 + 5 \times 7 = 40$ . The distribution of these electrons in  $\text{PCl}_5$  is as follows.



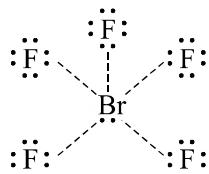
There are five lone pairs of electrons around P. Hence, the arrangement of these electrons around P will be triangular bipyramidal,

The hybridisation involved in this complex is  $\text{dsp}^3$ .

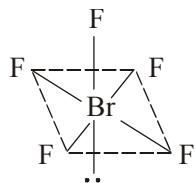


Hence, the shape of  $\text{PCl}_5$  is

- The valence electrons in  $\text{BrF}_5 = 7 + 5 \times 7 = 42$ . The distribution of these electrons in  $\text{BrF}_5$  is as follows.



There are six lone pairs of electrons around Br. Hence, the arrangement of these electrons around Br will be octahedral. The hybridization involved in this complex is  $\text{d}^2\text{sp}^3$ .



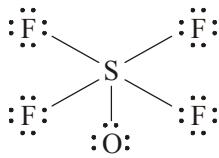
Hence, the shape of  $\text{BrF}_5$  is

15. *Molecular Structure of  $\text{OSF}_4$*

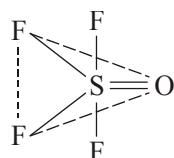
The total number of valence electrons to be distributed are 40 ( $= 6 + 6 + 4 \times 7$ ). These are distributed as shown in Fig. 5.2a.

There are five pairs of electrons around S atom. These will assume trigonal bipyramidal geometry around S atom. The structure of  $\text{OSF}_4$  is shown in Fig. 5.2b.

The hybridisation involved is  $\text{sp}^3\text{d}$  of sulphur orbitals. There is no lone pair of electrons in  $\text{OSF}_4$ .



**Fig. 5.2a**

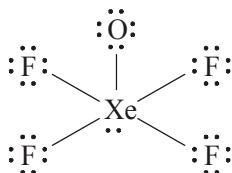
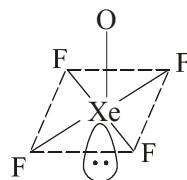


**Fig. 5.2b**

#### Structure of $\text{XeOF}_4$

The total number of valence electrons to be distributed are  $42 = 8 + 6 + 4 \times 7$ . These are distributed as shown in Fig. 5.3a.

There are six pairs of electrons around the central Xe atom. These assume octahedral geometry. The structure of  $\text{XeOF}_4$  is shown in Fig. 5.3b.

**Fig. 5.3a****Fig. 5.3b**

The hybridisation involved is  $\text{sp}^3\text{d}^2$  of Xe orbitals. There is one lone pair of electrons around Xe atom.

16. The corresponding acids of the given species respectively are  $\text{Ba}(\text{OH})_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{BO}_3$  and  $\text{HClO}_4$ . The decreasing order of acidity of these species is  $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{H}_2\text{CO}_3 > \text{H}_3\text{BO}_3 > \text{Ba}(\text{OH})_2$   
The conjugate bases follow the reverse order, i.e.  $\text{Cl}_2\text{O}_7^- < \text{SO}_3^- < \text{CO}_2^- < \text{B}_2\text{O}_3^- < \text{BaO}$

17. In the given compounds, oxygen is present as  $\text{O}_2$ ,  $\text{O}_2^+$  and  $\text{O}_2^-$ , respectively. For these species, we have

$$\begin{array}{ll} \text{O}_2 & \text{KK} (\sigma 2s)^2 (\sigma^*2s)^2 (\sigma 2p)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^*2p_x)^1 (\pi^*2p_y)^1 \\ \text{O}_2^+ & \text{KK} (\sigma 2s)^2 (\sigma^*2s)^2 (\sigma 2p)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^*2p_x)^1 \\ \text{O}_2^- & \text{KK} (\sigma 2s)^2 (\sigma^*2s)^2 (\sigma 2p)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^*2p_x)^2 (\pi^*2p_y)^1 \end{array}$$

The bond orders of these species as given by the expression

$$\text{BO} = (1/2) [\text{Number of (bonding - antibonding) electrons}]$$

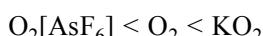
are as follows.

$$\text{For } \text{O}_2 \quad \text{BO} = \frac{1}{2} (8 - 4) = 2$$

$$\text{For } \text{O}_2^+ \quad \text{BO} = \frac{1}{2} (8 - 3) = 2.5$$

$$\text{For } \text{O}_2^- \quad \text{BO} = \frac{1}{2} (8 - 5) = 1.5$$

Since bond length is inversely proportional bond order, the increasing order of bond length of O—O is



### Subjective Type

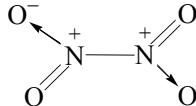
1. 80.1%

### HINTS AND SOLUTIONS

#### Straight Objective Type

9. Carbon tetrachloride is a nonpolar compound.
10.  $\text{CCl}_4$  has a regular tetrahedral structure.
11. Liquid HCl will not have hydrogen bond.
12.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  has electrovalent, covalent and coordinate covalent bonds.
13. NO has odd number of electrons. It will contain one unpaired electrons.
14. The bond between two identical nonmetallic atoms has a pair of electrons equally shared between them.
15. F being most electronegative will yield strongest hydrogen bond.

16. Sulphur dioxide involves  $sp^2$  hybridization of sulphur atomic orbitals.

17. The structure of  $N_2O_5$  is . It contains covalent and coordinate bond. In solid phase, it crystallises as  $NO_2^+ NO_3^-$ . The choice D will be correct in solid phase.

18.  $CH_3^+$  involves  $sp^2$  hybrid orbitals of carbon.

19. CO and  $CN^-$  involve the same number of electrons.

20.  $CO_2$  is a linear molecule.

21.  $BF_3$  will have zero dipole moment.

22.  $O_2^-$  has one unpaired electrons. It is paramagnetic.

23.  $PCl_3$  has a pyramidal shape.

24.  $NCO^-$  has a linear structure.

25.  $ClO_2^-$  has four paired electrons around Cl and thus it involves  $sp^3$  hybrid orbitals.

26. There are four hydrogen bonds around  $H_2O$  molecule.

27.  $H_2O_2$  has —OH polar bond and —O—O— nonpolar bond.

28.  $SO_2$  has  $sp^2$  hybridization of sulphur orbitals.

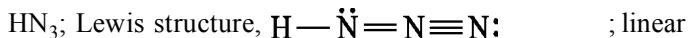
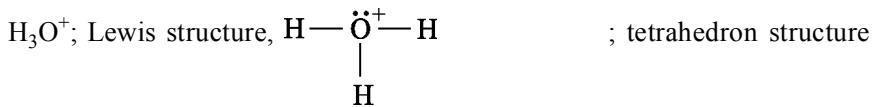
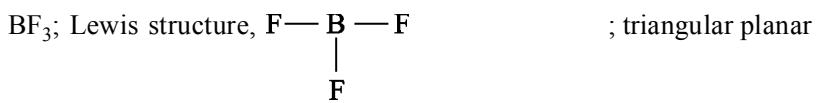
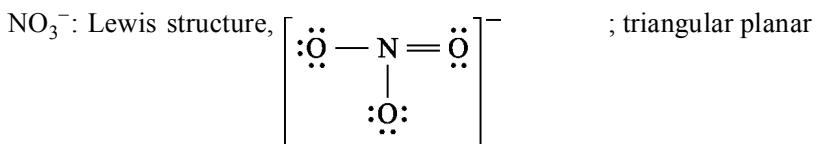
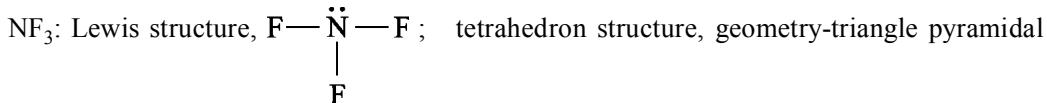
29.  $BF_3$  has  $sp^2$  hybridization of boron orbitals. Each BF bond is polar.

30. Molecular shapes of  $SF_4$ ,  $CF_4$  and  $XeF_4$  are different with 1, 0, 2 lone pairs of electrons, respectively.

31.  $NO_2^+$ ,  $NO_3^-$  and  $NH_4^+$  involve sp,  $sp^2$  and  $sp^3$  hybridization.

33. Hydration energy depends on the charge density (= charge/size) of positive ion.

35. Isostructural pairs have similar structures.



Thus, isostructural pairs are  $[NF_3, H_3O^+]$  and  $[NO_3^-, BF_3]$ .

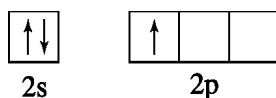
36. Calcium carbide is an ionic compound ( $Ca^{2+}C^{2-}$ ) which produces acetylene on reacting with water. Thus, the structure of  $C^{2-}$  is  $[C \equiv C]^{2-}$ . It has one  $\sigma$  and two  $\pi$  bonds.

37.  $CsBr_3$  may be represented as  $Cs^+ Br_3^-$ .

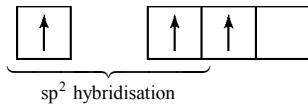
38.  $KHF_2 \rightarrow K^+ + HF_2^-$

39.  $NO_2^+$ ,  $BaO_2$  and  $AlO_2^-$  are even-electron species whereas  $KO_2$  is an odd-electron species.

40. Outer electronic configuration of boron atom



Electronic configuration of boron atom in  $\text{BF}_3$

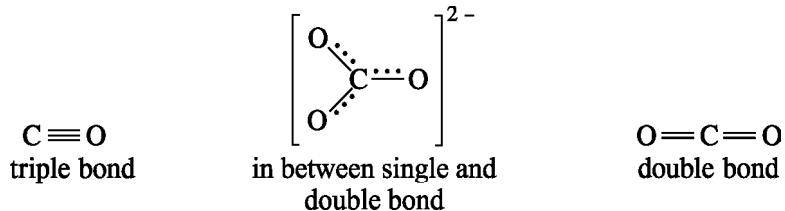


The geometry corresponding to  $\text{sp}^2$  hybridisation is trigonal planar.

41. The guiding rule for the bond length is

$$\text{triple bond} < \text{double bond} < \text{single bond}$$

The given chemical species are



Hence, the increasing order of the C—O bond length is

$$\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$$

42. The structure of  $\text{H}_2\text{S}$  is angular . Because of the different values of electro-negativity of S and H,

the bond S—H is polar and hence the dipole moment of  $\text{H}_2\text{S}$  is nonzero.

43. All the three species contain 10 valence electrons. Their molecular electronic configurations are represented as

$$(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\sigma 2p_z)^2$$

$$\text{Bond order} = \frac{\text{Bonding electrons} - \text{Antibonding electrons}}{2} = \frac{8 - 2}{2} = 3$$

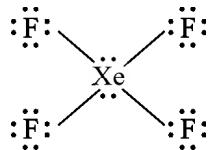
44. The structures of  $\text{NH}_3$ ,  $[\text{PtCl}_4]^{2-}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  are tetrahedral, square planar, triangle bipyramidal and triangular planar, respectively. Hence, the central atoms respectively involve  $\text{sp}^3$ ,  $\text{dsp}^2$ ,  $\text{dsp}^3$  and  $\text{sp}^2$  hybrid orbitals.

45. Both N and B attain tetrahedral geometry.

46. The species  $\text{O}_2^-$  has one unpaired electron.

47.  $\pi$ -electronic charge lies above and below molecular plane.

48. The total number of valence electrons in  $\text{XeF}_4$  are 36 ( $= 8 + 4 \times 7$ ). These are distributed as follows.



Thus, Xe contains six pairs of electrons around Xe out of which two are lone pairs. According VSEPR, these six pairs of electrons are distributed in the octahedral geometry.

49. The electronic configuration of  $\text{O}_2^-$  is  $\text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p)^2 (\pi 2p_x)^2 (\pi 2p_y)^2 (\pi^* 2p_x)^2 (\pi^* 2p_y)^1$ . It contains one unpaired electron and is thus paramagnetic. Its bond order is

$$\text{BO} = \frac{1}{2} [\text{Number of (bonding} - \text{antibonding)} \text{ electrons}] = \frac{1}{2} (8 - 5) = \frac{3}{2}$$

$$\text{The bond order of O}_2 \text{ is BO} = \frac{1}{2} (8 - 4) = 2$$

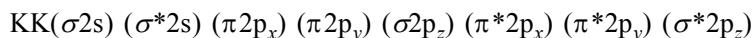
50. For the given species, we have

Species	Valence electrons	Lewis structure	Unpaired electrons
$\text{ClO}_3^-$	$7 + 6 \times 3 + 1 = 26$		1
$\text{XeF}_4$	$8 + 4 \times 7 = 36$		2
$\text{I}_3^-$	$7 \times 3 + 1 = 22$		3
$\text{SF}_4$	$6 + 4 \times 7 = 34$		1

51.  $\text{Na}_2\text{O}_2$  is  $(2\text{Na}^+)(\text{O}_2^{2-})$ . There is no unpaired electron either on  $\text{Na}^+$  or  $\text{O}_2^{2-}$ . Hence, it must be diamagnetic.  $\text{O}_3$  and  $\text{N}_2\text{O}$  have even-numbered electrons and thus are diamagnetic.

$\text{KO}_2$  is  $(\text{K}^+)(\text{O}_2^-)$ . The species  $\text{O}_2^-$  contains one unpaired electron. Hence, it must be paramagnetic.

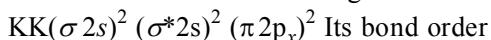
52. The diatomic species have the following scheme of molecular orbitals in the increasing order of energy.



The species  $\text{CO}$ ,  $\text{NO}^+$ ,  $\text{CN}^-$  and  $\text{N}_2$  have the same number ( $= 10$ ) of valence electrons while  $\text{NO}^-$  has 12 electrons. Thus,  $\text{NO}^-$  will have different bond order.

53. The species  $\text{P}_4$  has a tetrahedron structure. Each P involves  $\text{sp}^3$  hybrid orbital. hence, its p-character will be 75%.

54. The assumed electronic configuration of  $\text{B}_2$  would be

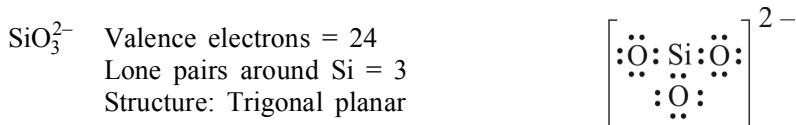
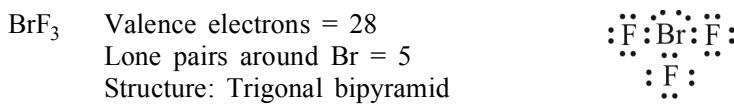
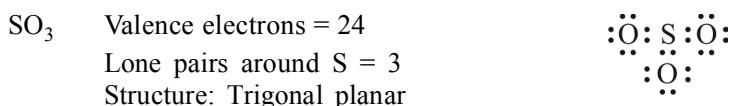


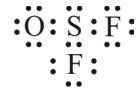
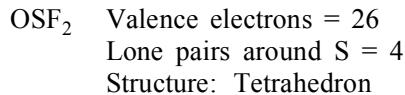
$$\begin{aligned} &= \frac{1}{2} \text{ (bonding - antibonding) electrons} \\ &= \frac{1}{2} (4 - 2) = 1 \end{aligned}$$

$$\begin{aligned} &= \frac{1}{2} (4 - 2) = 1 \end{aligned}$$

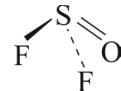
Since there is no unpaired electrons, the molecule  $\text{B}_2$  would be diamagnetic.

55. The Lewis structures are:



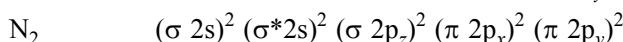
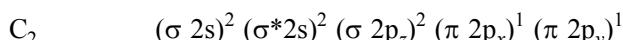
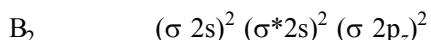


The structure of  $\text{OSF}_2$  is  
The shape of molecule is pyramidal.



- 56.** If  $2s - 2p$  mixing is not operative, the increasing order of energies of molecular orbitals for a diatomic molecule is  $(\sigma \ 2s) < (\sigma^* 2s) < \sigma \ 2p_z < \pi \ 2p_x = \pi \ 2p_y < \pi^* 2p_x = \pi^* 2p_y < (\sigma \ 2p_z)$

The electronic configurations of the given molecules are



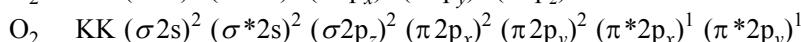
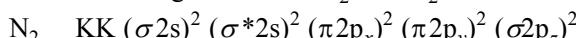
The species C<sub>2</sub> has two unpaired electrons and thus it is paramagnetic.

## **Multiple Correct-Choice Type**

1. Carbon dioxide, mercuric chloride and acetylene are linear molecules.
  2.  $\text{CN}^-$  and  $\text{NO}^+$  have the same number of electrons.
  3. The species  $\text{H}_3\text{O}^+$ ,  $\text{NH}_3$  and  $\text{CH}_3^-$  have same number of electrons.

## **Fill-in-the-blanks Type**

The molecular configurations of N<sub>2</sub> and O<sub>2</sub> are as follows:



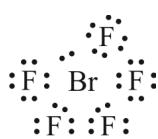
Conversion of  $\text{N}_2$  to  $\text{N}_2^+$  requires the removal of one outer electron from bonding  $\sigma 2p_z$  orbital. This will cause decrease of bond order and hence increase in bond length.

Conversion of  $O_2$  to  $O_2^+$  requires the removal of one outer electron from antibonding  $\pi$ 2p orbital. This will cause increase in bond order and hence decrease in bond length.

## **Integer Answer Type**

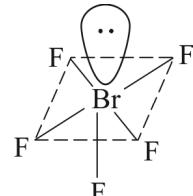
1. Number of valence electrons =  $6 \times 7 = 42$

Lewis structure is

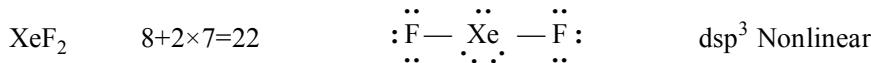
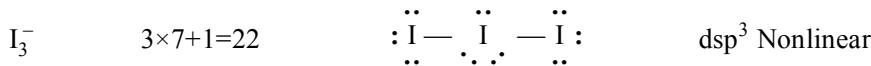
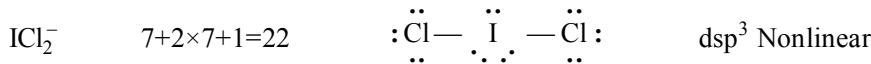
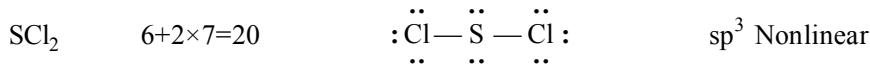
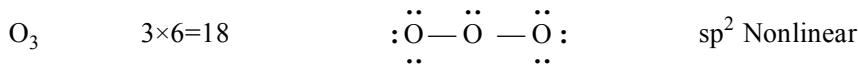
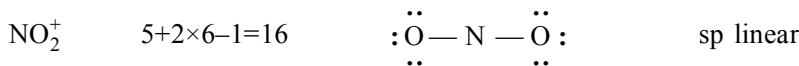
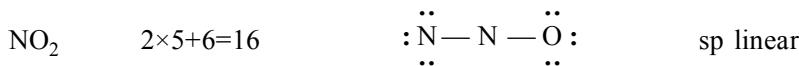
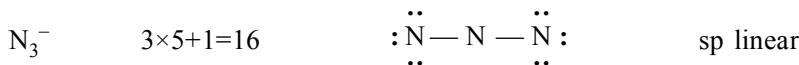


There are six pairs of electrons around Br. Their arrangement is octahedral.

The structure of  $\text{BrF}_5$  is a square based pyramid. The presence of lone pair distorts the regular geometry. The central Br atom is displaced slightly below the plane. The bond angle F—Br—F is expected to be **four**.



2. The valence electrons, their distributions, involved hybridization of the central atom in the given molecules/ions are as follows.



There are **four** molecules/ion(s) which are linear without involving d orbitals in hybridization.

### True/False Type

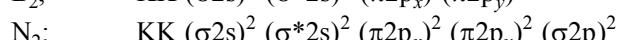
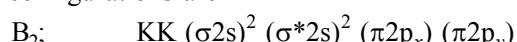
9. This statement is true only if the molecule has a centre of symmetry or its structure is such that the vector addition of the moments of the different bonds leads to a net zero dipole moment (e.g.,  $\text{CCl}_4$ ).

### Reasoning Type

3. Statement-1 is true while statement-2 is false.

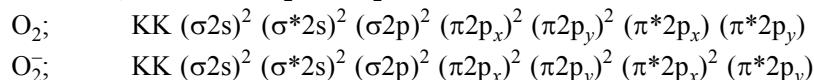
### Matrix Match Type

1. For  $\text{B}_2$  and  $\text{N}_2$ , because of s-p mixing, the energy of  $\pi 2p$  orbitals lies below that of  $\sigma 2p$  orbital. Their electronic configurations are



In  $\text{O}_2$ , no s-p mixing occurs and thus  $E(\sigma 2p) < E(\pi 2p_x)$  or  $E(\pi 2p_y)$ .

The electronic configurations of  $O_2$  and  $O_2^-$  are



The bond order (BO) is defined as

$$BO = \frac{1}{2} [\text{Number of (bonding} - \text{antibonding)} \text{ electrons}]$$

$N_2$  and  $O_2$  have  $BO \geq 2$ .

Adding electron implies reduction. It is energy stabilised step if it is added to the bonding molecular orbital. Removing electron implies oxidation. It is energy stabilised step if it is removed from an antibonding molecular orbital.

Thus, the matching goes as follows.

- |                |                 |
|----------------|-----------------|
| (a) p, r and t | (b) s, t        |
| (c) p, q       | (d) p, q and s. |

2. Identification of the items P and Q of **List-I** with the correct choice in the **List-II** is sufficient to choose the correct answer in the code.

The item P involves two d orbitals. There is end to end overlap between two identical types of lobes which leads to  $\sigma$  bonding orbital. Hence, P involves d – d  $\sigma$  bonding, which is the item 2 of the List-II.

The item Q of List-I involves p and d orbitals. There is side ways overlap between the same type of lobes, which leads to  $\pi$  bonding orbital. Hence, Q involves p – d  $\pi$  bonding, which is the item 3 of List-II.

Hence, the **choice (c)** of the given code is correct.

Rest of matchings follow automatically. The item R involves p and d orbitals. There is side ways overlap between different types of lobes, which leads to p – d  $\pi$  antibonding. Thus R in the List-I matches with the item 1 of the List-II.

The item S involves d – d  $\sigma$  antibonding.

## Subjective Type

1. We have

Dipole moment corresponding to 100% ionic character of KCl

$$\begin{aligned} &= (1.602 \times 10^{-19} \text{ C}) (2.6 \times 10^{-10} \text{ m}) \\ &= 4.1652 \times 10^{-29} \text{ C m} \end{aligned}$$

Actual dipole moment of KCl =  $3.336 \times 10^{-29}$  C m

$$\begin{aligned} \text{Percentage ionic character} &= \frac{3.336 \times 10^{-29} \text{ C m}}{4.1652 \times 10^{-29} \text{ C m}} \times 100 \\ &= 80.1 \end{aligned}$$



# ENERGETICS

6

## Straight Objective Type

1. The difference between heats of reaction at constant pressure and constant volume for the reaction  $2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$  in  $\text{kJ mol}^{-1}$  is  
(a)  $-7.43$       (b)  $+3.72$       (c)  $-3.72$       (d)  $+7.43$       (1991)
2. The products of combustion of an aliphatic thiol ( $\text{RSH}$ ) at  $298\text{ K}$  are  
(a)  $\text{CO}_2(\text{g}), \text{H}_2\text{O}(\text{g})$  and  $\text{SO}_2(\text{g})$       (b)  $\text{CO}_2(\text{g}), \text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$   
(c)  $\text{CO}_2(\text{l}), \text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{g})$       (d)  $\text{CO}_2(\text{g}), \text{H}_2\text{O}(\text{l})$  and  $\text{SO}_2(\text{l})$       (1992)
3. Molar heat capacity of water in equilibrium with ice at constant pressure is  
(a) zero      (b) infinity  
(c)  $40.45\text{ kJ K}^{-1}\text{ mol}^{-1}$       (d)  $75.48\text{ J K}^{-1}\text{ mol}^{-1}$       (1997)
4. Standard molar enthalpy of formation of  $\text{CO}_2$  is equal to  
(a) zero  
(b) the standard molar enthalpy of combustion of gaseous carbon  
(c) the sum of standard molar enthalpies of formation of  $\text{CO}$  and  $\text{O}_2$   
(d) the standard molar enthalpy of combustion of carbon(graphite)      (1997)
5. The  $\Delta_f H^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8\text{ kJ mol}^{-1}$  respectively. The standard enthalpy change (in  $\text{kJ mol}^{-1}$ ) for the reaction  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$  is  
(a)  $524.1$       (b)  $41.2$       (c)  $-262.5$       (d)  $-41.2$       (2000)
6. In thermodynamics, a process is called reversible when  
(a) surroundings and system change into each other  
(b) there is no boundary between system and surroundings  
(c) the surroundings are always in equilibrium with the system  
(d) the system changes into the surroundings spontaneously      (2001)
7. Which one of the following statements is false?  
(a) Work is a state function  
(b) Temperature is a state function  
(c) Change in the state is completely defined when the initial and final states are specified  
(d) Work appears at the boundary of the system      (2001)
8. One mole of a non-ideal gas undergoes a change of state  $(2.0\text{ atm}, 3.0\text{ L}, 95\text{ K}) \rightarrow (4.0\text{ atm}, 5.0\text{ L}, 245\text{ K})$  with a change in internal energy,  $\Delta U = 30.0\text{ L atm}$ . The change in enthalpy ( $\Delta H$ ) of the process in  $\text{L atm}$  is  
(a)  $40.0$       (b)  $42.3$   
(c)  $44.0$       (d) not defined, because pressure is not constant      (2002)

9. For which one of the following equations is  $\Delta_f H^\circ$  equal to  $\Delta_r H^\circ$ ?
- (a)  $\text{CH}_4(\text{g}) + 2\text{Cl}_2(\text{g}) \longrightarrow \text{CH}_2\text{Cl}_2(\text{l}) + 2\text{HCl}(\text{g})$       (b)  $\text{Xe}(\text{g}) + 2\text{F}_2(\text{g}) \longrightarrow \text{XeF}_4(\text{g})$
- (c)  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g})$       (d)  $\text{N}_2(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{N}_2\text{O}_3(\text{g})$       (2003)
10. Two moles of an ideal gas undergoes isothermal reversible expansion from 2 L to 8 L at 300 K. The enthalpy change of the gas is
- (a) 11.4 kJ      (b) -11.4 kJ      (c) zero      (d) 4.8 kJ      (2004)
11. The standard enthalpy and entropy of vaporization of a liquid are 25  $\text{kJ mol}^{-1}$  and 100  $\text{J K}^{-1} \text{mol}^{-1}$ , respectively. The normal boiling point of the liquid is
- (a) 200 K      (b) 250 K      (c) 400 K      (d) 500 K      (2004)
12. One mole of a monatomic ideal gas expands adiabatically at initial temperature  $T$  against a constant external pressure of 1 atm from one litre to three litres. The final temperature of the gas is
- (a)  $T$       (b)  $T/3^{(5R/2)}$       (c)  $T - 2 \text{ K}/(1.5 \times 0.082)$       (d)  $T + 2 \text{ K}/(1.5 \times 0.082)$       (2005)
13. The reaction  $\text{A} \rightarrow \text{B}$  proceeds through the following steps  $\text{A} \rightarrow \text{C} \rightarrow \text{D} \rightarrow \text{B}$ . If  $\Delta S(\text{A} \rightarrow \text{C}) = 60 \text{ eu}$ ,  $\Delta S(\text{C} \rightarrow \text{D}) = 20 \text{ eu}$  and  $\Delta S(\text{B} \rightarrow \text{D}) = 10 \text{ eu}$ , the entropy change for  $\text{A} \rightarrow \text{B}$  would be
- (a) 70 eu      (b) -70 eu      (c) 90 eu      (d) -90 eu      (2006)
14. If for an ideal gas, the ratio of pressure and volume is constant and is equal to 1  $\text{atm L}^{-1}$ , the molar heat capacity at constant pressure would be
- (a)  $(3/2) R$       (b)  $2R$       (c)  $(5/2) R$       (d) zero      (2006)
15. For the process  $\text{H}_2\text{O}(1, 1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(\text{g}, 1 \text{ bar}, 373 \text{ K})$ , the correct set of thermodynamic parameters is
- (a)  $\Delta G = 0$ ,  $\Delta S = +\text{ve}$       (b)  $\Delta G = 0$ ,  $\Delta S = -\text{ve}$       (c)  $\Delta G = +\text{ve}$ ,  $\Delta S = 0$       (d)  $\Delta G = -\text{ve}$ ,  $\Delta S = +\text{ve}$       (2007)
16. The value of  $\log_{10}K$  for a reaction  $\text{A} \rightleftharpoons \text{B}$  is  
(Given:  $\Delta_r H_{298\text{K}} = -54.07 \text{ kJ mol}^{-1}$ ,  $\Delta_r S^\circ_{298\text{K}} = 10 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ ).
- (a) 5      (b) 10      (c) 95      (d) 100      (2007)
17. The bond energy (in  $\text{kcal mol}^{-1}$ ) of a C—C single bond is approximately
- (a) 1      (b) 10      (c) 100      (d) 1000      (2010)
18. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is
- (a)  $\text{Br}_2(\text{g})$       (b)  $\text{Cl}_2(\text{g})$       (c)  $\text{H}_2\text{O}(\text{g})$       (d)  $\text{CH}_4(\text{g})$       (2010)
19. Using the data provided, calculate the multiple bond energy of a C≡C bond in  $\text{C}_2\text{H}_2$ .
- |   |   |
|---|---|
| $2\text{C}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g})$ | $\Delta H_1 = 225 \text{ kJ mol}^{-1}$  |
| $2\text{C}(\text{s}) \rightarrow 2\text{C}(\text{g})$                                   | $\Delta H_2 = 1410 \text{ kJ mol}^{-1}$ |
| $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$                                  | $\Delta H_3 = 330 \text{ kJ mol}^{-1}$  |
- Take the bond energy of C—H bond equal to 350  $\text{kJ mol}^{-1}$ .
- (a) 1165  $\text{kJ mol}^{-1}$       (b) 837  $\text{kJ mol}^{-1}$       (c) 865  $\text{kJ mol}^{-1}$       (d) 815  $\text{kJ mol}^{-1}$       (2012)
20. The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and glucose(s) at 25 °C are  $-400 \text{ kJ mol}^{-1}$ ,  $-300 \text{ kJ mol}^{-1}$  and  $-1300 \text{ kJ mol}^{-1}$ , respectively. The standard enthalpy of combustion per gram of glucose at 25 °C is
- (a) +2900 kJ      (b) -2900 kJ      (c) -16.11 kJ      (d) +16.11 kJ      (2013)

21. For the process  $\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$  at  $T = 100^\circ\text{C}$  and 1 atm pressure, the correct choice is

- (a)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} > 0$       (b)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} < 0$   
 (c)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} > 0$       (d)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} < 0$       (2014)

### Multiple Correct-Choice Type

1. Identify the intensive quantities from the following:

- (a) Enthalpy      (b) Temperature      (c) Volume      (d) Refractive index      (1993)

2. The following is (are) endothermic reaction(s):

- (a) Combustion of methane      (b) Decomposition of water  
 (c) Dehydrogenation of ethane to ethylene      (d) Conversion of graphite to diamond      (1999)

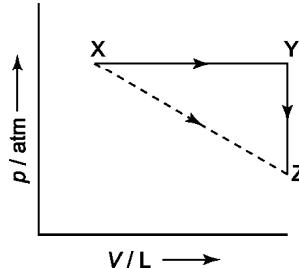
3. Among the following, the state function(s) is/are

- (a) Internal energy      (b) Irreversible expansion work  
 (c) Reversible expansion work      (d) Molar enthalpy      (2009)

4. Among the following, the intensive property is (properties are)

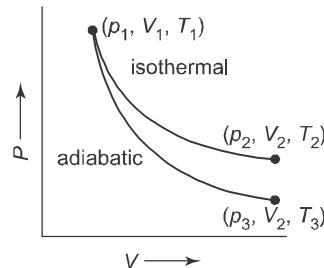
- (a) molar conductivity      (b) electromotive force  
 (c) resistance      (d) heat capacity      (2010)

5. For an ideal gas, consider only  $p$ - $V$  work in going from an initial state X to the final state Z. The final state can be reached by either of the two paths shown in the figure. Which of the following choice (s) is/are correct ? (Take  $\Delta S$  as the change in entropy and  $w$  as work done.)



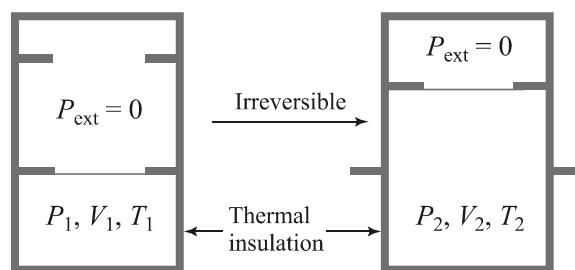
- (a)  $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$       (b)  $w_{X \rightarrow Z} = w_{X \rightarrow Y} + w_{Y \rightarrow Z}$   
 (c)  $w_{X \rightarrow Y \rightarrow Z} = w_{X \rightarrow Y}$       (d)  $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Y}$       (2012)

6. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?



- (a)  $T_1 = T_2$       (b)  $T_2 > T_1$   
 (c)  $w_{\text{isothermal}} > w_{\text{adiabatic}}$       (d)  $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$       (2012)

7. An ideal gas in a thermally insulated vessel at internal pressure  $P_1$ , volume  $V_1$  and absolute temperature  $T_1$  expands irreversibly against zero external pressure as shown in the diagram.



The final internal pressure, volume and absolute temperature of the gas are  $P_2$ ,  $V_2$  and  $T_2$ , respectively. For this expansion

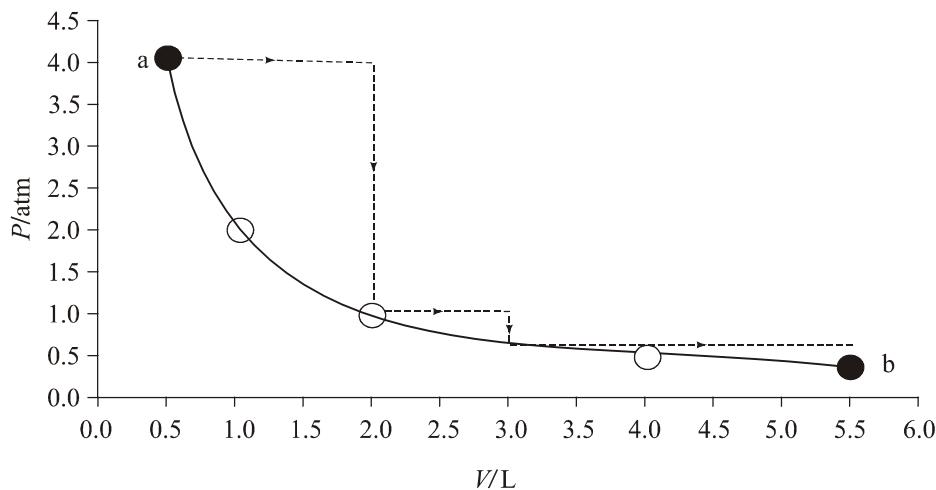
- (a)  $q = 0$       (b)  $T_2 = T_1$       (c)  $P_2V_2 = P_1V_1$       (d)  $P_2V_2^\gamma = P_1V_1^\gamma$       (2014)

### Fill-in-the-Blanks Type

- A system is said to be \_\_\_\_\_ if it can neither exchange matter nor energy with the surroundings. (1993)
- The heat content of the product is more than that of the reactants in an \_\_\_\_\_ reaction. (1993)
- When Fe(s) is dissolved in aqueous hydrochloric acid in a closed vessel, the work done is \_\_\_\_\_. (1997)
- Enthalpy is an \_\_\_\_\_ property. (1997)

### Integer Answer Type

- In a constant volume calorimeter, 3.5 g of a gas with relative molar mass 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is  $2.5 \text{ kJ K}^{-1}$ , the numerical value of the energy of combustion of the gas in  $\text{kJ mol}^{-1}$  is \_\_\_\_\_. (2009)
- One mole of an ideal gas is taken from **a** to **b** along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is  $w_s$  and that along the dotted line path is  $w_d$ , then the integer closest to the ratio  $w_d/w_s$  is \_\_\_\_\_. (2010)



(2010)

3. All the energy released from the reaction  $X \rightarrow Y$ .  $\Delta G^\circ = -193 \text{ kJ mol}^{-1}$  is used for oxidizing  $M^+$  as  $M^+ \rightarrow M^{3+} + 2e^-$ ,  $E^\circ = -0.25\text{V}$ . Under standard conditions, the number of moles of  $M^+$  oxidized when one mole of  $X$  is converted to  $Y$  is \_\_\_\_\_. [1F = 96500 C mol $^{-1}$ ] (2015)

### True/False Type

1. First law of thermodynamics is not adequate in predicting the direction of the process. (1982)  
 2. All combustion reactions are exothermic in nature. (1983)

### Reasoning Type

The question 1 below consists of an ‘Assertion’ in column 1 and the ‘Reason’ in column 2. Use the following key to choose the appropriate answer.

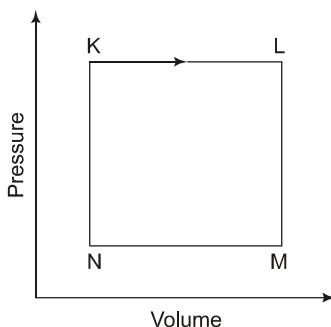
- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.
- (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
- (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
- (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

- | <b>Assertion(Column I)</b>   | <b>Reason(Column II)</b>                                      |
|--|---|
| 1. The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.   | The volume occupied by the molecules of an ideal gas is zero. |
| 2. STATEMENT-1: For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero and<br>STATEMENT-2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.  |   |
| (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1<br>(b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1<br>(c) STATEMENT-1 is True, STATEMENT-2 is False<br>(d) STATEMENT-1 is False, STATEMENT-2 is True | (2008)  |
| 3. STATEMENT-1: There is a natural asymmetry between converting work to heat and converting heat to work.<br>and<br>STATEMENT-2: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.   |   |
| (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1<br>(b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1<br>(c) STATEMENT-1 is True, STATEMENT-2 is False<br>(d) STATEMENT-1 is False, STATEMENT-2 is True | (2008)  |

### Linked Comprehension Type

#### Passage-1

A fixed mass  $m$  of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



1. The succeeding operations that enable this transformation of states are
 

(a) Heating, cooling, heating, cooling	(b) Cooling, heating, cooling, heating
(c) Heating, cooling, cooling, heating	(d) Cooling, heating, heating, cooling
2. The pair of isochoric processes among the transformation of states is
 

(a) K to L and L to M	(b) L to M and N to K
(c) L to M and M to N	(d) M to N and N to K

(2013)

#### Passage-2

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (**Expt. 1**). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (-57.0 kJ mol<sup>-1</sup>), this experiment could be used to measure the calorimeter constant.

In a second experiment (**Expt. 2**), 100 mL of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to **Expt. 1**) where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 J g<sup>-1</sup> K<sup>-1</sup> and density of all solutions as 1.0 g mL<sup>-1</sup>)

1. Enthalpy of dissociation (in kJ mol<sup>-1</sup>) of acetic acid obtained from the **Expt. 2** is
 

(a) 1.0	(b) 10.0	(c) 24.5	(d) 51.4
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2. The pH of the solution after **Expt. 2** is
 

(a) 2.8	(b) 4.7	(c) 5.0	(d) 7.0
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### Matrix Match Type

1. Match the transformation in **Column I** with the appropriate option(s) in **Column II**.

<b>Column I</b>	<b>Column II</b>
(a) $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$	(p) phase transition
(b) $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(q) allotropic change
(c) $2\text{H} \longrightarrow \text{H}_2(\text{g})$	(r) $\Delta H$ is positive
(d) $\text{P(white, solid)} \longrightarrow \text{P(red, solid)}$	(s) $\Delta S$ is positive

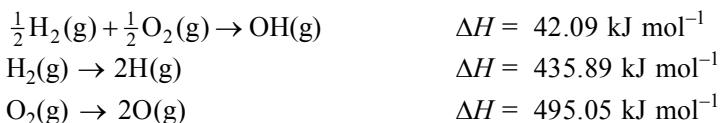
(2011)

2. Match the thermodynamic processes given under Column I with the expressions given under Column II:

Column I	Column II	(2015)
(a) Freezing of water at 273 K and 1 atm	(p) $q = 0$	
(b) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(q) $w = 0$	
(c) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(r) $\Delta S_{\text{sys}} < 0$	
(d) Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(s) $\Delta U = 0$ (t) $\Delta G = 0$	

### Subjective Type

1. The enthalpies of the following reactions are shown alongwith.



Calculate the O—H bond energy for the hydroxyl radical. (1981)

2. The standard enthalpies of formation at 298 K for  $\text{CCl}_4(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{HCl}(\text{g})$  are  $-106.7$ ,  $-241.8$ ,  $-393.7$  and  $-92.5 \text{ kJ mol}^{-1}$ , respectively. Calculate  $\Delta H_{298\text{K}}^{\circ}$  for the reaction  $\text{CCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g})$ . (1982)

3. The standard molar enthalpies of combustion of  $\text{C}_2\text{H}_2(\text{g})$ , C(graphite) and  $\text{H}_2(\text{g})$  are  $-1299.63$ ,  $-393.51$ ,  $-285.85 \text{ kJ mol}^{-1}$ , respectively. Calculate the standard enthalpy of formation of  $\text{C}_2\text{H}_2(\text{g})$ . (1983)

4. Given the following standard enthalpies of reactions.

- (i) Enthalpy of formation of water  $= -285.8 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of combustion of acetylene  $= -1299.6 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of combustion of ethylene  $= -1410.8 \text{ kJ mol}^{-1}$

Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume ( $25^\circ\text{C}$ ). (1984)

5. The bond dissociation enthalpy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are  $435$ ,  $243$  and  $431 \text{ kJ mol}^{-1}$ , respectively. Calculate the enthalpy of formation of  $\text{HCl}$  gas. (1985)

6. The standard molar enthalpies of formation of ethane, carbon dioxide and liquid water are  $-88.3$ ,  $-393.7$  and  $-285.8 \text{ kJ mol}^{-1}$ , respectively. Calculate the standard molar enthalpy of combustion of ethane. (1986)

7. An intimate mixture of ferric oxide,  $\text{Fe}_2\text{O}_3$ , and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per  $\text{cm}^3$  of the mixture. Given:

$$\Delta_f H(\text{Al}_2\text{O}_3, \text{s}) = -1669 \text{ kJ mol}^{-1}; \quad \Delta_f H(\text{Fe}_2\text{O}_3, \text{s}) = -833 \text{ kJ mol}^{-1}$$

Density of  $\text{Fe}_2\text{O}_3 = 5.2 \text{ g cm}^{-3}$ ;      Density of Al =  $2.7 \text{ g cm}^{-3}$  (1988)

8. The standard enthalpy of combustion at  $25^\circ\text{C}$  of hydrogen, cyclohexene ( $\text{C}_6\text{H}_{10}$ ) and cyclohexane ( $\text{C}_6\text{H}_{12}$ ) are  $-241$ ,  $-3800$  and  $-3920 \text{ kJ mol}^{-1}$ , respectively. Calculate the standard enthalpy of hydrogenation of cyclohexene. (1989)

9. An athlete is given  $100 \text{ g}$  of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) of energy equivalent to  $1560 \text{ kJ}$ . He utilizes  $50\%$  of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is  $44 \text{ kJ mol}^{-1}$ . (1989)

10. Using the data given below, calculate the bond enthalpy of C—C and C—H bonds.

$$\Delta_c H^{\circ}(\text{ethane}) = -1556.5 \text{ kJ mol}^{-1}; \quad \Delta_c H^{\circ}(\text{propane}) = -2117.5 \text{ kJ mol}^{-1}$$

$$\text{C(graphite)} \rightarrow \text{C(g)}; \quad \Delta H = 719.7 \text{ kJ mol}^{-1}$$

$$\text{Bond enthalpy of H—H} = 435.1 \text{ kJ mol}^{-1}$$

$$\Delta_f H^{\circ}(\text{H}_2\text{O}, 1) = -284.5 \text{ kJ mol}^{-1}; \quad \Delta_f H^{\circ}(\text{CO}_2, \text{g}) = -393.3 \text{ kJ mol}^{-1} \quad (1990)$$

11. A gas mixture consisting of 3.67 litres of ethylene and methane on complete combustion at 25 °C produces 6.11 litres of CO<sub>2</sub>. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1423 and – 891 kJ mol<sup>-1</sup>, respectively, at 25 °C. (1991)

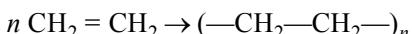
12. Determine the enthalpy of the reaction  $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$  at 25 °C using the given enthalpy of combustion values under standard conditions:

Compound:	H <sub>2</sub> (g)	CH <sub>4</sub> (g)	C <sub>2</sub> H <sub>6</sub> (g)	C(graphite)
ΔH/kJ mol <sup>-1</sup> :	– 285.8	– 890.0	– 1560.0	– 393.5

The standard enthalpy of formation of C<sub>3</sub>H<sub>8</sub>(g) is – 103.8 kJ mol<sup>-1</sup>. (1992)

13. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as the required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with  $x$  litre/hour of CH<sub>4</sub> and  $6x$  litre/hour of O<sub>2</sub>) is to be readjusted for butane, C<sub>4</sub>H<sub>10</sub>. In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Enthalpies of combustion: CH<sub>4</sub> = 809 kJ mol<sup>-1</sup>; C<sub>4</sub>H<sub>10</sub> = 2878 kJ mol<sup>-1</sup>. (1993)

14. The polymerisation of ethylene to linear polyethylene is represented by the reaction



where  $n$  has a large integral value. Given that the average enthalpies of bond dissociation for C=C and C—C at 298 K are + 590 and + 331 kJ mol<sup>-1</sup> respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K. (1994)

15. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. Bond energy of I<sub>2</sub> is 240 kJ mol<sup>-1</sup>. (1995)

16. The enthalpy change involved in the oxidation of glucose is – 2880 kJ mol<sup>-1</sup>. Twenty-five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose. (1997)

17. Compute the enthalpy of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Enthalpy of vaporization of liquid methyl alcohol = 38 kJ/mol. Enthalpy of gaseous atoms from the elements in their standard states: H, 218 kJ/mol; C, 715 kJ/mol; O, 249 kJ/mol.

Average bond enthalpy: C—H, 415 kJ/mol; C—O, 356 kJ/mol, and O—H, 463 kJ/mol (1997)

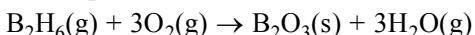
18. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and propene(g) are – 393.5, – 285.8 and 20.42 kJ mol<sup>-1</sup>, respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ mol<sup>-1</sup>. (1998)

19. Estimate the average S—F bond enthalpy in SF<sub>6</sub>. The values of standard enthalpy of formation of SF<sub>6</sub>(g), S(g) and F(g) are: – 1100, 275 and 80 kJ mol<sup>-1</sup> respectively.

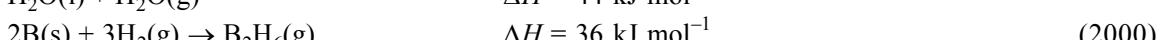
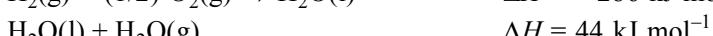
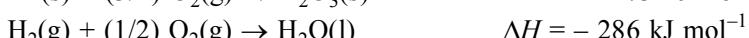
20. A sample of argon gas at 1 atm pressure and 27 °C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process. C<sub>V, m</sub> for argon is 12.48 J K<sup>-1</sup> mol<sup>-1</sup>. (2000)

21. Show that the reaction CO(g) + (1/2)O<sub>2</sub>(g) → CO<sub>2</sub>(g) at 300 K is spontaneous and exothermic, when the standard entropy change is – 0.094 kJ mol<sup>-1</sup> K<sup>-1</sup>. The standard Gibbs free energies of formation for CO<sub>2</sub> and CO are – 394.4 and – 137.2 kJ mol<sup>-1</sup>, respectively. (2000)

22. Diborane is a potential rocket fuel which undergoes combustion according to the reaction



From the following data, calculate the enthalpy change for the combustion of diborane.



23. The standard molar enthalpies of formation of cyclohexane(1) and benzene(1) at 25 °C are –156 and +49 kJ mol<sup>–1</sup> respectively. The standard enthalpy of hydrogenation of cyclohexene(1) at 25 °C is –119 kJ mol<sup>–1</sup>. Use these data to estimate the magnitude of the resonance energy of benzene. (1996)
24. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175 °C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A), 95.2% 2-pentyne(B) and 3.5% of 1,2-pentadiene (C). The equilibrium was maintained at 175 °C. Calculate  $\Delta G^\circ$  for the following equilibria:

$$B = A \quad \Delta G_1^\circ = ?$$

$$B = C \quad \Delta G_2^\circ = ?$$

From the calculated value of  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  indicate the order of stability of A, B and C. Write a reasonable reaction mechanism sharing all intermediates leading to A, B and C.

25. Two moles of a perfect gas undergo the following processes:
- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
  - a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
  - a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).
- Sketch with labels each of the processes on the same *p*-*V* diagram.
  - Calculate the total work (*w*) and the total heat charge (*q*) involved in the above processes.
  - What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process? (2002)
26. One mole of a liquid (2 bar, 100 mL) is taken in an adiabatic container and the pressure increases steeply to 100 bar. This is followed by a decrease of volume to 98 mL at a constant pressure of 100 bar. Determine  $\Delta U$  and  $\Delta H$ . (2004)
27. The reaction  $2\text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$  is carried out under constant volume (1 L). Two moles of CO and 1 mol of O<sub>2</sub> produces one mole of CO<sub>2</sub>. At constant temperature (500 K),  $\Delta_r H = -560 \text{ kJ mol}^{-1}$ . What will be the change in internal energy ( $\Delta U$ ) if the initial and final pressures were 70 atm and 40 atm, respectively. Assume the gases to deviate from the ideal gas behaviour to a large extent. Given: 1 L atm = 0.1 kJ. (2006)

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (b)  | 3. (b)  | 4. (d)  | 5. (b)  | 6. (c)  | 7. (a)  |
| 8. (c)  | 9. (b)  | 10. (c) | 11. (b) | 12. (c) | 13. (a) | 14. (b) |
| 15. (a) | 16. (b) | 17. (c) | 18. (b) | 19. (d) | 20. (c) | 21. (b) |

### Multiple Correct-Choice Type

- |             |                  |                  |             |
|-------------|------------------|------------------|-------------|
| 1. (b), (d) | 2. (b), (c), (d) | 3. (a), (d)      | 4. (a), (b) |
| 5. (a), (c) | 6. (a), (d)      | 7. (a), (b), (c) |             |

### Fill-in-the-Blanks Type

- |             |                |         |              |
|-------------|----------------|---------|--------------|
| 1. isolated | 2. endothermic | 3. zero | 4. extensive |
|-------------|----------------|---------|--------------|

### Integer Answer Type

- |      |      |      |
|------|------|------|
| 1. 9 | 2. 2 | 3. 4 |
|------|------|------|

**True/False Type**

1. True                    2. True

**Reasoning Type**

1. (b)                    2. (d)                    3. (b)

**Linked Comprehension Type****Passage-1**

1. (c)                    2. (b)

**Passage-2**

1. (a)                    2. (b)

**Matrix Match Type**

- |   |                                      |                                      |  |
|---|--------------------------------------|--------------------------------------|--|
| 1. (a) $\leftrightarrow$ (p), (r), (s); | (b) $\leftrightarrow$ (r), (s);      | (c) $\leftrightarrow$ (t);           | (d) $\leftrightarrow$ (p), (q), (t)      |
| 2. (a) $\leftrightarrow$ (r), (t);      | (b) $\leftrightarrow$ (p), (q), (s); | (c) $\leftrightarrow$ (p), (q), (s); | (d) $\leftrightarrow$ (p), (q), (s), (t) |

**Subjective Type**

- |  |   |   |                                 |
|--|---|---|---------------------------------|
| 1. 423.38 kJ mol <sup>-1</sup>   | 2. -173.4 kJ mol <sup>-1</sup>                          | 3. 226.76 kJ mol <sup>-1</sup>  | 4. -172.12 kJ mol <sup>-1</sup> |
| 5. -92 kJ mol <sup>-1</sup>  | 6. -1556.5 kJ mol <sup>-1</sup>                         | 7. 3.906 kJ g <sup>-1</sup> ; 16.47 kJ cm <sup>-3</sup>   |                                 |
| 8. -121 kJ mol <sup>-1</sup>   | 9. 319.14 g   | 10. 414.0 kJ mol <sup>-1</sup> ; 344.3 kJ mol <sup>-1</sup>   |                                 |
| 11. 50.88 kJ   | 12. -55.7 kJ mol <sup>-1</sup>                          | 13. (0.28 x) L h <sup>-1</sup> of C <sub>4</sub> H <sub>10</sub> ; (5.48 x) L h <sup>-1</sup> of O <sub>2</sub> |                                 |
| 14. -72 kJ mol <sup>-1</sup>   | 15. 2.16 $\times$ 10 <sup>-20</sup> J atm <sup>-1</sup> | 16. 4.80 km   | 17. -266 kJ mol <sup>-1</sup>   |
| 18. -2091.32 kJ mol <sup>-1</sup>  | 19. 309.2 kJ mol <sup>-1</sup>                          | 20. -117.25 J   | 21. -285.4 kJ mol <sup>-1</sup> |
| 22. -2035 kJ mol <sup>-1</sup>   | 23. -152 kJ mol <sup>-1</sup>                           | 24. Stability of isomers: B > C > A   |                                 |
| 25. $w = 622.1 \text{ J} ; q = -w$<br>$\Delta U = 0 ; \Delta H = 0 ; \Delta S = 0$ |   | 26. 20 J ; 970 J  | 27. -273 kJ                     |

**HINTS AND SOLUTIONS****Straight Objective Type**

- $\Delta H - \Delta U = (\Delta v_g)RT = (-3)(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = -7.43 \text{ kJ mol}^{-1}$
- At 298 K, the products are CO<sub>2</sub>(g), H<sub>2</sub>O(l) and SO<sub>2</sub>(g).
- On adding heat, no change in temperature occurs. Hence,  $C = q/T = \infty$ .
- For CO<sub>2</sub>(g), the standard enthalpy of formation and standard enthalpy of combustion of gaseous carbon (graphite) represent one and the same equation.
- For the given equation, we have

$$\begin{aligned}\Delta_r H &= \Delta_f H(\text{CO, g}) + \Delta_f H(\text{H}_2\text{O, g}) - \Delta_f H(\text{CO}_2, \text{ g}) - \Delta_f H(\text{H}_2, \text{ g}) \\ &= (-110.5 - 241.8 + 393.5 - 0) \text{ kJ mol}^{-1} = 41.2 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}
 8. \Delta H &= \Delta U + \Delta(pV) = \Delta U + (p_2V_2 - p_1V_1) \\
 &= 30.0 \text{ L atm} + [(4.0 \text{ atm})(5.0 \text{ L}) - (2.0 \text{ atm})(3.0 \text{ L})] \\
 &= 30.0 \text{ L atm} + 14.0 \text{ L atm} \\
 &= 44.0 \text{ L atm}
 \end{aligned}$$

9. For  $\Delta_f H^\circ$ , the product should be a single species with stoichiometric coefficient equal to one. The reactants must be elements in their stable states of aggregation at 1 atm pressure.
10. At constant temperature, both  $\Delta U$  and  $\Delta H$  are zero, as the quantities for an ideal gas depend only on the temperature.
11. At the normal boiling point, we will have  $\Delta G = 0$ . Hence, from  $\Delta G = \Delta H - T\Delta S$ , we get

$$T = \frac{\Delta H}{\Delta S} = \frac{25 \times 10^3 \text{ J mol}^{-1}}{100 \text{ JK}^{-1} \text{ mol}^{-1}} = 250 \text{ K}$$

12. From first law of thermodynamics, we have

$$dU = dq + dw$$

For adiabatic expansion,  $dq = 0$ . Hence

$$dU = dw$$

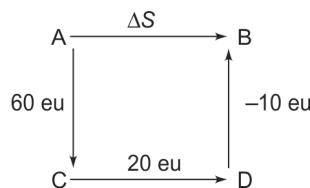
$$\text{or } nC_{V, \text{m}} \Delta T = -p \Delta V$$

$$\text{i.e. } (1 \text{ mol}) \left( \frac{3}{2} R \right) (T_f - T) = -(1 \text{ atm}) (3L - 1L)$$

$$\text{or } T_f = T - \frac{(1 \text{ atm})(2L)}{(1 \text{ mol})(1.5 \times 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})}$$

$$= T - \frac{2 \text{ K}}{1.5 \times 0.082}$$

13. The given information may be represented as follows.



$$\begin{aligned}
 \text{Hence, } \Delta S(A \rightarrow B) &= \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) + \Delta S(D \rightarrow B) \\
 &= 60 \text{ eu} + 20 \text{ eu} - 10 \text{ eu} \\
 &= 70 \text{ eu}
 \end{aligned}$$

14. By definition,

$$H = U + pV$$

$$\text{Hence } C_{p, \text{m}} = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p$$

For the given ideal gas, we will have

$$pV = RT \Rightarrow \{(1 \text{ atm L}^{-1}) V\} V = RT$$

or  $V^2 = \frac{RT}{(1 \text{ atm L}^{-1})}$

Hence  $2V \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{(1 \text{ atm L}^{-1})}$

or  $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{2V(1 \text{ atm L}^{-1})}$

Also  $U = \frac{3}{2}RT \Rightarrow \left(\frac{\partial U}{\partial T}\right)_p = \frac{3}{2}R$

With these,  $C_{p,m} = \frac{3}{2}R + p \left\{ \frac{R}{2V(1 \text{ atm L}^{-1})} \right\} = \frac{3}{2}R + \frac{R}{2}$   
 $= 2R$

- 15.** The conversion of  $\text{H}_2\text{O(l)}$  into  $\text{H}_2\text{O(g)}$  at 1 bar and 373 K is a reversible process. Hence

$$\Delta G = 0$$

and  $\Delta S = \frac{\Delta H}{T} = +\text{ve}$  ( $\because \Delta H$  is positive)

- 16.** For the given reaction

$$\begin{aligned}\Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ \\ &= (-54070 \text{ J mol}^{-1}) - (298 \text{ K})(10 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -57050 \text{ J mol}^{-1}\end{aligned}$$

Now using the expression  $\Delta_r G^\circ = -RT \ln K^\circ$ , we get

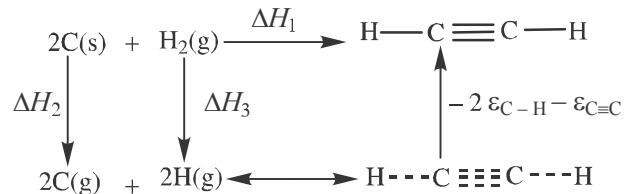
$$(-57050 \text{ J mol}^{-1}) = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})(2.303 \log K^\circ)$$

Hence,  $\log K^\circ = \frac{57050}{2.303 \times 8.314 \times 298} = \frac{57050}{5705} = 10$

- 17.** The bond energies given by the choices (a) and (b) are too low while that given by the choice (d) is too high.

- 18.** By definition, the standard molar enthalpy of formation of every element in its stable state of aggregation at one atmosphere pressure and at specified temperature is assigned a zero value. Only  $\text{Cl}_2(\text{g})$  is at its standard state of aggregation at 298 K.

- 19.** Consider the following transformations.



According to Hess's law  $\Delta H_1 = \Delta H_2 + \Delta H_3 - 2\epsilon_{\text{C}-\text{H}} - \epsilon_{\text{C}\equiv\text{C}}$

This gives

$$\epsilon_{\text{C}\equiv\text{C}} = \Delta H_2 + \Delta H_3 - \Delta H_1 - 2\epsilon_{\text{C}-\text{H}} = (1410 + 330 - 225 - 2 \times 350) \text{ kJ mol}^{-1} = 815 \text{ kJ mol}^{-1}$$

20. The combustion reaction of glucose is  $C_6H_{12}O_6(s) + 6 O_2(g) \rightarrow 6 CO_2(g) + 6 H_2O(l)$

$$\begin{aligned}\text{Hence } \Delta_c H^\circ &= 6 \Delta_f H^\circ(CO_2) + 6 \Delta_f H^\circ(H_2O) - \Delta_f H^\circ(C_6H_{12}O_6) \\ &= [6(-400) + 6(-300) - (-1300)] \text{ kJ mol}^{-1} \\ &= -2900 \text{ kJ mol}^{-1}\end{aligned}$$

The molar mass of glucose is

$$\begin{aligned}M &= 6 M_C + 12 M_H + 6 M_O = (6 \times 12 + 12 \times 1 + 6 \times 16) \text{ g mol}^{-1} \\ &= 180 \text{ g mol}^{-1}\end{aligned}$$

Hence, the standard enthalpy of combustion per gram of glucose is

$$\Delta H^\circ = \frac{\Delta_c H^\circ}{M} = \frac{-2900 \text{ kJ mol}^{-1}}{180 \text{ g mol}^{-1}} = -16.11 \text{ kJ g}^{-1}$$

21. For the conversion of  $H_2O(l) \rightarrow H_2O(g)$ , the system absorbs heat from the surroundings.

Thus  $q_{\text{system}} = + \text{ve}$  and  $q_{\text{surroundings}} < 0$

The transformation  $H_2O(l) \rightarrow H_2O(g)$  at 1 atm and 100 °C is reversible. Hence

$$\Delta S_{\text{system}} = \frac{q_{\text{system}}}{T} > 0$$

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T} < 0$$

### Multiple Correct-Choice Type

3. Internal energy and molar enthalpy are state functions.
  4. The intensive property does not depend on the size or quantity of a substance. Of the given physical quantities, molar conductivity and electromotive force are independent of the size of the system.
  5. Entropy  $S$  is a state function. The entropy change in going from one state to another does not depend upon the path(s) followed. The work done is path-dependent function. The change of state from Y to Z is a constant volume process and the work involved ( $-p dV$ ) will be zero.
- The choice (a) is correct as  $S$  is a state function. The choice (c) is also correct as  $w_{Y \rightarrow Z}$  is zero. The choices (b) and (d) are incorrect.
6. We will have

$T_1 = T_2$  as the expansion is isothermal.

$T_3 < T_1$  as the adiabatic expansion involves cooling.

$|w_{\text{isothermal}}| > |w_{\text{adiabatic}}|$  as the area under the isothermal curve is greater than that under adiabatic curve.

$\Delta U_{\text{isothermal}} = 0$  as temperature remains constant while  $\Delta U_{\text{adiabatic}} < 0$  as the expansion occurs at the expense of internal energy.

**Note:** The choice (c) is correct if the magnitude of the work is considered. Since expansion carries negative sign as per IUPAC recommendations, the choice (c) will not be correct if the negative sign is also considered.

7. The expression of work is  $w = -p_{\text{ext}} dV$ . Since  $p_{\text{ext}} = 0$ , we have  $w = 0$

Since the gas is thermally insulated,  $q = 0$

Since  $\Delta U = q + w$ , we have  $\Delta U = 0$

Since  $\Delta U = 0$ , the temperature of the gas remains constant. Hence,  $T_2 = T_1$

From Boyle's law  $P_2 V_2 = P_1 V_1$  at constant temperature.

The choice (d) is not applicable as the expansion is not reversible.

## Fill-in-the-Blanks Type

### Integer Answer Type

1. Heat released during the combustion of 3.5 g of the gas =  $C \Delta T = (2.5 \text{ kJ K}^{-1}) (0.45 \text{ K}) = 1.125 \text{ kJ}$

For combustion of 1 mol of the gas,

$$\text{heat released} = (1.125 \text{ kJ}) (28 \text{ g}/3.5 \text{ g}) = 9 \text{ kJ}$$

2. The solid line represents an isotherm as the product of  $PV$  is constant throughout. The product of  $PV$  is (4 atm) (0.5 L) i.e. 2 atm L. The work done along the solid line is equal to area under the line and is given by the expression

$$\begin{aligned}-w_s &= n(RT) \ln (V_2/V_1) = (1 \text{ mol}) (2 \text{ atm L}) \ln (5.5/0.5) \\ &= 4.796 \text{ L atm mol}^{-1}\end{aligned}$$

The work done along the dotted line (which is sum of the areas under each line) is

$$\begin{aligned}-w_d &= (4 \text{ atm}) [(2.0 - 0.5) \text{ L mol}^{-1}] + (1 \text{ atm}) [(3.0 - 2.0) \text{ L mol}^{-1}] \\ &\quad + (0.667 \text{ atm}) [(5.5 - 3.0) \text{ L mol}^{-1}] \\ &= (6 + 1 + 1.667) \text{ L atm mol}^{-1} = 8.667 \text{ L atm mol}^{-1} \\ (-w_d)/(-w_s) &= 8.667/4.796 = 1.81\end{aligned}$$

3. The free energy change involved in the reaction  $\text{M}^{3+} \rightarrow \text{M}^{3+} + 2\text{e}^-$  is

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ = -(2) (96500 \text{ C mol}^{-1}) (-0.25 \text{ V}) \\ &= 48250 \text{ J mol}^{-1}\end{aligned}$$

The number of moles of  $\text{M}^+$  oxidized is

$$n = \frac{-\Delta G^\circ (\text{X} \rightarrow \text{Y})}{\Delta G^\circ (\text{M}^+ \rightarrow \text{M}^{3+})} = \frac{193 \times 10^3 \text{ J mol}^{-1}}{48250 \text{ J mol}^{-1}} = 4$$

## Reasoning Type

- Work done by the gas is zero and the internal energy of an ideal gas depends only on temperature.
- STATEMENT-1 is false, as the Gibbs energy of reaction is zero and not its standard Gibbs energy. STATEMENT-2 is true as  $\Delta G = \text{negative}$ , i.e.  $\Delta G = G_{\text{final}} - G_{\text{initial}} = -\text{ve}$ , i.e.  $G_{\text{final}}$  is less than  $G_{\text{initial}}$ .
- Work can be completely converted into heat while heat cannot be completely converted into work. Statement-2 is correct explanation of statement-1.

## Linked Comprehension Type

### Passage-1

- The operation K to L involves constant pressure and increase in volume. The increase in volume is accompanied with increase of temperature (Charles law), thus heating is observed.

The operation L to M involves constant volume and decrease in pressure. The decrease in pressure is accompanied with decrease in temperature, thus cooling is observed. Similarly, M to N is accompanied with cooling and that N to K is accompanied with heating.

- The processes L to M and N to K involves constant volume and thus are isochoric processes.

### Passage-2

- The calorimeter constant will be

$$C = \frac{\Delta_{\text{new}} H}{\Delta T} = \frac{57.6 \text{ kJ mol}^{-1}}{5.7 \text{ K}} \approx 10 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

The enthalpy of dissociation of acetic acid will be

$$\Delta_{\text{dis}} H = C(5.7 \text{ K} - 5.6 \text{ K}) = (10 \text{ kJ K}^{-1} \text{ mol}^{-1}) (0.1 \text{ K}) = 1 \text{ kJ mol}^{-1}$$

2. After Expt 2, the solution (after taking into account the dilution) will contain 0.5 M each in acetic acid and sodium acetate. Its pH will be

$$\text{pH} = \text{p}K_a + \log \left\{ \frac{[\text{salt}]}{[\text{Acid}]} \right\} = -\log (2.0 \times 10^{-5}) + \log \left( \frac{0.5 \text{M}}{0.5 \text{M}} \right) = 4.7$$

### Matrix Match Type

1. (a) This transformation involves: (p) phase transformation, (r) absorption of heat, i.e.  $\Delta H$  positive and (s) increase in entropy, i.e.  $\Delta S$  positive, as gaseous product is produced.
- (b) This transformation involves: (r) absorption of heat, i.e.  $\Delta H$  positive and (s) increase in entropy, i.e.  $\Delta S$  positive as gaseous product is produced.
- (c) The transformation involves: (s) decrease in entropy as there is decrease in gaseous species.
- (d) The transformation involves: (p) phase transition, (q) allotropic change. The transformation white P to red P involves  $\Delta H = -\text{ve}$  and  $\Delta S = -\text{ve}$ , since white P  $\rightarrow$  red P  $\Delta H = -17.6 \text{ kJ mol}^{-1}$   $\Delta S = \Delta H/T = -\text{ve}$
2. (a) Freezing of water of 273 K and 1 atm is accompanied with decrease in entropy (i.e.  $\Delta S_{\text{sys}} < 0$ ) and  $\Delta G = 0$  (as the process is at equilibrium.)
- (b) Expansion of an ideal gas against vacuum is accompanied with  $q = 0$ ,  $w = 0$ , and  $\Delta U = 0$
- (c) Mixing of ideal gases is accompanied with  $q = 0$ ,  $\Delta U = 0$  and  $w = 0$ .
- (d) Reversible heating of a gas followed by cooling to the *same state* is accompanied with  $q = 0$ ,  $w = 0$ ,  $\Delta U = 0$  and  $\Delta G = 0$

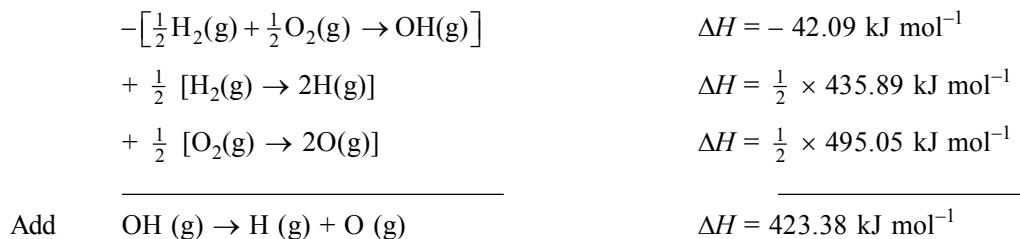
Hence, the matching go as follows:

- (a)  $\rightarrow$  (r), (t); (b)  $\rightarrow$  (p), (q), (s); (c)  $\rightarrow$  (p), (q), (s); (d)  $\rightarrow$  (p), (q), (s), (t)

### Subjective Type

1. We have to calculate the enthalpy of the reaction  $\text{OH(g)} \rightarrow \text{O(g)} + \text{H(g)}$

From the given reactions, this can be obtained as follows.



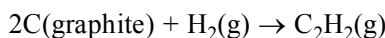
2. The enthalpy change of the given reaction will be given as

$$\begin{aligned} \Delta H^\circ &= \Delta_f H^\circ(\text{CO}_2, \text{g}) + 4\Delta_f H^\circ(\text{HCl, g}) - \Delta_f H^\circ(\text{CCl}_4, \text{g}) - 2\Delta_f H^\circ(\text{H}_2\text{O, g}) \\ &= (-393.7 - 4 \times 92.5 + 106.7 + 2 \times 241.8) \text{ kJ mol}^{-1} = -173.4 \text{ kJ mol}^{-1}. \end{aligned}$$

3. The given data are:

- (i)  $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2} \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$   $\Delta H^\circ = -1299.63 \text{ kJ mol}^{-1}$
- (ii)  $\text{C(graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   $\Delta H^\circ = -393.51 \text{ kJ mol}^{-1}$
- (iii)  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$   $\Delta H^\circ = -285.85 \text{ kJ mol}^{-1}$

We have to determine  $\Delta H$  for the reaction

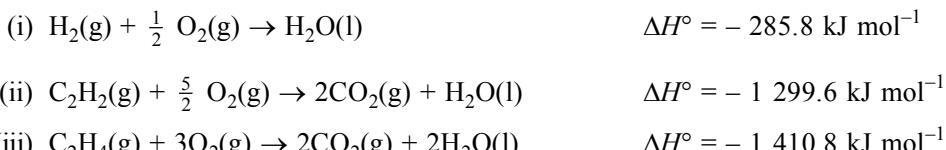


This equation can be obtained by the following manipulation:

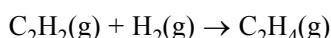
$$\text{Eq. (ii)} + \text{Eq. (iii)} - \text{Eq. (i)}$$

$$\begin{aligned}\text{Hence, } \Delta H^\circ &= \Delta H_{(\text{ii})}^\circ + \Delta H_{(\text{iii})}^\circ - \Delta H_{(\text{i})}^\circ = (-2 \times 393.51 - 285.85 + 1299.63) \text{ kJ mol}^{-1} \\ &= 226.76 \text{ kJ mol}^{-1}.\end{aligned}$$

**4.** The given data are:



We have to find  $\Delta U$  of the reaction



This equation can be obtained by the following manipulation.

$$\text{Eq. (ii)} + \text{Eq. (i)} - \text{Eq. (iii)}$$

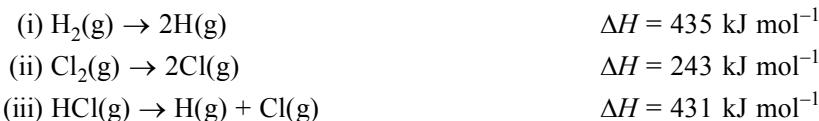
$$\begin{aligned}\text{Hence, } \Delta H^\circ &= \Delta H_{(\text{ii})}^\circ + \Delta H_{(\text{i})}^\circ - \Delta H_{(\text{iii})}^\circ = (-1299.6 - 285.8 + 1410.8) \text{ kJ mol}^{-1} \\ &= -174.6 \text{ kJ mol}^{-1}\end{aligned}$$

Now for the given reaction  $\Delta v_g = -1$

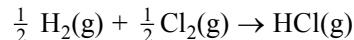
Hence, using the expression  $\Delta H^\circ = \Delta U^\circ + (\Delta v_g)RT$  we get

$$\begin{aligned}\Delta U^\circ &= \Delta H^\circ - (\Delta v_g)RT = -174.6 \text{ kJ mol}^{-1} - (-1)(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \\ &= (-174.6 + 2.48) \text{ kJ mol}^{-1} = -172.12 \text{ kJ mol}^{-1}.\end{aligned}$$

**5.** The given data are



We have to find  $\Delta H$  for the reaction



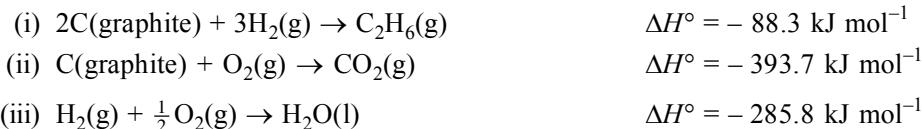
This equation can be obtained by the following manipulation.

$$\frac{1}{2} \text{Eq. (i)} + \text{Eq. (ii)} - \text{Eq. (iii)}$$

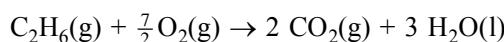
Hence, carrying out the corresponding manipulation on  $\Delta H$ s, we get

$$\Delta H = +\frac{1}{2} \Delta H_{(\text{i})} + \frac{1}{2} \Delta H_{(\text{ii})} - \Delta H_{(\text{iii})} = \left( \frac{1}{2} \times 435 + \frac{1}{2} \times 243 - 431 \right) \text{ kJ mol}^{-1} = -92 \text{ kJ mol}^{-1}.$$

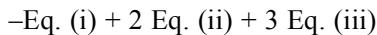
**6.** The given data are:



We have to find  $\Delta H^\circ$  for the reaction



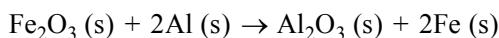
This equation can be obtained by the following manipulations.



Carrying out the corresponding manipulations on  $\Delta H^\circ$ s, we get

$$\begin{aligned}\Delta H^\circ &= -\Delta H_{(\text{i})}^\circ + 2\Delta H_{(\text{ii})}^\circ + 3\Delta H_{(\text{iii})}^\circ = (88.3 - 2 \times 393.7 - 3 \times 285.8) \text{ kJ mol}^{-1} \\ &= -1556.5 \text{ kJ mol}^{-1}.\end{aligned}$$

**7.** The reaction involved is



The enthalpy change of this reaction is

$$\Delta H = \Delta_f H(\text{Al}_2\text{O}_3, \text{s}) - \Delta_f H(\text{Fe}_2\text{O}_3, \text{s}) = (-1669 + 833) \text{ kJ mol}^{-1} = -836 \text{ kJ mol}^{-1}$$

Total mass of the reactants = Molar mass of  $\text{Fe}_2\text{O}_3$  + 2 Molar mass of Al

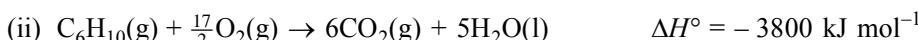
$$= 160 \text{ g} + (2 \times 27) \text{ g} = 214 \text{ g}$$

$$\text{Heat evolved per unit mass of the reactants} = \frac{836 \text{ kJ}}{214 \text{ g}} = 3.906 \text{ kJ g}^{-1}$$

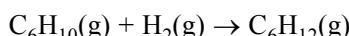
$$\text{Total volume of the reactants} = \frac{160 \text{ g}}{5.2 \text{ g cm}^{-3}} + 2 \frac{27}{2.7 \text{ g cm}^{-3}} = 50.77 \text{ cm}^3$$

$$\text{Heat evolved per unit volume of the reactants} = \frac{836 \text{ kJ}}{50.77 \text{ cm}^3} = 16.47 \text{ kJ cm}^{-3}.$$

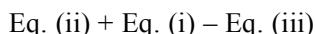
**8.** The given data are:



We have to calculate the enthalpy change for the reaction



This equation can be obtained by the following manipulations.



Carrying out the corresponding manipulations on  $\Delta H^\circ$ s, we get

$$\Delta H^\circ = \Delta H_{(\text{ii})}^\circ + \Delta H_{(\text{i})}^\circ - \Delta H_{(\text{iii})}^\circ = (-3800 - 241 + 3920) \text{ kJ mol}^{-1} = -121 \text{ kJ mol}^{-1}.$$

**9.** Energy available from 100 g glucose = 1560 kJ

$$\text{Energy utilized by athlete} = \frac{1}{2} \times 1560 \text{ kJ}$$

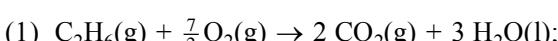
$$\text{Energy unutilized by athlete} = \frac{1}{2} \times 1560 \text{ kJ.}$$

$$\text{Enthalpy of evaporation of water} = 44 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\text{Amount of water to be converted into vapours from unused energy} &= \frac{78 \text{ kJ}}{44 \text{ kJ mol}^{-1}} \\ &= 17.73 \text{ mol}\end{aligned}$$

$$\text{Mass of water perspired} = 17.73 \times 18 \text{ g} = 319.14 \text{ g.}$$

**10.** From the enthalpy of combustion of ethane and propane, we write

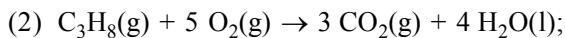


$$\Delta_c H = 3\Delta_f H(H_2O, l) + 2\Delta_f H(CO_2, g) - \Delta_f H(C_2H_6, g)$$

Thus,

$$\Delta_f H(C_2H_6, g) = -\Delta_c H + 3\Delta_f H(H_2O, l) + 2\Delta_f H(CO_2, g)$$

$$\begin{aligned} &= (1556.5 - 3 \times 284.5 - 2 \times 393.3) \text{ kJ mol}^{-1} \\ &= -83.6 \text{ kJ mol}^{-1} \end{aligned}$$



$$\Delta_c H = 3\Delta_f H(CO_2, g) + 4\Delta_f H(H_2O, l) - \Delta_f H(C_3H_8, g)$$

Thus

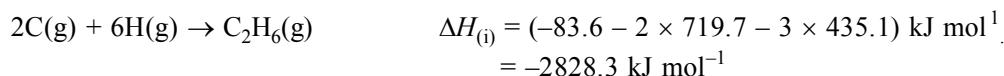
$$\Delta_f H(C_3H_8, g) = -\Delta_c H + 3\Delta_f H(CO_2, g) + 4\Delta_f H(H_2O, l)$$

$$\begin{aligned} &= (217.5 - 3 \times 393.5 - 4 \times 284.5) \text{ kJ mol}^{-1} \\ &= -101.0 \text{ kJ mol}^{-1} \end{aligned}$$

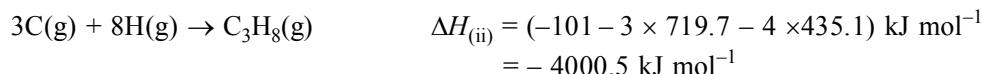
To calculate the  $\varepsilon_{C-H}$  and  $\varepsilon_{C-C}$ , we carry out the following manipulations.



Add \_\_\_\_\_



Add \_\_\_\_\_



Now

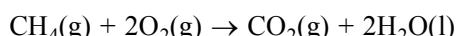
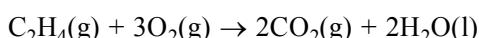
$$\Delta H_{(i)} = -\varepsilon_{C-C} - 6\varepsilon_{C-H} = -2828.3 \text{ kJ mol}^{-1}$$

$$\Delta H_{(ii)} = -2\varepsilon_{C-C} - 8\varepsilon_{C-H} = -4000.5 \text{ kJ mol}^{-1}$$

Solving for  $\varepsilon_{C-C}$  and  $\varepsilon_{C-H}$ , we get

$$\varepsilon_{C-C} = 414.0 \text{ kJ mol}^{-1} \text{ and } \varepsilon_{C-H} = 344.3 \text{ kJ mol}^{-1}$$

**11.** The combustion reactions are



Let  $V$  be the volume of  $C_2H_4(g)$  in the gaseous mixture of 3.67 L. From the chemical equations, we find that

Volume of  $CO_2(g)$  produced due to the combustion of  $C_2H_4(g)$  =  $2V$

Volume of  $CO_2(g)$  produced due to the combustion of  $CH_4(g)$  =  $3.67 L - V$

Equating the latter with  $6.11 L - 2V$ , we get

$$3.67 L - V = 6.11 L - 2V \quad \text{or} \quad V = 2.44 L$$

Hence, in the original mixture, we have

$$\text{Volume of } C_2H_4(g) \text{ per litre of the mixture} = \left( \frac{2.44 \text{ L}}{3.67 \text{ L}} \right) (1 \text{ L}) = 0.665 \text{ L}$$

$$\text{Volume of } CH_4(g) \text{ per litre of the mixture} = 1.0 \text{ L} - 0.665 \text{ L} = 0.335 \text{ L}$$

Now, Volume of 1 mol of any gas at 25 °C = (22.414 L)  $\left(\frac{298 \text{ K}}{273 \text{ K}}\right)$  = 24.467 L

Hence, Heat released due to the combustion of C<sub>2</sub>H<sub>4</sub>(g) = (1423 kJ)  $\left(\frac{0.665 \text{ L}}{24.467 \text{ L}}\right)$  = 38.68 kJ

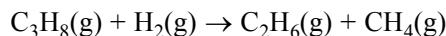
Heat released due to the combustion of CH<sub>4</sub>(g) = (891 kJ)  $\left(\frac{0.335 \text{ L}}{24.467 \text{ L}}\right)$  = 12.20 kJ

Total heat released = (38.68 + 12.20) kJ = 50.88 kJ.

**12.** The given data are:

- |  |  |
|--|--|
| (i) H <sub>2</sub> (g) + $\frac{1}{2}$ O <sub>2</sub> (g) → H <sub>2</sub> O(l)  | $\Delta H = -285.8 \text{ kJ mol}^{-1}$  |
| (ii) CH <sub>4</sub> (g) + 2O <sub>2</sub> (g) → CO <sub>2</sub> (g) + 2H <sub>2</sub> O(l)                              | $\Delta H = -890.0 \text{ kJ mol}^{-1}$  |
| (iii) C <sub>2</sub> H <sub>6</sub> (g) + $\frac{7}{2}$ O <sub>2</sub> (g) → 2CO <sub>2</sub> (g) + 3H <sub>2</sub> O(l) | $\Delta H = -1560.0 \text{ kJ mol}^{-1}$ |
| (iv) C(graphite) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)  | $\Delta H = -393.5 \text{ kJ mol}^{-1}$  |
| (v) 3C(graphite) + 4H <sub>2</sub> (g) → C <sub>3</sub> H <sub>8</sub> (g)   | $\Delta H = -103.8 \text{ kJ mol}^{-1}$  |

We have to determine  $\Delta H$  of the reaction



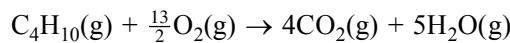
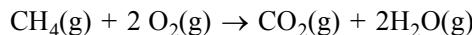
This equation can be obtained by the following manipulations.

$$-\text{Eq. (v)} - \text{Eq. (iii)} - \text{Eq. (ii)} + 3 \text{ Eq. (iv)} + 5 \text{ Eq. (i)}$$

Carrying out the corresponding manipulations on  $\Delta H$ s, we get

$$\Delta H = (103.8 + 1560 + 890 - 3 \times 393.5 - 5 \times 285.8) \text{ kJ mol}^{-1} = -55.7 \text{ kJ mol}^{-1}.$$

**13.** The combustion reactions are



$$\text{Calorific value of CH}_4 = \frac{809}{16} \text{ kJ g}^{-1}$$

$$\text{Calorific value of C}_4\text{H}_{10} = \frac{2878}{58} \text{ kJ g}^{-1}$$

Mass of C<sub>4</sub>H<sub>10</sub> having the same calorific output as that of CH<sub>4</sub> =  $\left(\frac{809}{16}\right)\left(\frac{58}{2878}\right) \text{ g}$

Amount of C<sub>4</sub>H<sub>10</sub> having the same calorific output as that of CH<sub>4</sub> =  $\frac{809}{16 \times 2878} \text{ mol}$

Now,  $\frac{1}{16}$  mol CH<sub>4</sub> requires the supply  $x \text{ L h}^{-1}$  of CH<sub>4</sub>

$\frac{809}{16 \times 2878} \text{ mol C}_4\text{H}_{10}$  requires the supply of  $\frac{x \text{ L h}^{-1}}{(1/16)}\left(\frac{809}{16 \times 2878}\right) = (0.28 x) \text{ L h}^{-1}$  of C<sub>4</sub>H<sub>10</sub>

The corresponding supply of O<sub>2</sub> =  $(0.28 x) \left(3 \times \frac{13}{2}\right) \text{ L h}^{-1} = (5.48 x) \text{ L h}^{-1}$

14. In polymerisation, 1 double bond ( $\text{C}=\text{C}$ ) is replaced by two single  $\text{C}-\text{C}$  bonds. For the polymerisation of 1 mol of ethylene, 1 mol of  $\text{C}=\text{C}$  bonds are replaced by 2 mol of  $\text{C}-\text{C}$  bonds. Hence

$$\Delta H = -2 \varepsilon_{\text{C}-\text{C}} + \varepsilon_{\text{C}=\text{C}} = \{-2(331) + 590\} \text{ kJ mol}^{-1} = -72 \text{ kJ mol}^{-1}.$$

15. The dissociation reaction is  $\text{I}_2 \rightarrow 2\text{I}$

Bond energy per single bond is

$$\varepsilon = \frac{240 \text{ kJ mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 3.985 \times 10^{-22} \text{ kJ} = 3.985 \times 10^{-19} \text{ J}$$

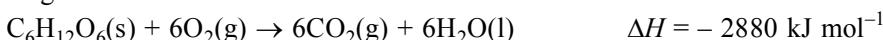
Energy of 1 photon of wavelength 4500 Å is

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{(4500 \times 10^{-10} \text{ m})} = 4.417 \times 10^{-19} \text{ J}$$

Of the energy  $4.417 \times 10^{-19} \text{ J}$ , the energy consumed to break  $\text{I}_2$  molecules is  $3.985 \times 10^{-19} \text{ J}$ . The remaining energy is used in imparting kinetic energy to the two iodine atoms. Hence

$$\text{Kinetic energy per iodine atom} = \frac{(4.417 - 3.985) \times 10^{-19} \text{ J}}{2} = 2.16 \times 10^{-20} \text{ J}.$$

16. We are given that



Enthalpy consumed in muscular work =  $(2880 \text{ kJ})(25/100) = 720 \text{ kJ}$

$$\text{Amount of glucose in 120 g} = \left( \frac{120 \text{ g}}{180 \text{ g mol}^{-1}} \right) = 0.6667 \text{ mol}$$

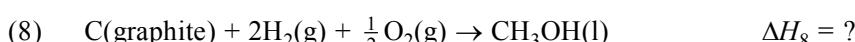
$$\begin{aligned} \text{Enthalpy available for muscular work from 120 g of glucose} &= (720 \text{ kJ mol}^{-1})(0.6667 \text{ mol}) \\ &= 480 \text{ kJ} \end{aligned}$$

$$\text{Distance to which a person can move} = \left( \frac{1 \text{ km}}{100 \text{ kJ}} \right) (480 \text{ kJ}) = 4.80 \text{ km}$$

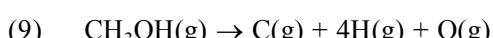
17. The given data are as follows.

(1)	$\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g})$	$\Delta H_1 = 38 \text{ kJ mol}^{-1}$
(2)	$\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$	$\Delta H_2 = 218 \text{ kJ mol}^{-1}$
(3)	$\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$	$\Delta H_3 = 715 \text{ kJ mol}^{-1}$
(4)	$\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$	$\Delta H_4 = 249 \text{ kJ mol}^{-1}$
(5)	$\text{C}-\text{H}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	$\Delta H_5 = 415 \text{ kJ mol}^{-1}$
(6)	$\text{C}-\text{O}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{O}(\text{g})$	$\Delta H_6 = 356 \text{ kJ mol}^{-1}$
(7)	$\text{O}-\text{H}(\text{g}) \rightarrow \text{O}(\text{g}) + \text{H}(\text{g})$	$\Delta H_7 = 463 \text{ kJ mol}^{-1}$

We have to calculate the enthalpy of formation of liquid methyl alcohol, i.e.,



First of all, we calculate the enthalpy of reaction



from the data on bond enthalpies. This is given as

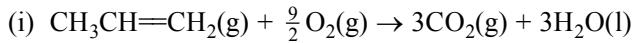
$$\Delta H_9 = 3 \Delta H_5 + \Delta H_6 + \Delta H_7 = (3 \times 415 + 356 + 463) \text{ kJ mol}^{-1} = 2064 \text{ kJ mol}^{-1}$$

Equation (8) can be generated as follows

$$\text{Eq. (3)} + 4 \cdot \text{Eq. (2)} + \text{Eq. (4)} - \text{Eq. (9)} - \text{Eq. (1)}$$

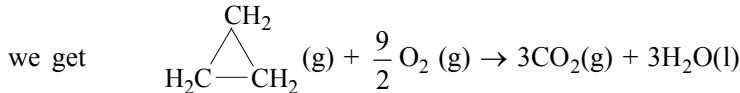
$$\begin{aligned} \text{Hence, } \Delta H &= \Delta H_3 + 4\Delta H_2 + \Delta H_4 - \Delta H_9 - \Delta H_1 \\ &= (715 + 4 \times 218 + 249 - 2064 - 38) \text{ kJ mol}^{-1} = -266 \text{ kJ mol}^{-1} \end{aligned}$$

**18.** For the reaction



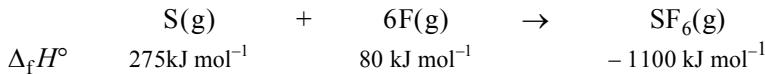
$$\begin{aligned} \Delta_f H &= 3\Delta_f H(\text{CO}_2, \text{g}) + 3\Delta_f H(\text{H}_2\text{O}, \text{l}) - \Delta_f H(\text{CH}_3\text{CH}=\text{CH}_2) \\ &= [3(-393.5) + 3(-285.8) - (20.42)] \text{ kJ mol}^{-1} = -2058.32 \text{ kJ mol}^{-1} \end{aligned}$$

To the reaction (i), if we add the reaction



$$\text{Hence, } \Delta_c H(\text{cyclopropane}) = (-2058.32 - 33.0) \text{ kJ mol}^{-1} = -2091.32 \text{ kJ mol}^{-1}$$

**19.** To calculate the average S—F bond enthalpy, we determine the enthalpy change for the following reaction.



$$\begin{aligned} \Delta_f H^\circ &= \Delta_f H^\circ(\text{SF}_6, \text{g}) - [\Delta_f H^\circ(\text{S, g}) + 6 \Delta_f H^\circ(\text{F, g})] \\ &= [-1100 - (275 + 6 \times 80)] \text{ kJ mol}^{-1} = -1855 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Hence, } \varepsilon(\text{S} - \text{F}) = \frac{-\Delta_f H^\circ(\text{SF}_6, \text{g})}{6} = \frac{1855 \text{ kJ mol}^{-1}}{6} = 309.2 \text{ kJ mol}^{-1}$$

**20.** For a reversible expansion of an ideal gas, we have

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \quad \text{where} \quad \gamma = C_{p,m}/C_{V,m}$$

For a monatomic gas (assumed to be ideal),

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{V,m} + R}{C_{V,m}} = 1 + \frac{R}{C_{V,m}} = 1 + \frac{8.314}{12.48} = 1.6662$$

$$\text{Hence, } T = \left( \frac{V_1}{V_2} \right)^{\gamma-1} T_1 = \left( \frac{1.25}{2.50} \right)^{0.6662} (300 \text{ K}) = 189.0 \text{ K}$$

The enthalpy change in the given process would be  $\Delta H = nC_{p,m} \Delta T$

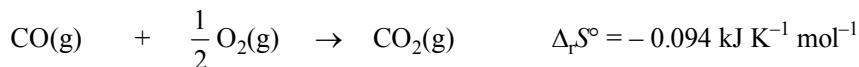
$$\text{where } n = \frac{pV}{RT} = \frac{(101.325 \text{ kPa})(1.25 \text{ dm}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 0.0508 \text{ mol}$$

$$C_{p,m} = C_{V,m} + R = (12.48 + 8.314) \text{ J K}^{-1} \text{ mol}^{-1} = 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta T = T_2 - T_1 = (189.0 - 300) \text{ K} = -111 \text{ K}$$

$$\begin{aligned} \text{Hence } \Delta H &= nC_{p,m} \Delta T = (0.0508 \text{ mol})(20.794 \text{ J K}^{-1} \text{ mol}^{-1})(-111 \text{ K}) \\ &= -117.25 \text{ J} \end{aligned}$$

**21.** For the given reaction, we have



$$\Delta_f G^\circ = -137.2 \text{ kJ mol}^{-1} \quad -394.4 \text{ kJ mol}^{-1}$$

The standard free-energy change of the reaction is

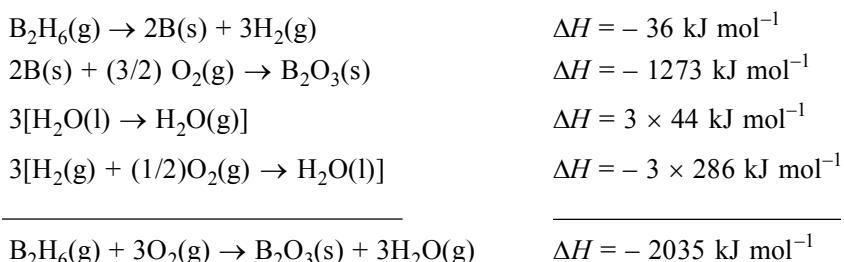
$$\Delta_r G^\circ = \Delta_f G^\circ(\text{CO}_2, \text{g}) - \Delta_f G^\circ(\text{CO, g}) = (-394.4 + 137.2) \text{ kJ mol}^{-1} = -257.2 \text{ kJ mol}^{-1}$$

Since  $\Delta_r G^\circ$  is negative, the reaction is spontaneous. The enthalpy change of the reaction is

$$\Delta_r H^\circ = \Delta_r G^\circ - T\Delta_r S^\circ = (-257.2 + 300)(-0.094) \text{ kJ mol}^{-1} = -285.4 \text{ kJ mol}^{-1}$$

Since  $\Delta_r H^\circ$  is negative, the reaction is exothermic.

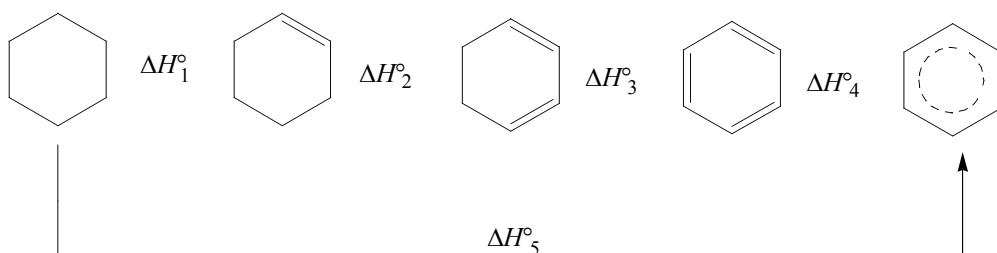
**22.** The given reaction can be obtained as follows.



**23.** The reaction corresponding to the hydrogenation of cyclohexene(l) is



This implies that the generation of one double bond in cyclohexene requires  $119 \text{ kJ mol}^{-1}$  of enthalpy. To calculate the resonance energy, we may proceed as follows.



Now,

$$\Delta H_1^\circ = \Delta H_2^\circ = \Delta H_3^\circ = 119 \text{ kJ mol}^{-1}$$

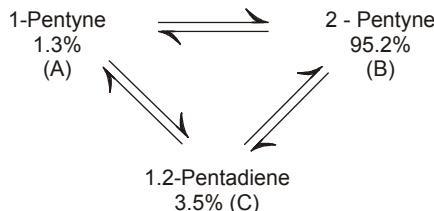
$$\Delta H_4^\circ = \text{resonance energy}$$

$$\begin{aligned} \Delta H_5^\circ &= \Delta H_f^\circ(\text{benzene}) - \Delta H_f^\circ(\text{cyclohexane}) \\ &= [49 - (-156)] \text{ kJ mol}^{-1} \\ &= 205 \text{ kJ mol}^{-1} \end{aligned}$$

According to Hess's law, we have

$$\begin{aligned} \Delta H_4^\circ &= \Delta H_5^\circ - (\Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ) \\ &= (205 - 3 \times 119) \text{ kJ mol}^{-1} \\ &= -152 \text{ kJ mol}^{-1} \end{aligned}$$

24. We have



For the equilibrium  $B \rightleftharpoons A$ , we get

$$K_{\text{eq}1} = \frac{[A]_{\text{eq}}}{[B]_{\text{eq}}} = \frac{1.3}{95.2} = 1.366 \times 10^{-2}$$

$$\begin{aligned}\Delta G_1^\circ &= -R_T \ln K_{\text{eq}1} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(448 \text{ K}) \ln (3.666 \times 10^{-2}) \\ &= 15991 \text{ J mol}^{-1}\end{aligned}$$

For the equilibrium  $B \rightleftharpoons C$ , we get

$$K_{\text{eq}2} = \frac{[C]_{\text{eq}}}{[B]_{\text{eq}}} = \frac{3.5}{95.2} = 3.676 \times 10^{-2}$$

$$\begin{aligned}\Delta G_2^\circ &= -R_T \ln K_{\text{eq}2} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(448 \text{ K}) \ln (3.676 \times 10^{-2}) \\ &= 12304 \text{ J mol}^{-1}\end{aligned}$$

For the equilibrium  $B \rightleftharpoons A$ , we have

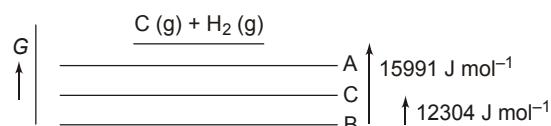
$$\Delta G_1^\circ = \Delta_f G_A^\circ - \Delta_f G_B^\circ = 15991 \text{ J mol}^{-1}$$

or  $\Delta_f G_A^\circ = \Delta_f G_B^\circ + 15991 \text{ J mol}^{-1}$

Similarly for  $B \rightleftharpoons C$ , we have

$$\Delta_f G_C^\circ = \Delta_f G_B^\circ + 12304 \text{ J mol}^{-1}$$

Diagrammatically, we have



Hence, the order of stability of isomers is  $B > C > A$

(Note: This also follows from the percentages of B, C and A in the equilibrium mixture.)

25. (i) The  $p$ - $V$  diagram of the given processes a, b and c are shown in Fig. C-1.

- (a) Reversible isobaric expansion  $(1 \text{ atm}, 20 \text{ L}) \longrightarrow (1 \text{ atm}, 40 \text{ L})$
- (b) Reversible isochoric expansion  $(1 \text{ atm}, 40 \text{ L}) \longrightarrow (0.5 \text{ atm}, 40 \text{ L})$
- (c) Reversible isothermal compression  $(0.5 \text{ atm}, 40 \text{ L}) \longrightarrow (1 \text{ atm}, 20 \text{ L})$

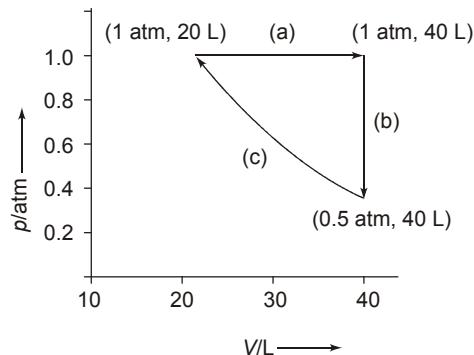


Fig. C-1

(ii) Work involved in the given processes are as follows.

$$\begin{aligned} \text{Process a} \quad w_1 &= p(\Delta V) = (1 \text{ atm}) (40 \text{ L} - 20 \text{ L}) = 20 \text{ atm L} \\ &= 20 \times 101.325 \text{ J} = 2026.5 \text{ J} \end{aligned}$$

$$\text{Process b} \quad w_2 = 0, \text{ since the process occurs at constant volume}$$

$$\begin{aligned} \text{Process c} \quad w_3 &= nRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_2}{V_1} \\ &= (1 \text{ atm}) (20 \text{ L}) \ln (20 \text{ L}/40 \text{ L}) = -13.86 \text{ atm L} \\ &= -13.86 \times 101.325 \text{ J} = -1404.4 \text{ J} \end{aligned}$$

The total work done is

$$\begin{aligned} w &= w_1 + w_2 + w_3 = 2026.5 \text{ J} + 0 - 1404.4 \text{ J} \\ &= 622.1 \text{ J} \end{aligned}$$

Since the given processes constitute a cyclic process,  $\Delta U = 0$ , and from the first law of thermodynamics, we get

$$q = -w = -622.1 \text{ J}$$

Since the given processes constitute a cyclic process,  $\Delta U = 0$ , and from the first law of thermodynamics, we get

$$q = -w = -622.1 \text{ J}$$

(iii) Since the overall process is a cyclic process,

$$\Delta U = 0 \quad \Delta H = 0 \quad \text{and} \quad \Delta S = 0$$

**26.** From the first law of thermodynamics, we have

$$dU = dq + dw$$

Since the processes occur adiabatically,  $dq = 0$ . This gives

$$dU = dw$$

For the first process liquid(2 bar, 100 mL)  $\longrightarrow$  liquid(100 bar, 100 mL);  $dV = 0$ .

Hence  $dw = -pdV = 0$ . For this process  $dU = 0$  or  $\Delta U = 0$ .

For the second process



$$w = -p \Delta V = -(100 \text{ bar}) (98 \text{ mL} - 100 \text{ mL}) = 200 \text{ bar mL}$$

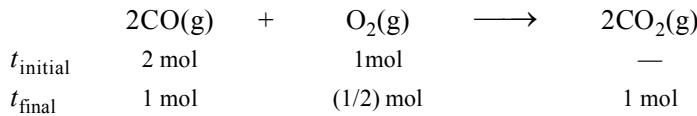
Hence, for both the processes  $\Delta U = 0 + 200 \text{ bar mL} = 200 \text{ bar mL}$

$$= (200) (10^5 \text{ N m}^{-2}) (10^{-2} \text{ m})^3 = 20 \text{ J}$$

$$\Delta H = \Delta U + \Delta(PV) = 200 \text{ bar mL} + [(100 \text{ bar}) (98 \text{ mL}) - (2 \text{ bar}) (100 \text{ mL})]$$

$$= 100 \text{ bar mL} + 9600 \text{ bar mL} = 9700 \text{ bar mL} = 9700 (10^5 \text{ N m}^{-2}) (10^{-2} \text{ m})^3 = 970 \text{ J}$$

**27.** We have



It is given that

$$\Delta_r H = 2\Delta_f H(\text{CO}_2) - 2\Delta_f H(\text{CO}) - \Delta_f H(\text{O}_2) = -560 \text{ kJ mol}^{-1}$$

$$\text{Now } H_{\text{initial}} = (2 \text{ mol}) \Delta_f H(\text{CO}) + (1 \text{ mol}) \Delta_f H(\text{O}_2)$$

$$H_{\text{final}} = (1 \text{ mol}) \Delta_f H(\text{CO}) + \left(\frac{1}{2} \text{ mol}\right) \Delta_f H(\text{O}_2) + (1 \text{ mol}) \Delta_f H(\text{CO}_2)$$

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

$$= (1 \text{ mol}) \Delta_f H(\text{CO}_2) - (1 \text{ mol}) \Delta_f H(\text{CO}) - \left(\frac{1}{2} \text{ mol}\right) \Delta_f H(\text{O}_2)$$

$$= \left(\frac{1}{2} \text{ mol}\right) \Delta_r H = \left(\frac{1}{2} \text{ mol}\right) (-560 \text{ kJ mol}^{-1}) = -280 \text{ kJ}$$

Since  $H = U + pV$ , we have

$$\Delta U = \Delta H - \Delta(pV)$$

$$= \Delta H - V \Delta p \quad (\text{since } V \text{ is constant})$$

Substituting the data, we get

$$\Delta U = -280 \text{ kJ} - (1 \text{ L}) \{40 \text{ atm} - 70 \text{ atm}\} = -280 \text{ kJ} + (30 \text{ L atm}) \left(\frac{0.1 \text{ kJ}}{1 \text{ L atm}}\right)$$

$$= -273 \text{ kJ}$$



# CHEMICAL EQUILIBRIA

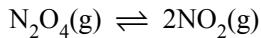
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## SECTION-I

### Straight Objective Type

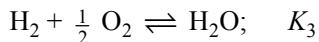
1. The oxidation of  $\text{SO}_2$  by  $\text{O}_2$  to  $\text{SO}_3$  is an exothermic reaction. The yield of  $\text{SO}_3$  will be maximum if
  - (a) temperature is increased and pressure is kept constant
  - (b) temperature is reduced and pressure is increased
  - (c) both temperature and pressure are increased
  - (d) both temperature and pressure are reduced(1981)
2. For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , the equilibrium constant  $K_p$  changes with
  - (a) total pressure
  - (b) catalyst
  - (c) the amounts of  $\text{H}_2$  and  $\text{I}_2$  present
  - (d) temperature(1981)
3. The equilibrium,  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is attained at  $25^\circ\text{C}$  in a closed container and an inert gas, helium, is introduced. Which of the following statements are correct?
  - (a) Concentrations of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  are changed
  - (b) More chlorine is formed
  - (c) Concentration of  $\text{SO}_2$  is reduced
  - (d) More  $\text{SO}_2\text{Cl}_2$  is formed(1989)
4. One mole of  $\text{N}_2\text{O}_4(\text{g})$  at  $300\text{ K}$  is kept in a closed container under one atmosphere. It is heated to  $600\text{ K}$  when  $20\%$  by mass of  $\text{N}_2\text{O}_4(\text{g})$  decomposes to  $\text{NO}_2(\text{g})$ . The resultant pressure is
  - (a)  $1.2\text{ atm}$
  - (b)  $2.4\text{ atm}$
  - (c)  $2.0\text{ atm}$
  - (d)  $1.0\text{ atm}$(1996)
5. For the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  at a given temperature, the equilibrium amount of  $\text{CO}_2(\text{g})$  can be increased by
  - (a) adding a suitable catalyst
  - (b) adding an inert gas
  - (c) decreasing the volume of the container
  - (d) increasing the amount of  $\text{CO}(\text{g})$(1998)
6. Pure ammonia is placed in a vessel at a temperature where its dissociation constant ( $K_p$ ) is appreciable. At equilibrium:
  - (a)  $K_p$  does not change significantly with pressure
  - (b)  $\alpha$  does not change with pressure
  - (c) concentration of  $\text{NH}_3$  does not change with pressure
  - (d) concentration of  $\text{H}_2$  is less than that of nitrogen(1984)

7. For the chemical reaction  $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$ , the amount of  $X_3Y$  at equilibrium is affected by
- (a) temperature and pressure
  - (b) temperature only
  - (c) pressure only
  - (d) temperature, pressure and catalyst
8. For the reversible reaction,  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  at  $500^\circ C$ , the value of  $K_p$  is  $1.44 \times 10^{-5}$  when partial pressure is measured in atmospheres. The corresponding value of  $K_c$ , with concentration in mol L<sup>-1</sup>, is
- (a)  $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
  - (b)  $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
  - (c)  $1.44 \times 10^{-5}/(0.082 \times 773)^2$
  - (d)  $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$
9. When two reactants, A and B are mixed to give products C and D, the reaction quotient,  $Q$ , at the initial stages of the reaction
- (a) is zero
  - (b) decreases with time
  - (c) is independent of time
  - (d) increases with time
10. At constant temperature, the equilibrium constant ( $K_p$ ) for the decomposition reaction  $N_2O_4 \rightleftharpoons 2NO_2$  is expressed by  $K_p = (4x^2p)/(1 - x^2)$ , where  $p$  = pressure,  $x$  = extent of decomposition. Which one of the following statements is true?
- (a)  $K_p$  increases with increase of  $p$
  - (b)  $K_p$  increases with increase of  $x$
  - (c)  $K_p$  increases with decrease of  $x$
  - (d)  $K_p$  remains constant with change in  $p$  and  $x$
11. Consider the following equilibrium in a closed container:



At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant ( $K_p$ ) and degree of dissociation ( $\alpha$ )?

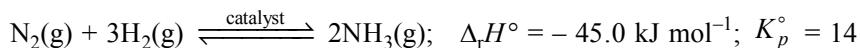
- (a) neither  $K_p$  nor  $\alpha$  changes
  - (b) both  $K_p$  and  $\alpha$  change
  - (c)  $K_p$  changes, but  $\alpha$  does not change
  - (d)  $K_p$  does not change, but  $\alpha$  changes
12. The following equilibria are given:



The equilibrium constant of the reaction  $2NH_3 + \frac{5}{2} O_2 \rightleftharpoons 2NO + 3H_2O$  in terms of  $K_1$ ,  $K_2$  and  $K_3$  is

- (a)  $K_1 K_2 / K_3$
- (b)  $K_1 K_3^2 / K_2$
- (c)  $K_2 K_3^3 / K_1$
- (d)  $K_1 K_2 K_3$

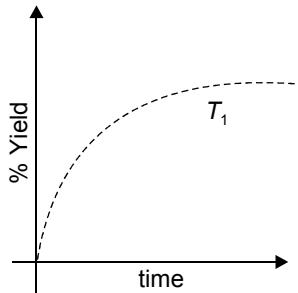
13. Haber-Bosch process for the manufacture of  $NH_3$  is based on the reaction



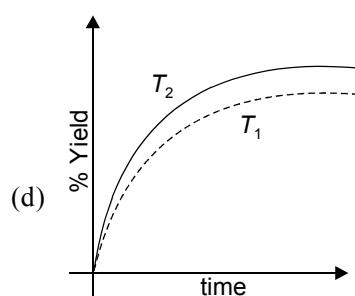
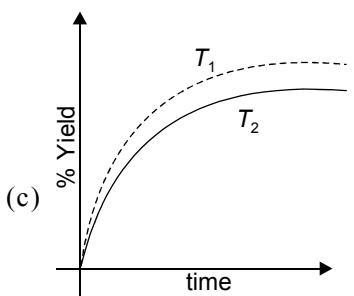
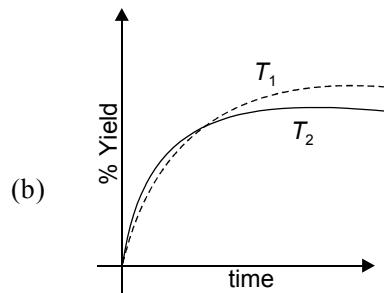
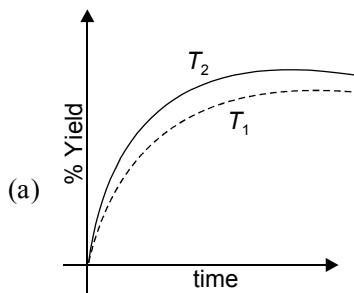
Which of the following information regarding the above reaction is correct?

- (a) On adding  $N_2$ , the equilibrium is shifted to right side with an increase in entropy.
- (b) The equilibrium constant  $K_p^\circ$  increases with increase in temperature.
- (c) At equilibrium,  $2G_m(NH_3) = G_m(N_2) + 3G_m(H_2)$  where  $G_m$  represents the molar Gibbs function of the species enclosed within the brackets.
- (d) The use of catalyst helps increasing the rate of forward reaction more than that of backward reaction thereby increasing the yield of  $NH_3$ .

14. The % yield of ammonia as a function of time in the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ;  $\Delta H < 0$  at  $(P, T_1)$  is given below:



If this reaction is conducted at  $(P, T_2)$ , with  $T_2 > T_1$ , the % yield of ammonia as a function of time is represented by



(2015)

### Multiple Correct-Choice Type

1. For the gas phase reaction



carried out in a vessel, the equilibrium concentration of  $\text{C}_2\text{H}_4$  can be increased by

- (a) increasing the temperature
- (b) decreasing the pressure
- (c) removing some  $\text{H}_2$
- (d) adding some  $\text{C}_2\text{H}_6$

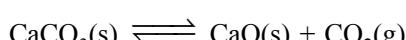
(1984)

2. When  $\text{NaNO}_3$  is heated in a closed vessel, oxygen is liberated and  $\text{NaNO}_2$  is left behind. At equilibrium

- (a) addition of  $\text{NaNO}_2$  favours reverse reaction
- (b) addition of  $\text{NaNO}_3$  favours forward reaction
- (c) increasing temperature favours forward reaction
- (d) increasing pressure favours reverse reaction

(1986)

3. For the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , the forward reaction at constant temperature is favoured by
- introducing an inert gas at constant volume
  - introducing chlorine gas at constant volume
  - introducing an inert gas at constant pressure
  - increasing the volume of the container
  - introducing  $\text{PCl}_5$  at constant volume.
- (1991)
4. The equilibrium  $2\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^0 + \text{Cu}^{\text{II}}$  in aqueous medium at  $25^\circ\text{C}$  shifts towards the left in the presence of
- $\text{NO}_3^-$
  - $\text{Cl}^-$
  - $\text{SCN}^-$
  - $\text{CN}^-$
- (2011)
5. The thermal dissociation equilibrium of  $\text{CaCO}_3(\text{s})$  is studied under different conditions.



For this equilibrium, the correct statement(s) is (are)

- $\Delta H$  is dependent on  $T$
- $K$  is independent of the initial amount of  $\text{CaCO}_3$
- $K$  is dependent on the pressure of  $\text{CO}_2$  at a given  $T$
- $\Delta H$  is independent of the catalyst

(2013)

### Fill-in-the-Blanks Type

- A ten-fold increase in pressure on the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  at equilibrium results in \_\_\_\_\_ in  $K_p$ .  
(1996)
- For a given reversible reaction, at a fixed temperature equilibrium constants  $K_p$  and  $K_c$  are related by \_\_\_\_\_.  
(1994)
- For a gaseous reaction  $2\text{B} \rightarrow \text{A}$ , the equilibrium constant  $K_p$  is \_\_\_\_\_ to/than  $K_c$ .  
(1997)

### True/False Type

- Aluminium chloride is a Lewis acid because it can donate electrons.  
(1982)
- Silver fluoride is fairly soluble in water.  
(1982)
- Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water.  
(1984)
- Addition of ammonium chloride to a solution containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia.  
(1985)
- The solubility of  $\text{Zn}(\text{OH})_2$  is greater in an acidic or basic medium than in neutral water.  
(1982)
- If the equilibrium constant for the reaction  $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$  is  $K$ , then for the backward reaction  $\text{AB} \rightleftharpoons \frac{1}{2}\text{A}_2 + \frac{1}{2}\text{B}_2$ , the equilibrium constant is  $1/K$ .  
(1984)
- When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs.  
(1984)

### Reasoning Type

- In the following question are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code among a, b, c and d which are defined below.

**Code**

- (a) Both S and E are true, and E is the correct explanation of S.
- (b) Both S and E are true but E is not the correct explanation of S
- (c) S is true but E is false
- (d) S is false but E is true.

**Statement**

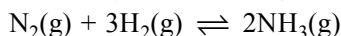
The endothermic reaction are favoured at lower temperature and the exothermic reactions are favoured at higher temperature

**Explanation**

When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

**Subjective Type**

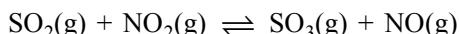
- One mole of nitrogen is mixed with three moles of hydrogen in a 4-litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:



calculate the equilibrium constant  $K_c$ . What will be the value of  $K_c$  for the following equilibrium?

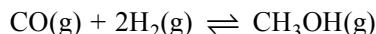


- One mole of  $\text{N}_2$  and 3 mol of  $\text{PCl}_5$  placed in a 100-litre vessel are heated to  $227^\circ\text{C}$ . The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of  $\text{PCl}_5$  and  $K_p$  for the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ . (1984)
- The equilibrium constant of the reaction  $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$  at  $100^\circ\text{C}$  is 50. If a one-litre flask containing one mole of  $\text{A}_2$  is connected to a two-litre flask containing two moles of  $\text{B}_2$ , what amount of  $\text{AB}$  will be formed at  $373\text{ K}$ ? (1985)
- At a certain temperature, equilibrium constant ( $K_c$ ) is 16 for the reaction



If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentrations of  $\text{NO}$  and  $\text{NO}_2$ ? (1987)

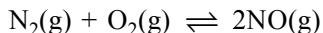
- $\text{N}_2\text{O}_4$  is 25% dissociated at  $37^\circ\text{C}$  and 1 atm pressure. Calculate (i)  $K_p$  and (ii) the percentage dissociation at 0.1 atm and  $37^\circ\text{C}$ . (1988)
- The equilibrium constant  $K_p$  of the reaction  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$  is  $900\text{ atm}^{-1}$  at  $800\text{ K}$ . A mixture containing  $\text{SO}_3$  and  $\text{O}_2$  having initial partial pressures of 1 atm and 2 atm, respectively, is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at  $800\text{ K}$ . (1989)
- For the reaction  $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$ , hydrogen gas is introduced into a five-litre flask at  $327^\circ\text{C}$  containing 0.2 mol of  $\text{CO}(\text{g})$  and a catalyst until the pressure is 4.92 atm. At this point, 0.1 mol of  $\text{CH}_3\text{OH}(\text{g})$  is formed. Calculate the equilibrium constants  $K_p$  and  $K_c$ . (1990)
- 0.15 mol of CO taken in a 2.5 L flask is maintained at  $705\text{ K}$  along with a catalyst so that the following reaction takes place



Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mol of methanol is formed. Calculate (a)  $K_p$  and  $K_c$  and (b) the final pressure if the same amount of CO and  $\text{H}_2$  as before are used, but with no catalyst so that the reaction does not take place. (1993)

- At temperature  $T$ , a compound  $\text{AB}_2(\text{g})$  dissociates according to the reaction  $2\text{AB}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g}) + \text{B}_2(\text{g})$  with a degree of dissociation,  $x$ , which is small compared with unity. Deduce the expression for  $x$  in terms of the equilibrium constant,  $K_p$  and the total pressure  $P$ . (1994)
- For the reaction  $\text{Ag}(\text{CN})_2^- \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-$ , the equilibrium constant at  $25^\circ\text{C}$  is  $4.0 \times 10^{-19}$ . Calculate the silver ion concentration in a solution which was originally 0.10 molar in  $\text{KCN}$  and 0.03 molar in  $\text{AgNO}_3$ . (1994)

11. A sample of air consisting of N<sub>2</sub> and O<sub>2</sub> was heated to 2500 K until the equilibrium



was established with an equilibrium constant  $K_c = 2.1 \times 10^{-3}$ . At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fractions of N<sub>2</sub> and O<sub>2</sub>. (1997)

12. For the reaction, N<sub>2</sub>O<sub>5</sub>(g) = 2NO<sub>2</sub>(g) + 0.5 O<sub>2</sub>(g), calculate the mole fraction of N<sub>2</sub>O<sub>5</sub>(g) decomposed at constant volume and temperature, if the initial pressure is 600 mmHg and the pressure at any time is 960 mmHg. Assuming ideal gas behaviour. (1998)

13. When 3.06 g of solid NH<sub>4</sub>HS is introduced into a two-litre evacuated flask at 27 °C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate  $K_c$  and  $K_p$  for the reaction at 27 °C. (ii) What would happen to equilibrium when more solid NH<sub>4</sub>HS is introduced into the flask? (1999)

14. (a) The reaction N<sub>2</sub>O<sub>4</sub>(g) ⇌ 2NO<sub>2</sub>(g) is carried out at 298 K and 20 bar. Five moles of each of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> are taken initially. Determine  $\Delta_f G$  and  $K_p^\circ$  at 298 K. Given:  $\Delta_f G^\circ(\text{N}_2\text{O}_4) = 100 \text{ kJ mol}^{-1}$  and  $\Delta_f G^\circ(\text{NO}_2) = 50 \text{ kJ mol}^{-1}$ .

- (b) The reaction proceeds at a initial pressure of 20 bar. Determine the direction in which the reaction proceeds to achieve equilibrium. Also determine the amounts of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> when the reaction attains equilibrium. (2004)

## ANSWERS

### Straight Objective Type

- |        |        |                |         |         |         |         |
|--------|--------|----------------|---------|---------|---------|---------|
| 1. (b) | 2. (d) | 3. (No choice) | 4. (b)  | 5. (d)  | 6. (a)  | 7. (a)  |
| 8. (d) | 9. (d) | 10. (d)        | 11. (d) | 12. (c) | 13. (c) | 14. (c) |

### Multiple Correct-Choice Type

1. (a), (b), (c), (d)    2. (c), (d)    3. (c), (d), (e)    4. (b), (c), (d)    5. (a), (b), (d)  
4. The equilibrium constant of the reaction is

$$K_p = p_{\text{CO}_2}$$

Since  $K_p$  is a constant at a given  $T$ , the value of  $p_{\text{CO}_2}$  will be independent of  $p_{\text{CO}_2}$  at a given  $T$ . The remaining three statements are correct.

Therefore, the **choices (a), (b) and (d)** are correct.

### Fill-in-the-Blanks Type

1. No change    2.  $K_p = K_c(RT)^{\Delta v g}$     3. smaller

### True/False Type

1. False    2. True    3. True    4. True    5. True    6. False    7. True

## Reasoning Type

1. (d)

## Subjective Type

1.  $1.49 \times 10^{-5} (\text{mol L}^{-1})^2$
2. 0.333; 0.205 atm
3. 1.868 mol
4. 1.6 mol L<sup>-1</sup>; 0.4 mol L<sup>-1</sup>
5. 0.267 atm; 63%
6.  $p(\text{SO}_2) = 0.023 \text{ atm}$ ;  $p(\text{O}_2) = 2.0115 \text{ atm}$ ;  $p(\text{SO}_3) = 0.977 \text{ atm}$
7. 0.115 atm<sup>-2</sup>; 27.78 (mol L<sup>-1</sup>)<sup>-2</sup>
8. 0.04513 atm<sup>-2</sup>; 150.85 (mol L<sup>-1</sup>)<sup>2</sup>; 12.20 atm
9.  $x = (2K_p/P)^{1/3}$
10.  $7.5 \times 10^{-18} \text{ M}$
11.  $x(\text{N}_2) = 0.79$ ;  $x(\text{O}_2) = 0.21$
12. 0.407
13. (i)  $4.90 \times 10^{-2} \text{ atm}^2$ ;  $8.1 \times 10^{-5} \text{ M}^2$ ; (ii) No effect
14. (a) 5705.8 J mol<sup>-1</sup>;  $K_p^\circ = 1$  (b)  $n(\text{N}_2\text{O}_4) = 6.667 \text{ mol}$ ;  $n(\text{NO}_2) = 1.667 \text{ mol}$

## HINTS AND SOLUTIONS

### Straight Objective Type

1. The reaction is  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ ;  $\Delta H = -\text{ve}$ . Since the reaction is exothermic, more of SO<sub>3</sub> will be formed if temperature is lowered.

Since the reaction involves decrease in the gaseous phase, increase in pressure will cause the formation of more of SO<sub>3</sub>.

2. The equilibrium constant of a reaction is independent of total pressure, catalyst and concentrations of species. It depends only on temperature.
3. Adding inert gas at constant volume increases pressure of the system. Since  $K_p$  is independent of pressure, the equilibrium will not be affected. Thus, none of the given choices is correct.

4. The reaction is  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$   
 $1 \text{ mol} - x \qquad \qquad \qquad 2x$

Total amount of gases = 1 mol + x

Since 20% by mass of N<sub>2</sub>O<sub>4</sub> is decomposed,  $x = 0.2 \text{ mol}$ . Hence

$$P_{300\text{K}} = \frac{1.2 \text{ mol}}{1 \text{ mol}} \times 1 \text{ atm} = 1.2 \text{ atm.}$$

Since temperature is doubled, pressure will also be doubled, i.e., 2.4 atm.

5. Since the given equilibrium involves  $\Delta v_g = 0$ , there will be no effect of adding an inert gas and decreasing the volume of the container. A catalyst can help in achieving the equilibrium rapidly without affecting the equilibrium amounts of the species involved in the reaction.

Only increasing the amount of a reactant can shift the equilibrium to the right side, thus causing the increase in the equilibrium amount of a product.

6.  $K_p$  depends only on temperature. The dissociation of NH<sub>3</sub> is  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ . Since  $\Delta v_g \neq 0$ ,  $\alpha$  will depend on the pressure.
7. The given reaction will be exothermic in nature due to the formation of three X—Y bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species. Hence, the reaction will

be affected by both temperature and pressure. The use of a catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

8. The expression relating  $K_p$  and  $K_c$  is  $K_p = K_c (RT)^{\Delta v_g}$

where  $\Delta v_g$ , the change in stoichiometric number of gaseous species in the chemical equation, is -2.

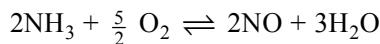
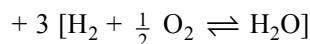
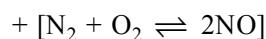
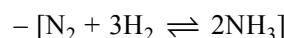
Hence,  $K_p = K_c (RT)^{-2}$  or  $K_c = K_p / (RT)^2$

9. For the reaction  $A + B \rightarrow C + D$ , the reaction quotient is defined as  $Q = \frac{[C][D]}{[A][B]}$

In the initial stages of the reaction, the concentrations of C and D increase while those of A and B decrease. Hence, the value of  $Q$  increases with time.

10.  $K_p$  of an equilibrium reaction depends only on temperature. However, the degree of dissociation will change in accordance with Le-Chatelier's principle.

11. The given reaction can be obtained as follows.



Hence,

$$K = K_2 K_3^3 / K_1$$

12. At equilibrium,  $\Delta G$  of the reaction is zero.

14. The given reaction is exothermic in nature. As per Le-Chatelier principle, the yield of  $NH_3$  will decrease with increase in temperature. Therefore, the choice (c) is correct.

## Multiple Correct-Choice Type

1. The reaction is exothermic and involves decrease in the number of gaseous species. The equilibrium concentration of the reactant  $C_2H_4$  can be increased by increasing temperature and decreasing pressure. It can also be increased by removing  $H_2$  (one of the reactants) and adding some  $C_2H_6$  (i.e. product).

2. The reaction is  $2NaNO_3(s) \rightleftharpoons 2NaNO_2(s) + O_2(g)$ .

Since  $NaNO_3$  and  $NaNO_2$  are solids, addition of these species do not affect equilibrium.

Since the reaction involves heating, the forward reaction will be favoured by increasing temperature.

Since the reaction involves increase in the gaseous species, increasing pressure favours reverse reaction.

3. Introducing an inert gas at constant volume will not affect the equilibrium. Introducing  $Cl_2(g)$  at constant volume will move the equilibrium in the reverse direction.

Introducing an inert gas at constant pressure will increase the volume of container. The equilibrium will shift in the direction of more number of gaseous species, i.e. forward direction. Introducing  $PCl_5(g)$  will also favour forward direction.

4. The ions  $Cl^-$ ,  $SCN^-$  and  $CN^-$  form precipitate with  $Cu^+$ . Hence, the equilibrium is shifted towards left side.

5. The equilibrium constant of the reaction is

$$K_p = p_{CO_2}$$

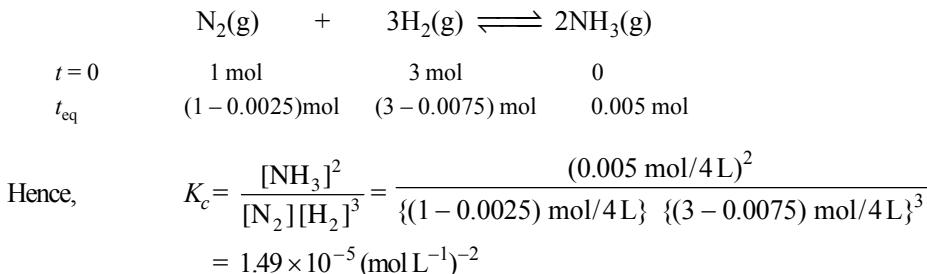
Since  $K_p$  is a constant at a given  $T$ , the value of  $p_{CO_2}$  will be independent of  $p_{CO_2}$  at a given  $T$ . The remaining three statements are correct.

## True/False Type

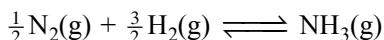
1. Lewis acid accepts pair of electrons and does not donate them.
3. This is due to formation of  $\text{Na}^+\text{AgCl}_2^-$ .
5.  $\text{Zn}(\text{OH})_2$  is an amphoteric species. In acidic medium, it exists as  $\text{Zn}^{2+}$  while in alkaline solution as  $\text{Zn}(\text{OH})_4^{2-}$ .
6. For  $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$  ;  $K_{\text{eq}} = [\text{AB}]^2 / [\text{A}_2][\text{B}_2]$   
 $\text{For } \text{AB} \rightleftharpoons \frac{1}{2} \text{A}_2 + \frac{1}{2} \text{B}_2 ; K'_{\text{eq}} = [\text{A}_2]^{1/2}[\text{B}_2]^{1/2} / [\text{AB}]$   
 Obviously,  $K'_{\text{eq}} = 1 / \sqrt{K_{\text{eq}}}$ .
7. Decreasing pressure causes evaporation of liquid for which energy comes from within the system causing cooling of the system.

## Subjective Type

1. From the given data, we write

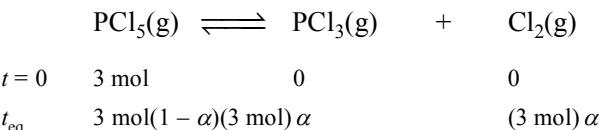


The equilibrium constant for the reaction



would be,  $K'_c = \sqrt{K_c} = 3.86 \times 10^{-3} (\text{mol L}^{-1})^{-1}$

2. If  $\alpha$  is the degree of dissociation of  $\text{PCl}_5(\text{g})$ , we will have



Total amount of gases in the vessel

$$n = n(\text{N}_2) + n(\text{PCl}_5) + n(\text{PCl}_3) + n(\text{Cl}_2) = 1 \text{ mol} + 3 \text{ mol}(1 - \alpha) + (3 \text{ mol})\alpha + (3 \text{ mol})\alpha$$

$$= 4 \text{ mol} + (3 \text{ mol})\alpha \quad (1)$$

From the given value of equilibrium pressure, we find that

Total amount of gases,

$$n = \frac{pV}{RT} = \frac{(2.05 \text{ atm})(100 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1})(500 \text{ K})} = 5.0 \text{ mol} \quad (2)$$

Equating Eqs (1) and (2), we get

$$4 \text{ mol} + (3 \text{ mol})\alpha = 5 \text{ mol}$$

**7.10** IIT Chemistry: Topic-wise Solved Questions

$$\text{or } \alpha = \frac{1 \text{ mol}}{3 \text{ mol}} = 0.333$$

$$\text{Now } n(\text{PCl}_5) = 3 \text{ mol} (1 - 0.333) = 2 \text{ mol}$$

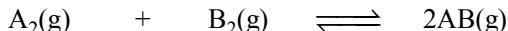
$$n(\text{PCl}_3) = n(\text{Cl}_2) = (3 \text{ mol}) (0.333) = 1 \text{ mol}$$

$$p(\text{PCl}_5) = \frac{n(\text{PCl}_5)}{n} p_{\text{eq}} = \frac{2}{5} \times 2.05 \text{ atm} = 0.82 \text{ atm}$$

$$p(\text{PCl}_3) = p(\text{Cl}_2) = \frac{1}{5} \times 2.05 \text{ atm} = 0.41 \text{ atm}$$

$$\text{Hence, } K_p = \frac{p(\text{PCl}_3) \cdot p(\text{Cl}_2)}{p(\text{PCl}_5)} = \frac{(0.41 \text{ atm})^2}{0.82 \text{ atm}} = 0.205 \text{ atm}$$

**3.** We have



$t = 0$	1 mol	2 mol		
$t_{\text{eq}}$	1 mol - $x$	2 mol - $x$		$2x$

Since for the given reaction,  $\Delta v_g = 0$ , we will have

$$K_p = K_n = \frac{n_{\text{AB}}^2}{n_{\text{A}_2} n_{\text{B}_2}} = \frac{(2x)^2}{(1 \text{ mol} - x)(2 \text{ mol} - x)} = 50$$

$$\text{or } 46x^2 - 50(3 \text{ mol})x + 100 \text{ mol}^2 = 0$$

$$\text{which gives } x = 0.934 \text{ mol}$$

$$\text{Hence, } n(\text{AB}) = 2x = 1.868 \text{ mol.}$$

**4.** We have



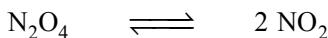
$t = 0$	1 mol	1 mol	1 mol	1 mol
$t_{\text{eq}}$	1 mol - $x$	1 mol - $x$	1 mol + $x$	1 mol + $x$

$$\text{Hence, } K_c = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{\{(1 \text{ mol} + x)/1 \text{ L}\}^2}{\{(1 \text{ mol} - x)/1 \text{ L}\}^2} = 16$$

$$\text{or } \frac{1 \text{ mol} + x}{1 \text{ mol} - x} = 4 \text{ or } x = \frac{3}{5} \text{ mol} = 0.6 \text{ mol}$$

$$\text{Hence, } [\text{NO}_2] = 0.4 \text{ mol L}^{-1} \quad \text{and} \quad [\text{NO}] = 1.6 \text{ mol L}^{-1}.$$

**5.** If  $\alpha$  is the degree of dissociation of  $\text{N}_2\text{O}_4$ , we will have



$t = 0$	$n$	
$t_{\text{eq}}$	$n(1 - \alpha)$	$n(2\alpha)$

Total amount of gases =  $n(1 + \alpha)$

$$\text{Now } p_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha} p \quad \text{and} \quad p_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha} p$$

$$\text{and } K_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{[2\alpha p/(1 + \alpha)]^2}{(1 - \alpha) p/(1 + \alpha)} = \frac{4\alpha^2}{1 - \alpha^2} p$$

It is given that when  $p = 1 \text{ atm}$ ,  $\alpha = 0.25$ . Hence,

$$K_p = \frac{4(0.25)^2}{1 - (0.25)^2} (1 \text{ atm}) = 0.267 \text{ atm}$$

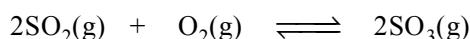
Now when  $p = 0.1 \text{ atm}$ , we will have

$$0.267 \text{ atm} = \frac{4\alpha^2}{1 - \alpha^2} (0.1 \text{ atm})$$

$$\text{Solving for } \alpha, \text{ we get } \alpha^2 = \frac{2.67}{6.67} = 0.4 \quad \text{or} \quad \alpha = 0.63$$

Hence, 63% of  $\text{N}_2\text{O}_4$  is dissociated at 0.1 atm and  $37^\circ\text{C}$ .

6. Since to start with  $\text{SO}_2$  is not present, it is expected that some of  $\text{SO}_3$  will decompose to give  $\text{SO}_2$  and  $\text{O}_2$  at equilibrium. If  $2x$  is the partial pressure of  $\text{SO}_3$  that is decreased at equilibrium, we would have



$t = 0$	0	2 atm	1 atm
$t_{\text{eq}}$	$2x$	$2 \text{ atm} + x$	$1 \text{ atm} - 2x$

$$\text{Hence, } K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2 (p_{\text{O}_2})} = \frac{(1 \text{ atm} - 2x)^2}{(2x)^2 (2 \text{ atm} + x)} = 900 \text{ atm}^{-1}$$

Assuming  $x \ll 2 \text{ atm}$ , we get

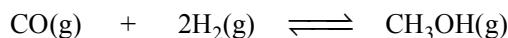
$$\frac{(1 \text{ atm} - 2x)^2}{(2x)^2 (2 \text{ atm})} = 900 \text{ atm}^{-1} \quad \text{or} \quad \frac{(1 \text{ atm} - 2x)^2}{(2x)^2} = 1800 \quad \text{or} \quad \frac{1 \text{ atm}}{2x} - 1 = 42.43$$

$$\text{or } x = \frac{1}{2 \times 43.43} \text{ atm} = 0.0115 \text{ atm}$$

Hence,  $p(\text{SO}_2) = 2x = 0.023 \text{ atm}$ ;  $p(\text{O}_2) = 2 \text{ atm} + x = 2.0115 \text{ atm}$

and  $p(\text{SO}_3) = 1 \text{ atm} - 2x = 0.977 \text{ atm}$

7. We have



$t = 0$	0.2 mol		
$t_{\text{eq}}$	0.1 mol	?	0.1 mol

Total amount of gas at equilibrium,

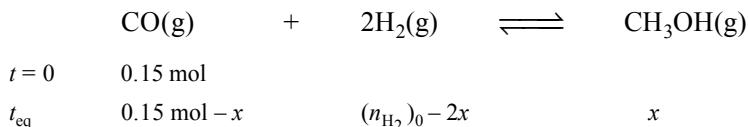
$$\frac{pV}{RT} = \frac{(4.92 \text{ atm})(5 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1})(600 \text{ K})} = 0.5 \text{ mol}$$

Hence, Amount of H<sub>2</sub> at equilibrium = 0.5 mol - 0.2 mol = 0.3 mol

$$\text{Now } K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.1 \text{ mol}/5\text{L})}{(0.1 \text{ mol}/5\text{L})(0.3 \text{ mol}/5\text{L})^2} = 27.78 (\text{mol L}^{-1})^{-2}$$

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{p_{\text{CO}} (p_{\text{H}_2})^2} = \frac{(0.1/0.5) \times 4.92 \text{ atm}}{\{(0.1/0.5) \times 4.92 \text{ atm}\} \cdot \{(0.3/0.5) \times 4.92 \text{ atm}\}^2} = 0.115 \text{ atm}^{-2}.$$

**8.** We have



It is given that 0.08 mol of CH<sub>3</sub>OH is formed at equilibrium. Hence,

$$n_{\text{CH}_3\text{OH}} = x = 0.08 \text{ mol} \quad \text{and} \quad n_{\text{CO}} = 0.15 \text{ mol} - x = 0.07 \text{ mol}$$

From the total pressure of 8.5 atm at equilibrium, we calculate the total amount of gases, i.e. CO, H<sub>2</sub> and CH<sub>3</sub>OH at equilibrium.

$$n_{\text{total}} = \frac{pV}{RT} = \frac{(8.5 \text{ atm})(2.5 \text{ L})}{(0.082 \text{ atm L K}^{-1} \text{ mol}^{-1})(705 \text{ K})} = 0.3676 \text{ mol}$$

Now, the amount of H<sub>2</sub> at equilibrium is given as

$$n_{\text{H}_2} = n_{\text{total}} - n_{\text{CO}} - n_{\text{CH}_3\text{OH}} = (0.3676 - 0.07 - 0.08) \text{ mol} = 0.2176 \text{ mol}$$

$$\text{Hence, } K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.08 \text{ mol}/2.5 \text{ L})}{(0.07 \text{ mol}/2.5 \text{ L})(0.2176 \text{ mol}/2.5 \text{ L})^2} = 150.85 (\text{mol L}^{-1})^{-2}$$

$$\text{Now } K_p = K_c(RT)^{\text{Avg}} = (150.85 \text{ mol}^{-2} \text{ L}^2) \cdot \{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(705 \text{ K})\}^{-2} = 0.04513 \text{ atm}^{-2}$$

Since  $n_{\text{H}_2} = (n_{\text{H}_2})_0 - 2x$ , we have

$$(n_{\text{H}_2})_0 = n_{\text{H}_2} + 2x = (0.2176 + 2 \times 0.08) \text{ mol} = 0.3776 \text{ mol}$$

Total amount of CO and H<sub>2</sub> in the reacting system before the reaction sets in is given as

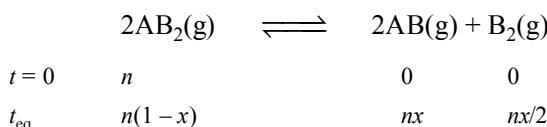
$$n_0 = (n_{\text{CO}})_0 + (n_{\text{H}_2})_0 = (0.15 + 0.3776) \text{ mol} = 0.5276 \text{ mol}$$

$$\text{Hence, } p_0 = \frac{n_0 RT}{V} = \frac{(0.5276 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(705 \text{ K})}{(2.5 \text{ L})} = 12.20 \text{ atm}$$

Alternatively,  $p_0$  may be calculated as given below.

$$\frac{p_0}{n_0} = \frac{p_1}{n_1} \quad \text{or} \quad p_0 = \left( \frac{8.5 \text{ atm}}{0.3676 \text{ mol}} \right) (0.5276 \text{ mol}) = 12.20 \text{ atm.}$$

**9.** Let  $n$  be the initial amount of AB<sub>2</sub>. We will have



Total amount of gases at equilibrium

$$n_{\text{total}} = n_{\text{AB}_2} + n_{\text{AB}} + n_{\text{B}_2} = n(1-x) + nx + nx/2 = n(1+x/2)$$

The partial pressures of the species at equilibrium would be

$$p_{\text{AB}_2} = \frac{n_{\text{AB}_2}}{n_{\text{total}}} P = \frac{n(1-x)}{n(1+x/2)} P = \frac{1-x}{1+x/2} P \approx P$$

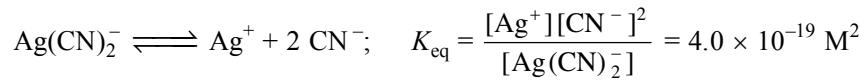
$$p_{AB} = \frac{n_{AB}}{n_{\text{total}}} P = \frac{nx}{n(1+x/2)} P = \frac{x}{1+x/2} P \approx xP$$

$$p_{B_2} = \frac{n_{B_2}}{n_{\text{total}}} P = \frac{nx/2}{n(1+x/2)} P = \frac{x/2}{1+x/2} P \approx \frac{x}{2} P$$

Now  $K_p = \frac{(p_{AB})^2 p_{B_2}}{(p_{AB_2})^2} = \frac{(xP)^2 \{(x/2)P\}}{P^2} = \frac{x^3}{2} P$

or  $x = \left(\frac{2K_p}{P}\right)^{1/3}$ .

**10.** We have



For the reaction  $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$  we will have,

$$K'_{\text{eq}} = \frac{1}{K_{\text{eq}}} = \frac{1}{4.0 \times 10^{-19} \text{ M}^2} = 0.25 \times 10^{19} \text{ M}^{-2}$$

The very large value of  $K'_{\text{eq}}$  implies almost complete conversion of  $\text{Ag}^+$  ion. The very small concentration of  $\text{Ag}^+$  ions will be left so as to satisfy the equilibrium constant. Let it be  $x$ . Hence



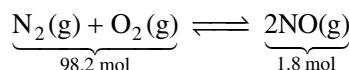
$t = 0$	0.03 M	0.1 M
$t_{\text{eq}}$	$x$	$(0.1 - 2 \times 0.03)M$ 0.03 M

Substituting these concentrations in the expression of  $K_{\text{eq}}$ , we get

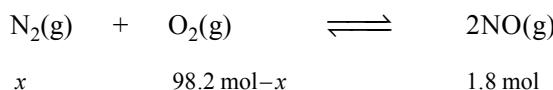
$$\frac{(x)(0.04 \text{ M})^2}{(0.03 \text{ M})} = 4.0 \times 10^{-19} \text{ M}^2$$

or  $x = [\text{Ag}^+] = \frac{(4.0 \times 10^{-19})(0.03)}{(0.04)^2} \text{ M} = 7.5 \times 10^{-18} \text{ M}$ .

**11.** Let there be 100 mol of the three gases at equilibrium. We will have



Let  $x$  be the amount of  $\text{N}_2$  in the mixture. Then



Using the equilibrium constant, we get

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 2.1 \times 10^{-3} \quad \text{i.e.} \quad \frac{(1.8 \text{ mol})^2}{x(98.2 \text{ mol} - x)} = 2.1 \times 10^{-3}$$

Solving for  $x$ , we get  $x = 78.56$  mol

In the original air sample. We will have

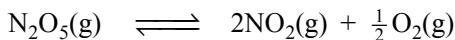
$$\text{Amount of N}_2 = (78.56 + 0.9) \text{ mol} = 79.46 \text{ mol}$$

$$\text{Amount of O}_2 = (98.2 - 78.56 + 0.9) \text{ mol} = 20.54 \text{ mol}$$

$$\text{Mole fraction of N}_2 = 0.79$$

$$\text{Mole fraction of O}_2 = 0.21$$

- 12.** If  $p$  is the partial pressure of  $\text{N}_2\text{O}_5$  that has decomposed,



$$600 \text{ mmHg} - p \quad 2p \quad p/2$$

$$\text{Pressure at any time} = (600 \text{ mmHg} - p) + 2p + p/2 = 600 \text{ mmHg} + (3/2)p$$

Equating this to 960 mmHg, we get

$$p = (2/3)(960 - 600) \text{ mmHg} = 244 \text{ mmHg}$$

The mole fraction of  $\text{N}_2\text{O}_5$  decomposed would be

$$x = \frac{244 \text{ mmHg}}{600 \text{ mmHg}} = 0.407$$

- 13.** The reaction along with the given data is

	$\text{NH}_4\text{HS}(\text{s})$	$\rightleftharpoons$	$\text{NH}_3(\text{g})$	$+$	$\text{H}_2\text{S}(\text{g})$
$t = 0$	3.06 g (= 0.06 mol)		0		0
$t_{\text{eq}}$	0.7 $\times$ 0.06 mol		0.3 $\times$ 0.06 mol = 0.018 mol		0.3 $\times$ 0.06 mol = 0.018 mol

- (i) The equilibrium constant  $K_c$  is

$$K_c = [\text{NH}_3][\text{H}_2\text{S}] = \left( \frac{0.018 \text{ mol}}{2 \text{ L}} \right) \left( \frac{0.018 \text{ mol}}{2 \text{ L}} \right) = 8.1 \times 10^{-5} (\text{mol/L})^2$$

The equilibrium constant  $K_p$  is

$$K_p = K_c (RT)^{\Delta v_g} = (8.1 \times 10^{-5} \text{ mol}^2/\text{L}^2) [(0.082 \text{ atm L mol}^{-1} \text{ K}^{-1})(300 \text{ K})]^2 = 4.90 \times 10^{-2} \text{ atm}^2$$

- (ii) There will not be any effect on the equilibrium by introducing more of solid  $\text{NH}_4\text{HS}$  as the equilibrium constant is independent of the quantity of solid.

- 14.** (a) Initially we have

$$p(\text{NO}_2) = x_{\text{NO}_2} p = \left( \frac{5 \text{ mol}}{10 \text{ mol}} \right) (20 \text{ bar}) = 10 \text{ bar}$$

$$p(\text{N}_2\text{O}_4) = x_{\text{N}_2\text{O}_4} p = \left( \frac{5 \text{ mol}}{10 \text{ mol}} \right) (20 \text{ bar}) = 10 \text{ bar}$$

$$Q_p = \frac{(p_{\text{NO}_2})^2}{p_{\text{N}_2\text{O}_4}} = \frac{(10 \text{ bar})^2}{(10 \text{ bar})} = 10 \text{ bar}$$

For the given reaction,

$$\Delta_r G^\circ = 2\Delta_f G^\circ(\text{NO}_2) - \Delta_f G^\circ(\text{N}_2\text{O}_4) = 2(50 \text{ kJ mol}^{-1}) - 100 \text{ kJ mol}^{-1} = 0$$

From the expression

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q_p^\circ$$

$$\begin{aligned} \text{we get } \Delta_r G &= 0 + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \ln (10) \\ &= (8.314 \times 298 \times 2.303) \text{ J mol}^{-1} \\ &= 5705.8 \text{ J mol}^{-1} \end{aligned}$$

The value of  $K_p^\circ$  of the reaction is given by  $\Delta_r G^\circ = -RT \ln K_p^\circ$ .

Since  $\Delta_r G^\circ = 0$ ,  $K_p^\circ = 1$

Since initially  $Q_p^\circ > K_p^\circ$ , the reaction will proceed in the reverse direction.

(b) We will have



$$5 \text{ mol} + x \quad 5 \text{ mol} - 2x ; \quad \text{total amount} = 10 \text{ mol} - x$$

where  $x$  is the amount of  $\text{N}_2\text{O}_4$  formed at equilibrium.

$$p_{\text{N}_2\text{O}_4} = \frac{5 \text{ mol} + x}{10 \text{ mol} - x} (20 \text{ bar}) \quad \text{and} \quad p_{\text{NO}_2} = \frac{5 \text{ mol} - 2x}{10 \text{ mol} - x} (20 \text{ bar})$$

Since  $K_p^\circ = 1$ , we get

$$\frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}^2} = 1 \text{ bar} \quad \text{or} \quad p_{\text{NO}_2}^2 = (1 \text{ bar}) p_{\text{N}_2\text{O}_4}$$

$$\text{or} \quad \left[ \frac{5 \text{ mol} - 2x}{10 \text{ mol} - x} (20) \right]^2 = \frac{5 \text{ mol} + x}{10 \text{ mol} - x} (20)$$

$$\text{or} \quad 20 (5 \text{ mol} - 2x)^2 = (5 \text{ mol} + x) (10 \text{ mol} - x)$$

$$\text{or} \quad 500 \text{ mol}^2 + 80 x^2 - 400 x \text{ mol} = 50 \text{ mol}^2 + 5 x \text{ mol} - x^2$$

$$\text{or} \quad 81 x^2 - 405 x \text{ mol} + 450 \text{ mol}^2 = 0$$

$$\text{or} \quad x = \frac{(405 \text{ mol}) \pm \sqrt{(405 \text{ mol})^2 - 4(81)(450 \text{ mol}^2)}}{2 \times 81}$$

This gives  $x = 3.333 \text{ mol}$  or  $x = 1.667 \text{ mol}$

Since  $2x$  cannot be more than 5 mol, we get

$$x = 1.667 \text{ mol}$$

$$\text{Hence, } n(\text{N}_2\text{O}_4) = 5 \text{ mol} + x = 6.667 \text{ mol}$$

$$n(\text{NO}_2) = 5 \text{ mol} - 2x = 1.667 \text{ mol}$$

## SECTION-II

### IONIC EQUILIBRIUM

#### Straight Objective Type

1. Of the given anions, the strongest Bronsted base is

(a)  $\text{ClO}^-$       (b)  $\text{ClO}_2^-$       (c)  $\text{ClO}_3^-$       (d)  $\text{ClO}_4^-$       (1981)

2. An acidic buffer solution can be prepared by mixing the solutions of

(a) ammonium acetate and acetic acid      (b) ammonium chloride and ammonium hydroxide  
 (c) sulphuric acid and sodium hydroxide      (d) sodium chloride and sodium hydroxide      (1981)



16. Which of the following solutions will have pH close to 1.0?
- 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH
  - 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH
  - 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH
  - 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH
- (1992)
17. If  $pK_b$  for fluoride ion at 25 °C is 10.83, the ionization constant of HF in water at this temperature is
- $1.74 \times 10^{-5}$
  - $3.52 \times 10^{-3}$
  - $6.75 \times 10^{-4}$
  - $5.38 \times 10^{-2}$
- (1997)
18. A certain buffer solution contains equal concentrations of HX and  $X^-$ . The  $K_b^o$  for  $X^-$  is  $10^{-10}$ . The pH of the buffer is
- 4
  - 7
  - 10
  - 14
- (1984)
19. A certain weak acid has a dissociation constant of  $1.0 \times 10^{-4}$ . The equilibrium constant for its reaction with a strong base is
- $1.0 \times 10^{-4}$
  - $1.0 \times 10^{-10}$
  - $1.0 \times 10^{10}$
  - $1.0 \times 10^{14}$
- (1984)
20. The solubility in mol dm<sup>-3</sup> of  $A_2X_3$  is  $y$ . Its solubility product is
- $6y^4$
  - $64y^4$
  - $36y^5$
  - $108y^5$
- (1997)
21. The pH of 0.1 M solution of the following salts increases in the order
- $NaCl < NH_4Cl < NaCN < HCl$
  - $HCl < NH_4Cl < NaCl < NaCN$
  - $NaCN < NH_4Cl < NaCl < HCl$
  - $HCl < NaCl < NaCN < NH_4Cl$
- (1999)
22. For a sparingly soluble salt  $A_pB_q$ , the relationship of its solubility product ( $K_{sp}$ ) with its solubility ( $s$ ) is
- $K_{sp} = s^{p+q} \cdot p^p \cdot q^q$
  - $K_{sp} = s^{p+q} \cdot p^q \cdot q^p$
  - $K_{sp} = s^{pq} \cdot p^p \cdot q^q$
  - $K_{sp} = s^{pq} \cdot (pq)^{p+q}$
- (2001)
23. Identify the correct order of solubility of  $Na_2S$ , CuS and ZnS in aqueous medium
- $CuS > ZnS > Na_2S$
  - $ZnS > Na_2S > CuS$
  - $Na_2S > CuS > ZnS$
  - $Na_2S > ZnS > CuS$
- (2002)
24. A weak acid HX has  $pK_a = 5$ . The per cent degree of hydrolysis of 0.1 M solution of salt NaX is
- 0.001%
  - 0.01%
  - 0.1%
  - 0.15%
- (2004)
25. 0.1 mol of  $CH_3NH_2$  ( $K_b^o = 6 \times 10^{-4}$ ) is added to 0.08 mol of HCl and the solution is diluted to 1 L. The hydrogen-ion concentration in the solution is
- $5 \times 10^{-5}$  M
  - $8 \times 10^{-2}$  M
  - $1.6 \times 10^{-11}$  M
  - $6.7 \times 10^{-11}$  M
- (2005)
26. An aqueous solution of carbonic acid ( $H_2CO_3$ ) contains
- $H_2CO_3$  only
  - $H_2CO_3, H^+, HCO_3^-$
  - $H_2CO_3, H^+, HCO_3^-, CO_3^{2-}$
  - $H_2CO_3, CO_2, H^+, HCO_3^-, CO_3^{2-}$
- (2006)
27. 2.5 mL of (2/5) M weak monoacidic base ( $K_b^o = 1 \times 10^{-12}$  at 25 °C) is titrated with (2/15) M HCl in water at 25°C. The concentration of  $H^+$  at equivalence point is ( $K_w^o = 1 \times 10^{-14}$  at 25 °C)
- $3.7 \times 10^{-13}$  M
  - $3.2 \times 10^{-7}$  M
  - $3.2 \times 10^{-2}$  M
  - $2.7 \times 10^{-2}$  M
- (2008)
28. Solubility product constants ( $K_{sp}$ ) of salts of types MX,  $MX_2$  and  $M_3X$  at temperature 'T' are  $4.0 \times 10^{-8}$  M<sup>2</sup>,  $3.2 \times 10^{-14}$  M<sup>3</sup> and  $2.7 \times 10^{-15}$  M<sup>4</sup>, respectively. Solubilities (mol dm<sup>-3</sup>) of the salts at temperature 'T' are in the order
- $MX > MX_2 > M_3X$
  - $M_3X > MX_2 > MX$
  - $MX_2 > M_3X > MX$
  - $MX > M_3X > MX_2$
- (2008)

29. The compound that is not a Lewis acid is  
 (a)  $\text{BF}_3$       (b)  $\text{AlCl}_3$       (c)  $\text{BeCl}_2$       (d)  $\text{SnCl}_4$       (1985)
30. Aqueous solutions of  $\text{HNO}_3$ ,  $\text{KOH}$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COONa}$  of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are)  
 (a)  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$       (b)  $\text{KOH}$  and  $\text{CH}_3\text{COONa}$   
 (c)  $\text{HNO}_3$  and  $\text{CH}_3\text{COONa}$       (d)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$       (2010)
31. The  $K_{\text{sp}}^{\circ}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at 298 K. The solubility (in mol L<sup>-1</sup>) of  $\text{Ag}_2\text{CrO}_4$  in 0.1 M  $\text{AgNO}_3$  solution is  
 (a)  $1.1 \times 10^{-11}$       (b)  $1.1 \times 10^{-10}$       (c)  $1.1 \times 10^{-12}$       (d)  $1.1 \times 10^{-9}$       (2013)

### Multiple Correct-Choice Type

1. Which of the following statement(s) is(are) correct?  
 (a) The pH of  $1.0 \times 10^{-8}$  M solution of HCl is 8  
 (b) The conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$   
 (c) Autoprotolysis constant of water increases with temperature  
 (d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point  $\text{pH} = (1/2) \text{p}K_a$ .      (1998)
2. A buffer solution can be prepared from a mixture of  
 (a) sodium acetate and acetic acid in water  
 (b) sodium acetate and hydrochloric acid in water  
 (c) ammonia and ammonium chloride in water  
 (d) ammonia and sodium hydroxide in water      (1999)

### Fill-in-the-Blanks Type

1. The conjugate base of  $\text{HSO}_4^-$  in aqueous solution is \_\_\_\_\_.      (1982)
2. An element that can exist as a positive ion in acidic medium and as a negative ion in basic medium is said to be \_\_\_\_\_.      (1984)
3. The basicity of phosphorous acid is \_\_\_\_\_.      (1990)
4. In the reaction  $\text{I}^- + \text{I}_2 \rightarrow \text{I}_3^-$ , the Lewis acid is \_\_\_\_\_.      (1997)
5. Among  $\text{PCl}_3$ ,  $\text{CH}_3^+$ ,  $\text{NH}_2^-$  and  $\text{NF}_3$ , \_\_\_\_\_ is least reactive towards water \_\_\_\_\_.      (1997)
6.  $(\text{CH}_3\text{OH}_2)^+$  is \_\_\_\_\_ acidic than  $(\text{CH}_3\text{NH}_3)^+$ .      (1997)

### Integer Answer Type

1. The dissociation constant of a substituted benzoic acid at 25 °C is  $1.0 \times 10^{-4}$  M. The pH of a 0.01 M solution of its sodium salt is \_\_\_\_\_.      (2009)
2. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is \_\_\_\_\_.  
 KCN       $\text{K}_2\text{SO}_4$        $(\text{NH}_4)_2\text{C}_2\text{O}_4$       NaCl       $\text{Zn}(\text{NO}_3)_2$   
 FeCl<sub>3</sub>       $\text{K}_2\text{CO}_3$        $\text{NH}_4\text{NO}_3$       LiCN      (2010)
3. In 1 L saturated solution of  $\text{AgCl}$  ( $K_{\text{sp}}(\text{AgCl}) = 1.6 \times 10^{-10}$  M<sup>2</sup>), 0.1 mol of  $\text{CuCl}$  ( $K_{\text{sp}}(\text{CuCl}) = 1.0 \times 10^{-6}$  M<sup>2</sup>) is added. The resultant concentration of  $\text{Ag}^+$  in the solution is  $1.6 \times 10^{-x}$  M. The value of "x" is \_\_\_\_\_.      (2011)

## Reasoning Type

The questions below (1 and 2) consist of an ‘*Assertion*’ in column 1 and the ‘*Reason*’ in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and reason is the CORRECT explanation of the *assertion*.
- (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
- (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
- (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

<i>Assertion</i> (column 1)	<i>Reason</i> (column 2)	
1. The value of van der Waals’ constant ‘ <i>a</i> ’ is larger for ammonia than for nitrogen.	Hydrogen bonding is present in ammonia.	(1998)
2. Sulphate is estimated as $\text{BaSO}_4$ and not as $\text{MgSO}_4$ .	Ionic radius of $\text{Mg}^{2+}$ is smaller than that of $\text{Ba}^{2+}$ .	(1998)

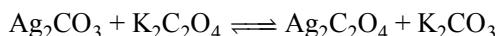
## Short Answer Type

1. The pH of an aqueous solution of sodium acetate is more than seven. (1982)
2. Acetic acid is less acidic in sodium acetate solution than in sodium chloride solution. (1986)
3. Ammonium chloride is acidic in liquid ammonia solvent. (1991)
4. Between  $\text{Na}^+$  and  $\text{Ag}^+$ , which is a stronger Lewis acid and why? (1997)
5. During the qualitative analysis of a mixture containing  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions,  $\text{H}_2\text{S}$  gas is passed through an acidified solution containing these ions in order to test  $\text{Cu}^{2+}$  alone. Explain briefly. (1998)
6. Will the pH of water be same at 55 °C and 25 °C? Explain. (2003)

## Subjective Type

1. What amount of sodium propanoate should be added to one litre of an aqueous solution containing 0.02 mol of propanoic acid to obtain a buffer solution of pH 4.75? What will be the pH if 0.01 mol of hydrogen chloride is dissolved in the above buffer solution? Compare the last pH value with the pH of 0.01 mol HCl solution. Dissociation constant of propanoic acid at 25°C is  $1.34 \times 10^{-5}$ . (1981)
2. Twenty mL of 0.2 M NaOH is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make pH of the solution 4.75. The ionization constant of acetic acid is  $1.8 \times 10^{-5}$ . (1982)
3. The dissociation constant of a weak acid HA is  $4.9 \times 10^{-8}$ . After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii)  $\text{OH}^-$  concentration in a decimolar solution of acid. Water has a pH of 7. (1983).
4. A solution contains a mixture of  $\text{Ag}^+$  (0.10 M) and  $\text{Hg}_2^{2+}$  (0.1 M) which are separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated. Given:  $K_{\text{sp}}(\text{AgI}) = 8.5 \times 10^{-17}$  and  $K_{\text{sp}}(\text{Hg}_2\text{I}_2) = 2.5 \times 10^{-26}$ . (1984)
5. The concentration of hydrogen ion in a 0.2 molar solution of formic acid is  $6.4 \times 10^{-3}$  mol L<sup>-1</sup>. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution? The dissociation constant of formic acid is  $2.4 \times 10^{-4}$  and the degree of dissociation of sodium formate is 0.75. (1985)

6. The solubility of  $\text{Mg}(\text{OH})_2$  in pure water is  $9.57 \times 10^{-3}$  g L<sup>-1</sup>. Calculate its solubility (g L<sup>-1</sup>) in 0.02 M  $\text{Mg}(\text{NO}_3)_2$  solution. (1986)
7. What is the pH of the solution when 0.2 mol of hydrochloric acid is added to one litre of solution containing (i) 1 M each of acetic acid and acetate ion and (ii) 0.1 M each of acetic acid and acetate ion? Assume that the total volume is one litre.  $K_a$  for acetic acid =  $1.8 \times 10^{-5}$ . (1987)
8. What amount of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 mol of NaCN. Given:  $K_{\text{ioniz}}(\text{HCN}) = 4.1 \times 10^{-10}$ . (1988)
9. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of ammonium chloride and 0.05 mol/L of ammonium hydroxide. Calculate the concentrations of aluminium and magnesium ions in solution. Given:  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ,  $K_{\text{sp}}(\text{Mg}(\text{OH})_2) = 8.9 \times 10^{-12}$  and  $K_{\text{sp}}(\text{Al}(\text{OH})_3) = 6 \times 10^{-32}$ . (1989)
10. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resultant solution will be twice the original value? Given:  $K_a$  (acetic acid) =  $1.8 \times 10^{-5}$ . (1990)
11. A 40.0 mL solution of a weak base, BOH is titrated with 0.1 N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid, respectively. Find the dissociation constant of the base. (1991)
12. The solubility product of  $\text{Ca}(\text{OH})_2$  at 25 °C is  $4.42 \times 10^{-5}$ . A 500 mL of saturated solution of  $\text{Ca}(\text{OH})_2$  is mixed with equal volume of 0.4 M NaOH. How much  $\text{Ca}(\text{OH})_2$  in milligrams is precipitated? (1992)
13. The pH of blood stream is maintained by a proper balance of  $\text{H}_2\text{CO}_3$  and  $\text{NaHCO}_3$  concentrations. What volumes of 5 M  $\text{NaHCO}_3$  solution should be mixed with a 10 mL sample of blood which is 2 M in  $\text{H}_2\text{CO}_3$ , in order to maintain a pH of 7.4?  $K_a$  for  $\text{H}_2\text{CO}_3$  in blood is  $7.8 \times 10^{-7}$ . (1993)
14. An aqueous solution of a metal bromide  $\text{MBr}_2$  (0.05 M) is saturated with  $\text{H}_2\text{S}$ . What is the minimum pH at which MS will precipitate?  $K_{\text{sp}}$  for MS =  $6.0 \times 10^{-21}$ , concentration of saturated  $\text{H}_2\text{S}$  = 0.1 M,  $K_1 = 10^{-7}$  and  $K_2 = 1.3 \times 10^{-13}$  for  $\text{H}_2\text{S}$ . (1993)
15. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. ( $\text{p}K_a$  of formic acid = 3.8 and  $\text{p}K_b$  of ammonia = 4.8.) (1995)
16. What is the pH of a 0.50 M aqueous NaCN solution?  $\text{p}K_b$  of  $\text{CN}^-$  is 4.70. (1996)
17. A sample of AgCl was treated with 5.00 mL of 1.5 M  $\text{Na}_2\text{CO}_3$  solution to give  $\text{Ag}_2\text{CO}_3$ . The remaining solution contained 0.0026 g of  $\text{Cl}^-$  per litre. Calculate the solubility product of AgCl. Given:  $(K_{\text{sp}}(\text{Ag}_2\text{CO}_3) = 8.2 \times 10^{-12} \text{ M}^3)$ . (1997)
18. An acid indicator, HIn differs in colour from its conjugate base ( $\text{In}^-$ ). The human eye is sensitive to colour differences only when the ratio  $[\text{In}^-]/[\text{HIn}]$  is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ( $K_a = 1.0 \times 10^{-5}$ )? (1997)
19. Given:  $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$ ,  $K_c = 6.2 \times 10^{-8} \text{ M}^2$  and  $K_{\text{sp}}$  of AgCl =  $1.8 \times 10^{-10} \text{ M}^2$  at 298 K. If ammonia is added to a water solution containing excess of a AgCl(s) only, calculate the concentration of complex in 1.0 M aqueous ammonia. (1998)
20. What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)? (1998)
21. The solubility of  $\text{Pb}(\text{OH})_2$  in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of  $\text{Pb}(\text{OH})_2$  in a buffer solution of pH = 8. (1999)
22. The solubility product of  $\text{Ag}_2\text{C}_2\text{O}_4$  at 25 °C is  $1.29 \times 10^{-11} \text{ mol}^3 \text{ L}^{-3}$ . A solution of  $\text{K}_2\text{C}_2\text{O}_4$  containing 0.1520 mol in 500 mL water is shaken at 25 °C with excess  $\text{Ag}_2\text{CO}_3$  till the following equilibrium is reached:



At equilibrium, the solution contains 0.0358 mol of  $\text{K}_2\text{CO}_3$ . Assuming the degree of dissociation of  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{CO}_3$  to be equal, calculate the solubility product of  $\text{Ag}_2\text{CO}_3$ . (1991, 1996)

23. The average concentration of  $\text{SO}_2$  in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of  $\text{SO}_2$  in water at 298 K is  $1.3653 \text{ mol L}^{-1}$  and  $\text{p}K_a$  of  $\text{H}_2\text{SO}_3$  is 1.92, estimate the pH of rain on that day. (2000)

24. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25 °C.
- Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
  - If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing;  $K_a$  of acetic acid is  $1.75 \times 10^{-5}$  mol L<sup>-1</sup>]. (2002)

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (a)  | 3. (d)  | 4. (b)  | 5. (b)  | 6. (d)  | 7. (d)  |
| 8. (a)  | 9. (d)  | 10. (a) | 11. (a) | 12. (d) | 13. (d) | 14. (b) |
| 15. (d) | 16. (d) | 17. (c) | 18. (a) | 19. (c) | 20. (d) | 21. (b) |
| 22. (a) | 23. (d) | 24. (b) | 25. (d) | 26. (d) | 27. (d) | 28. (d) |
| 29. (c) | 30. (d) | 31. (b) |         |         |         |         |

### Multiple Correct-Choice Type

1. (b), (c)    2. (a), (c)

### Fill-in-the-Blanks Type

1.  $\text{SO}_4^{2-}$     2. metalloid    3. two    4.  $\text{I}_2$     5.  $\text{NF}_3$     6. stronger

### Integer Answer Type

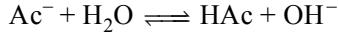
1. 8    2. 3    3. 7

### Reasoning Type

1. (b)    2. (b)

### Short Answer Type

1. Acetate ions hydrolyse  $\text{H}_2\text{O}$  producing  $\text{OH}^-$  ions:



Due to  $\text{OH}^-$  ions solution is alkaline due to which  $\text{pH} > 7$ .

2. Due to common ion  $\text{CH}_3\text{COO}^-$  from sodium acetate, the ionization of acetic acid is suppressed making acetic acid less acidic.

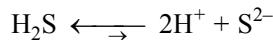
3. Liquid  $\text{NH}_3$  undergoes self ionization as  $2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$

Thus, all ammonium salts act as acid and amides act as base in liquid  $\text{NH}_3$ .

4.  $\text{Ag}^+$  is a stronger Lewis acid than  $\text{Na}^+$ . The latter has stable noble gas configuration and thus shows little tendency to accept lone pair of electrons.

5. The solubility products of CuS and ZnS are  $K_{\text{sp}}(\text{CuS}) \approx 10^{-38}$  and  $K_{\text{sp}}(\text{ZnS}) \approx 10^{-22}$

Since  $K_{sp}$  (CuS) <<  $K_{sp}$  (ZnS), very small concentration of  $S^{2-}$  is sufficient to cause the precipitation of  $Cu^{2+}$  ions. In order to have very small concentration of  $S^{2-}$  ions, acidic medium is used. Due to the common ion  $H^+$ , the ionisation of  $H_2S$  is suppressed:



The available concentration of  $S^{2-}$  ions in acidic medium causes only the precipitation of CuS and not that of ZnS.

6. The pH of water at 55 °C and 25 °C will be different. Since the ionization of water increases with increase in temperature, there will be more  $H^+$  at 55 °C as compared to that present at 25 °C. Hence, the pH of water at 55 °C will be lesser than the pH at 25 °C.

### Subjective Type

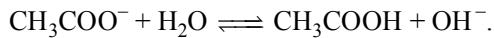
- |   |  |
|---|--|
| 1. $1.52 \times 10^{-2}$ mol                                    | 2. 4.568   |
| 3. (i) 0.07%; (ii) 4.15; (iii) $1.43 \times 10^{-10}$ M         | 4. $5 \times 10^{-13}$ mol L <sup>-1</sup> ; 99.83 |
| 5. 4.19   | 6. $8.7 \times 10^{-4}$ g L <sup>-1</sup>          |
| 7. 1  | 8. $8.85 \times 10^{-3}$ mol                       |
| 9. $[Al^{3+}] = 1.97 \times 10^{-17}$ M; $[Mg^{2+}] = 0.0423$ M | 10. 2.37; $2.7 \times 10^4$ L                      |
| 11. $1.83 \times 10^{-5}$                                       | 12. 743.33 mg                                      |
| 13. 78.34 mL  | 14. 0.98   |
| 15. 6.5   | 16. 11.5   |
| 17. $1.71 \times 10^{-10}$ M <sup>2</sup>                       | 18. 4 to 6   |
| 19. 0.054 M   | 20. 11.30  |
| 21. $1.20 \times 10^{-3}$ M                                     | 22. $3.97 \times 10^{-12}$ M <sup>3</sup>          |
| 23. 6.37  | 24. (i) $1.75 \times 10^{-4}$ ; 1 (ii) 4.76        |

### HINTS AND SOLUTIONS

### Straight Objective Type

2. An acidic buffer is prepared by mixing weak acid and salt of its conjugate base, e.g., acetic acid and ammonium acetate.
3. The pH of a  $10^{-8}$  M HCl will be less than 7 as it is an acidic solution.
4.  $K_w = [H^+] [OH^-]$ . For pure water  $[H^+] = [OH^-]$ . Hence,  $K_w = 10^{-12}$  M<sup>2</sup>
5. Only for choice b, ionic-product exceeds solubility product;  

$$[Ca^{2+}] [F^-]^2 = (10^{-2} \text{ M}) (10^{-3} \text{ M})^2 = 10^{-8} \text{ M}^3$$
6.  $Sn^{2+}$  is not precipitated by hydrochloric acid.
7. The pH of the solution at the equivalence point lies in the alkaline range. Hence, phenolphthalein is the best indicator.
8. The conjugate acid of  $NH_2^-$  is  $NH_3$ .
9. 0.1 M solution of sodium acetate is basic due to hydrolysis of acetate ion;



10. Both  $Bi^{3+}$  and  $Sn^{4+}$  are precipitated.
11. For choice a, the ionic-product exceeds solubility product;  $[Ag^+] [Cl^-] = (10^{-4} \text{ M}) = 10^{-8} \text{ M}^2$ .

12. The pH of stomach is lesser than  $pK_a$  while that of small intestine is greater than  $pK_a$ . Hence, aspirin is unionised in stomach while in small intestine it is present in the ionised form.
13. The solubility of hydroxides of alkaline-earth metals decreases down the group. Hence, the solubility product of  $\text{Ba}(\text{OH})_2$  will be minimum.
14.  $\text{Al}^{3+}$  is precipitated in the medium containing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ .
15. The conjugate acid-base pairs are  $(\text{HCl}, \text{Cl}^-)$  and  $(\text{CH}_3\text{COOH}_2^+, \text{CH}_3\text{COOH})$ .
16. Choice b is equivalent to 10 mL M/20 HCl. Its pH will be  $-\log(1/20) = \log 20 = 1.3010$ . Choice d is equivalent to 50 mL of M/10 HCl. Its pH will be  $-\log(1/10) = 1$ .
17. In solution  $K_w = K_a K_b$  or  $\text{p}K_w = \text{p}K_a + \text{p}K_b$ . The  $\text{p}K_a$  of HF will be  $14 - 10.83 = 3.17$ . Its  $K_a$  will be antilog ( $-3.17$ ) =  $6.76 \times 10^{-4}$ .
18.  $K_a^\circ(\text{HX}) = K_w^\circ / K_b^\circ(\text{X}^-) = 10^{-14} / 10^{-10} = 10^{-4}$   
 $\text{pH} = \text{p}K_a^\circ + \log([\text{salt}] / [\text{acid}]) = 4$

19. The reaction is  $\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$ . Its equilibrium constant is

$$K_{\text{eq}} = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}][\text{H}^+][\text{OH}^-]} = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 10^{10}$$

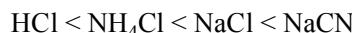
20.  $\text{A}_2\text{X}_3 \rightleftharpoons 2\text{A}^{3+} + 3\text{X}^{2-}$   
 $2y \quad 3y$

$$K_{\text{sp}} = [\text{A}^{3+}]^2 [\text{X}^{2-}]^3 = (2y)^2 (3y)^3 = 108y^5$$

21. The characteristics of the given solutions are:

$\text{NaCl}$	neutral solution
$\text{NH}_4\text{Cl}$	slightly acidic due to the reaction $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
$\text{NaCN}$	Slightly alkaline due to the reaction $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$
$\text{HCl}$	highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline i.e.



22.  $\text{A}_p\text{B}_q \rightleftharpoons p\text{A}^{q+} + q\text{B}^{p-}$

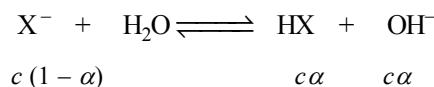
If  $s$  is the solubility of  $\text{A}_p\text{B}_q$ , then

$$[\text{A}^{q+}] = ps \text{ and } [\text{B}^{p-}] = qs$$

$$\text{Hence } K_{\text{sp}} = [\text{A}^{q+}]^p [\text{B}^{p-}]^q = (ps)^p (qs)^q = p^p q^q s^{(p+q)}$$

23. Sodium sulphide is soluble in water. The solubility product (and hence solubility) of  $\text{ZnS}$  is larger than that of  $\text{CuS}$ .

24. The hydrolysis constant of



$$\text{is } K_b = \frac{[\text{HX}][\text{OH}^-]}{[\text{X}^-]} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}^+][\text{X}^-]/[\text{HX}]} = \frac{K_w}{K_a} = \frac{10^{-14} \text{ M}^2}{10^{-5} \text{ M}} = 10^{-9} \text{ M}$$

Also  $K_b = \frac{[HX][OH^-]}{[X^-]} = \frac{c\alpha^2}{c[1-\alpha]} \approx c\alpha^2$

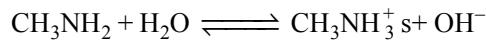
Hence,  $\alpha = \sqrt{K_b/c} = \sqrt{10^{-9} M / 0.1 M} = 10^{-4}$

The percent degree of hydrolysis is  $10^{-4} \times 100$ , i.e.  $10^{-2}\%$

**25.** We have

	$CH_3NH_2 + HCl \rightarrow CH_3NH_3^+ + Cl^-$
<i>Initially</i>	0.1 mol      0.08 mol      0      0
<i>Finally</i>	0.02 mol      -      0.08 mol      0.08 mol

The expression of  $K_b$  of  $CH_3NH_2$  is

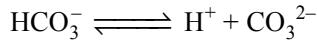
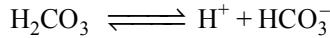
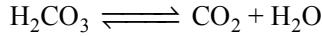


Hence,  $K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.08 \text{ mol})[OH^-]}{0.02 \text{ mol}}$

or  $[OH^-] = \frac{K_b}{4} = \frac{6 \times 10^{-4} M}{4} = 1.45 \times 10^{-4} M$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14} M^2}{1.5 \times 10^{-4} M} = 6.7 \times 10^{-11} M$$

**26.** An aqueous solution of carbonic acid involves the following equilibria.



Thus, the solution contains  $H_2CO_3$ ,  $CO_2$ ,  $H^+$ ,  $HCO_3^-$  and  $CO_3^{2-}$ .

**27.** Volume of (2/15) M HCl to neutralize the given 2.5 mL of (2/5)M weak monoacidic base is

$$V_{acid} = \frac{V_{base} M_{base}}{M_{acid}} = \frac{(2.5 \text{ mL}) \{(2/5)M\}}{\{(2/15)M\}} = 7.5 \text{ mL}$$

Total volume of solution at the equilibrium point is  $2.5 \text{ mL} + 7.5 \text{ mL} = 10.0 \text{ mL}$

Molarity of the salt ( $B^+Cl^-$ ) at the equivalence point is

$$M_{salt} = \frac{V_{base} M_{base}}{V_{total}} = \frac{(2.5 \text{ mL}) \{(2/5)M\}}{\{(10 \text{ mL})\}} = 0.1 \text{ M}$$

The cation of the salt formed undergoes hydrolysis  $B^+ + H_2O \rightleftharpoons BOH + H^+$ , the hydrolysis constant of this reaction is

$$K_h = \frac{[BOH][H^+]}{[B^+]}$$

Multiplying the dividing by  $[OH^-]$  in the solution, we get

$$K_h = \frac{[\text{BOH}]}{[\text{B}^+][\text{OH}^-]} [\text{H}^+] [\text{OH}^-] = \frac{K_w}{K_b} = \frac{10^{-14} \text{ M}^2}{10^{-12} \text{ M}} = 10^{-2} \text{ M}$$

In the solution,  $[\text{BOH}] = [\text{H}^+]$  and  $[\text{B}^+] = [\text{B}^+]_0 - [\text{H}^+]$ . Hence,

$$K_h = \frac{[\text{H}^+]^2}{[\text{B}^+]_0 - [\text{H}^+]} \text{ i.e. } [\text{H}^+]^2 + K_h [\text{H}^+] - K_h [\text{B}^+]_0 = 0$$

Substituting the values of  $K_h$  and  $[\text{B}^+]_0$ , we get

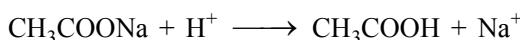
$$[\text{H}^+]^2 + (0.01 \text{ M}) [\text{H}^+] - 0.001 \text{ M}^2 = 0$$

Solving for  $[\text{H}^+]$ , we get

$$\begin{aligned} [\text{H}^+] &= \frac{-(0.01 \text{ M}) + \sqrt{(0.01 \text{ M})^2 + 4(0.001 \text{ M}^2)}}{2} \\ &= \frac{-(0.01 \text{ M}) + \sqrt{0.0041 \text{ M}^2}}{2} = \frac{(-0.01 + 0.064) \text{ M}}{2} = 0.027 \text{ M} \end{aligned}$$

28. For  $\text{MX}$ , we have  $\text{MX} \rightleftharpoons \text{M}^+ + \text{X}^-$ ;  $K_{sp} = [\text{M}^+] [\text{X}^-] = (s)(s) = s^2$   
Hence  $s = K_{sp}^{1/2} = (4.0 \times 10^{-8} \text{ M}^2)^{1/2} = 2 \times 10^{-4} \text{ M}$   
For  $\text{MX}_2$ , we have  $\text{MX}_2 \rightleftharpoons \text{M}^{2+} + 2\text{X}^-$ ;  $K_{sp} = [\text{M}^{2+}] [\text{X}^-]^2 = (s)(2s)^2 = 4s^3$   
Hence  $s = (K_{sp}/4)^{1/3} = (3.2 \times 10^{-14} \text{ M}^3/4)^{1/3} = 2 \times 10^{-5} \text{ M}$   
For  $\text{M}_3\text{X}$ , we have  $\text{M}_3\text{X} \rightleftharpoons 3\text{M}^+ + \text{X}^{3-}$ ;  $K_{sp} = [\text{M}^+]^3 [\text{X}^{3-}] = (3s)^3 (s) = 27s^4$   
Hence  $s = (K_{sp}/27)^{1/4} = (2.7 \times 10^{-15} \text{ M}^4/27)^{1/4} = 1.0 \times 10^{-4} \text{ M}$   
Hence, the solubility follows the order  $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

29.  $\text{BeCl}_2$  does not act as Lewis acid.  
30. Only the choice (d) contains constituents which can combine with the small amounts of acid or base added to the solution.



Thus, the pH of solution will not be affected significantly.

31. Given that  $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

The concentration of  $\text{CrO}_4^{2-}$  in 0.1 M solution of  $\text{AgNO}_3$  would be

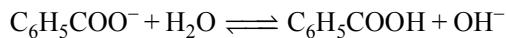
$$[\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.1 \times 10^{-12} \text{ M}^3}{(0.1 \text{ M})^2} = 1.1 \times 10^{-10} \text{ M}$$

### Multiple Correct-Choice Type

2. A buffer solution is obtained by mixing a weak acid/base with salt of its conjugate base/acid.

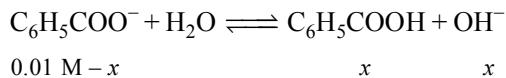
**Fill-in-the-Blanks Type****Integer Answer Type**

1. The benzoate anion will undergo hydrolysis as shown in the following



Its  $K_b = \frac{K_w}{K_a} = \frac{10 \times 10^{-14} \text{ M}^2}{1.0 \times 10^{-5} \text{ M}} = 1.0 \times 10^{-10} \text{ M}$

If  $x$  of  $\text{C}_6\text{H}_5\text{COO}^-$  reacts with water, we will have



Hence,  $K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}] + [\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{(x)(x)}{0.01 \text{ M} - x}$

Ignoring  $x$  in comparison to 0.01 M, we have

$$x = \sqrt{K_b(0.01 \text{ M})} = \sqrt{(10^{-10} \text{ M})(10^{-2} \text{ M})} = 10^{-6} \text{ M}$$

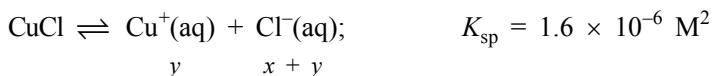
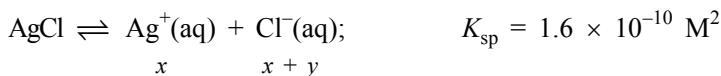
$$\text{pOH} = -\log \{[\text{OH}^-] / \text{mol dm}^{-3}\} = -\log (10^{-6}) = 6$$

$$\text{pH} = 14 - \text{pOH} = 8$$

2. The basic solution turns red litmus paper to blue.

The aqueous solution of  $\text{KCN}$ ,  $\text{K}_2\text{CO}_3$  and  $\text{LiCN}$  are alkaline due to the hydrolysis of anions.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  solution is acidic due to the fact that  $K_{a2}(\text{OxH}_2) > K_b(\text{NH}_4\text{OH})$ .

3. We have



Thus  $x(x + y) = 1.6 \times 10^{-10} \text{ M}^2 \quad (1)$

$$y(x + y) = 1.0 \times 10^{-6} \text{ M}^2 \quad (2)$$

On dividing, we get

$$\frac{x}{y} = \frac{1.6 \times 10^{-4}}{1.0 \times 10^{-6}} \Rightarrow y = \frac{x}{1.6 \times 10^{-4}} = 6250x$$

Substituting  $y$  in terms of  $x$  in Eq. (1), we get  $x(x + 6250x) = 1.6 \times 10^{-10} \text{ M}^2$

or  $x = \left( \frac{1.6 \times 10^{-10} \text{ M}^2}{6251} \right)^{1/2} = 1.6 \times 10^{-7} \text{ M}$

Hence, the correct answer is 7.

## Subjective Type

1. Using the expression

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get  $4.75 = -\log(1.34 \times 10^{-5}) + \log \frac{[\text{salt}]}{0.02 \text{ M}}$  which gives  $4.75 = 4.87 + \log \frac{[\text{salt}]}{0.02 \text{ M}}$

$$\text{or } \frac{[\text{salt}]}{0.02 \text{ M}} = 0.76 \quad \text{or} \quad [\text{salt}] = 1.52 \times 10^{-2} \text{ M}$$

Hence, Amount of sodium propanoate to be added  $= 1.52 \times 10^{-2} \text{ mol}$

The addition of 0.01 mol of hydrogen chloride converts the equivalent amount of sodium propanoate into propanoic acid. Hence, we will have

$$\text{pH} = 4.87 + \log \frac{(0.0152 - 0.01) \text{ mol L}^{-1}}{(0.02 + 0.01) \text{ mol L}^{-1}} = 4.87 + \log(0.173) = 4.87 - 0.76 = 4.11$$

The pH of 0.01 molar HCl solution would be

$$\text{pH} = -\log(0.01) = 2.$$

2. The addition of NaOH converts equivalent amount of acetic acid into sodium acetate. Hence,

$$\text{Concentration of acetic acid after the addition of sodium hydroxide} = \frac{30}{70} \times 0.2 \text{ M}$$

$$\text{Concentration of sodium acetate after the addition of sodium hydroxide} = \frac{20}{70} \times 0.2 \text{ M}$$

Hence, using the expression  $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$ , we get (1)

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log \left( \frac{20}{30} \right) = 4.745 - 0.177 = 4.568$$

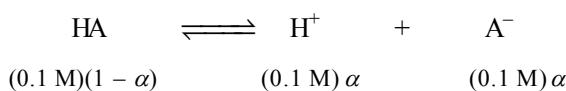
Let  $V$  be the additional volume of 0.2 M NaOH that need to be added to make pH of the solution equal to 4.74. Substituting this value in Eq. (1), we would get

$$4.74 = 4.745 + \log \left( \frac{20 \text{ mL} + V}{30 \text{ mL} - V} \right)$$

$$\text{or } \log \frac{20 \text{ mL} + V}{30 \text{ mL} - V} = -0.005 \quad \text{or} \quad \frac{20 \text{ mL} + V}{30 \text{ mL} - V} = 0.9866$$

$$\text{or } V = \frac{30 \text{ mL} \times 0.9866 - 20 \text{ mL}}{1.9866} = 4.83 \text{ mL.}$$

3. (i) If  $\alpha$  is the degree of dissociation of the weak acid HA, we will have



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(0.1\text{ M})\alpha^2}{1-\alpha}$$

Assuming  $\alpha \ll 1$ , we will have

$$K_a = (0.1\text{ M})\alpha^2$$

$$\text{or } \alpha = \sqrt{\frac{K_a}{0.1\text{ M}}} = \sqrt{\frac{4.9 \times 10^{-8}\text{ M}}{0.1\text{ M}}} = 7 \times 10^{-4}$$

$$\text{Hence, Percentage ionization} = \frac{7 \times 10^{-4}}{1} \times 100 = 7 \times 10^{-2}$$

(ii) We have

$$[H^+] = (0.1\text{ M})\alpha = 7 \times 10^{-5}\text{ M}$$

$$\text{pH} = -\log \{[H^+]/M\} = -\log (7 \times 10^{-5}) = 4.15$$

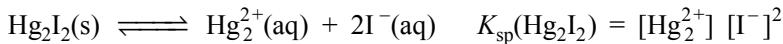
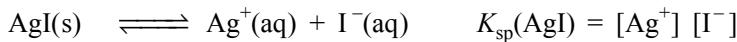
(iii) Since water has a pH = 7, we will have

$$[H^+] = [OH^-] = 10^{-7}\text{ M} \quad \text{or} \quad [H^+][OH^-] = 10^{-14}\text{ M}^2$$

Thus,  $[OH^-]$  in 0.1 M solution of acid would be

$$[OH^-] = \frac{10^{-4}\text{ M}^2}{[H^+]} = \frac{10^{-14}\text{ M}^2}{7 \times 10^{-5}\text{ M}} = 1.43 \times 10^{-10}\text{ M}$$

4. We have



Hence,

Concentration of  $I^-$  required to precipitate  $Ag^+$  ions

$$= \frac{K_{sp}(AgI)}{[Ag^+]} = \frac{8.5 \times 10^{-17} (\text{mol L}^{-1})^2}{(0.10 \text{ mol L}^{-1})} = 8.5 \times 10^{-16} \text{ mol L}^{-1}$$

Concentration of  $I^-$  required to precipitate  $Hg_2^{2+}$  ions

$$= \left( \frac{K_{sp}(Hg_2I_2)}{[Hg_2^{2+}]} \right)^{1/2} = \left( \frac{2.5 \times 10^{-26} (\text{mol L}^{-1})^3}{0.1 \text{ mol L}^{-1}} \right)^{1/2} = 5 \times 10^{-13} \text{ mol L}^{-1}$$

Since  $[I^-]$  required to precipitate  $Ag^+$  ions is lesser than that required for  $Hg_2^{2+}$ , it is  $Ag^+$  ions that are precipitated first. The precipitation of  $Ag^+$  will continue till  $[I^-]$  in solution becomes  $5 \times 10^{-13} \text{ mol L}^{-1}$  at which the second ion (i.e.  $Hg_2^{2+}$ ) will also start precipitating. At this stage, the concentration of  $Ag^+$  ions remaining in the solution is given as

$$[Ag^+]_{\text{left}} = \frac{8.5 \times 10^{-17} (\text{mol L}^{-1})^2}{(5 \times 10^{-13} \text{ mol L}^{-1})} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$$

$$\text{Hence, Percentage of } Ag^+ \text{ ions precipitated} = \frac{(0.1\text{ M} - 1.7 \times 10^{-4}\text{ M})}{0.1\text{ M}} \times 100 = 99.83.$$

5. Assuming that the addition of sodium formate suppresses the ionization of formic acid, we can use the expression

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

to compute pH of the solution. Since salt is 75 per cent dissociated, we will get

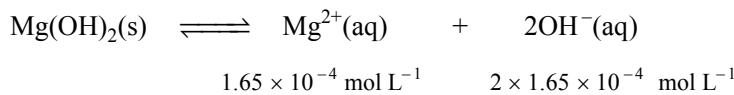
$$\text{pH} = -\log (2.4 \times 10^{-4}) + \log \frac{0.75}{0.2} = 3.62 + 0.57 = 4.19.$$

**6.** We have

Molar mass of  $\text{Mg(OH)}_2$  = 58 g mol<sup>-1</sup>

$$\text{Concentration of Mg(OH)}_2 \text{ in pure water} = \frac{9.57 \times 10^{-3} \text{ g L}^{-1}}{58 \text{ g mol}^{-1}} = 1.65 \times 10^{-4} \text{ mol L}^{-1}$$

It follows that



$$\begin{aligned} \text{Hence, } K_{\text{sp}}(\text{Mg(OH)}_2) &= [\text{Mg}^{2+}] [\text{OH}^-]^2 \\ &= (1.65 \times 10^{-4}) (2 \times 1.65 \times 10^{-4})^2 (\text{mol L}^{-1})^3 \\ &= 1.80 \times 10^{-11} (\text{mol L}^{-1})^3 \end{aligned}$$

Now in 0.02 M  $\text{Mg(NO}_3)_2$  solution, concentration of  $\text{Mg}^{2+}$  ions = 0.02 M  
The concentration of  $\text{OH}^-$  that can exist in 0.02 M  $\text{Mg(NO}_3)_2$  solution is

$$[\text{OH}^-] = \left( \frac{K_{\text{sp}}}{[\text{Mg}^{2+}]} \right)^{1/2} = \left( \frac{1.80 \times 10^{-11} (\text{mol L}^{-1})^3}{0.02 \text{ mol L}^{-1}} \right)^{1/2} = 3 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{Concentration of Mg(OH)}_2 \text{ in 0.02 M Mg(NO}_3)_2 \text{ solution} = \frac{1}{2} \times 3 \times 10^{-5} \text{ mol L}^{-1}$$

$$\begin{aligned} \text{Solubility of Mg(OH)}_2 \text{ in 0.02 M Mg(NO}_3)_2 \text{ solution} &= \left( \frac{1}{2} \times 3 \times 10^{-5} \text{ mol L}^{-1} \right) (58 \text{ g mol}^{-1}) \\ &= 8.7 \times 10^{-4} \text{ g L}^{-1}. \end{aligned}$$

**7.** (i) The addition of 0.2 mol of HCl would convert equivalent amount of acetate ions into acetic acid. Hence, after the addition of HCl, we will have

$$\text{Concentration of acetic acid} = 1.2 \text{ M}$$

$$\text{Concentration of acetate ions} = 0.8 \text{ M}$$

Hence, using the expression

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{we get } \text{pH} = -\log (1.8 \times 10^{-5}) + \log \frac{0.8}{1.2} = 4.745 - 0.176 = 4.569 \approx 4.57$$

(ii) The solution will now contain 0.2 M acetic acid and 0.1 M HCl. Assuming no ionization of acetic acid due to the common ion  $\text{H}^+$  from HCl, we find that

$$[\text{H}^+] \approx 0.1 \text{ M}$$

$$\text{Hence, } \text{pH} = -\log \{[\text{H}^+]/\text{M}\} = -\log (0.1) = 1.$$

**8.** The addition of HCl converts NaCN into HCN. Let  $x$  be the amount of HCl added. We will have

$$[\text{NaCN}] = 0.01 \text{ M} - x \quad \text{and} \quad [\text{HCN}] = x$$

Substituting these values along with pH and  $K_a$  in the expression,

$$\text{pH} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

we get

$$8.5 = -\log(4.1 \times 10^{-10}) + \log \frac{0.01 M - x}{x}$$

or

$$8.5 = 9.387 + \log \frac{0.01 M - x}{x} \quad \text{or} \quad \log \frac{0.01 M - x}{x} = -0.887$$

or

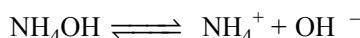
$$\frac{0.01 M - x}{x} = 0.13$$

or

$$x = \frac{0.01 M}{0.13} = 8.85 \times 10^{-3} \text{ M}$$

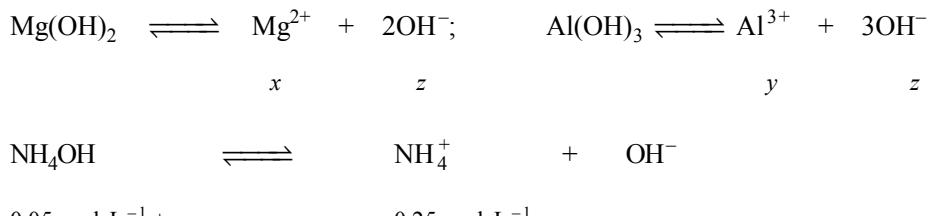
Hence, Amount of HCl to be added =  $8.85 \times 10^{-3}$  mol.

9. To start with we have a buffer solution containing  $0.25 \text{ mol L}^{-1}$  of  $\text{NH}_4\text{Cl}$  and  $0.05 \text{ mol L}^{-1}$  of  $\text{NH}_4\text{OH}$ . In the equilibrium reaction



we will have  $[\text{NH}_4\text{OH}] = 0.05 \text{ mol L}^{-1}$  and  $[\text{NH}_4^+] = 0.25 \text{ mol L}^{-1}$

The dissolution of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  create extra  $\text{OH}^-$  ions and thus cause the above equilibrium reaction to shift more towards left. If  $z$  is the concentration of  $\text{OH}^-$  ions in the resultant solution, we will have



where  $x$  and  $y$  are the solubilities of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ , respectively, and  $\alpha$  is the concentration of  $\text{NH}_4^+$  ions that is replaced by  $\text{NH}_4\text{OH}$ . We will have

$$K_{\text{sp}}(\text{Mg}(\text{OH})_2) = [\text{Mg}^{2+}][\text{OH}^-]^2 = xz^2 = 8.9 \times 10^{-12} \text{ M}^3 \quad (1)$$

$$K_{\text{sp}}(\text{Al}(\text{OH})_3) = [\text{Al}^{3+}][\text{OH}^-]^3 = yz^3 = 6 \times 10^{-32} \text{ M}^4 \quad (2)$$

$$K_b(\text{NH}_4\text{OH}) = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = \frac{(0.25 \text{ M} - \alpha)(z)}{0.05 \text{ M} + \alpha} = 1.8 \times 10^{-5} \text{ M} \quad (3)$$

Since the solution is electrically neutral, we will also have

$$2[\text{Mg}^{2+}] + 3[\text{Al}^{3+}] + [\text{NH}_4^+] = [\text{OH}^-] + [\text{Cl}^-]$$

i.e.

$$2x + 3y + (0.25 \text{ M} - \alpha) = z + 0.25 \text{ M}$$

or

$$2x + 3y - \alpha = z \quad (4)$$

From the values of solubility product constants, we may conclude that

$$y \ll x \quad \text{or} \quad 3y \ll 2x$$

With this, Eq. (4) becomes

$$2x - \alpha = z \quad \text{or} \quad \alpha = 2x - z \quad (5)$$

Moreover, due to the consumption of  $\text{OH}^-$  ions in Eq. (3), we may also expect that

$$z \ll 2x$$

(This may be verified from the final computed values of  $x$  and  $z$ .)

With this, Eq. (5) is simplified to

$$\alpha = 2x \quad (6)$$

Substituting this in Eq. (3), we get

$$\frac{(0.25 M - 2x)(z)}{0.05 M + 2x} = 1.8 \times 10^{-5} M$$

Replacing  $x$  in terms of  $z$  from Eq. (1), we get

$$\frac{\left(0.25 M - \frac{2 \times 8.9 \times 10^{-12} M^3}{z^2}\right)(z)}{0.05 M + 2 \left(\frac{8.9 \times 10^{-12} M^3}{z^2}\right)} = 1.8 \times 10^{-5} M$$

$$(0.25 M) z^3 - (0.05 M) (1.8 \times 10^{-5} M) z^2 - (2) (8.9 \times 10^{-12} M^3) z - 2 (8.9 \times 10^{-12} M^3) \times (1.8 \times 10^{-5} M) = 0$$

$$\text{or } z^3 = (3.6 \times 10^{-6} M) z^2 + (7.12 \times 10^{-11} M^2) z + 1.28 \times 10^{-15} M^3$$

The above expression may be solved by the method of successive approximation. We may start with  $z = 10^{-5}$  M and substitute this in the right hand side of the above expression and then take cube root of this to get new refined value of  $z$ . This refined value is again substituted in the right hand side and get the second refined value. This is continued till the two successive values of  $z$  agree within the allowed accuracy, say up to two decimals. Carrying out the above approximation, we get

Cycle No.	$[\text{OH}^-]/M$
1	$1.0 \times 10^{-5}$
2	$1.33 \times 10^{-5}$
3	$1.42 \times 10^{-5}$
4	$1.45 \times 10^{-5}$
5	$1.45 \times 10^{-5}$

Thus, taking  $[\text{OH}^-] = 1.45 \times 10^{-5}$  M, we get

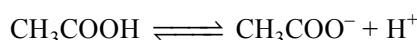
$$\text{From Eq. (1)} \quad [\text{Mg}^{2+}] = \frac{8.9 \times 10^{-12} M^3}{(1.45 \times 10^{-5} M)^2} = 0.0423 M$$

$$\text{From Eq. (2)} \quad [\text{Al}^{3+}] = \frac{6 \times 10^{-32} M^4}{(1.45 \times 10^{-5} M)^3} = 1.97 \times 10^{-17} M$$

From the above results, the approximations made in solving the above problem is justified as

$$[\text{Al}^{3+}] \ll [\text{Mg}^{2+}] \quad \text{and} \quad [\text{OH}^-] \ll 2 [\text{Mg}^{2+}]$$

10. We have



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]_0 - [\text{H}^+]} \approx \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]_0}$$

$$\text{Hence, } [\text{H}^+] = (K_a [\text{CH}_3\text{COOH}]_0)^{1/2} = (1.8 \times 10^{-5})^{1/2} \text{ mol L}^{-1} = 4.30 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log \{[\text{H}^+]/\text{mol L}^{-1}\} = -\log (4.3 \times 10^{-3}) = 2.37$$

Now the pH of the diluted solution would be  $\text{pH} = 2 \times 2.37$

which gives  $-\log \{[\text{H}^+]/\text{mol L}^{-1}\} = 2 \times 2.37$

$$\text{or } \left( \frac{[\text{H}^+]}{\text{mol L}^{-1}} \right)^{1/2} = 4.30 \times 10^{-3}$$

$$\text{or } [\text{H}^+] = 1.8 \times 10^{-5} \text{ mol L}^{-1}$$

Substituting this in the expression

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{COOH}]_0 - [\text{H}^+]}$$

$$\text{we get } 1.8 \times 10^{-5} \text{ mol L}^{-1} = \frac{(1.8 \times 10^{-5} \text{ mol L}^{-1})^2}{[\text{CH}_3\text{COOH}]_0 - (1.8 \times 10^{-5} \text{ mol L}^{-1})}$$

$$\text{This gives } [\text{CH}_3\text{COOH}]_0 = 3.6 \times 10^{-5} \text{ mol L}^{-1}$$

Volume of dilute acetic acid containing 1 mol of acid would be

$$V = \frac{1 \text{ mol}}{3.65 \times 10^{-5} \text{ mol L}^{-1}} = 2.7 \times 10^4 \text{ L.}$$

- 11.** Let  $N_{\text{base}}$  be the normality of the base BOH. Substituting the given data in the expression

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

we get

$$(i) \quad 14 - 10.04 = \text{p}K_b + \log \left( \frac{5.0 \times 0.1}{40.0 \times N_{\text{base}} - 5.0 \times 0.1} \right) \quad (1)$$

$$(ii) \quad 14 - 9.14 = \text{p}K_b + \log \left( \frac{20.0 \times 0.1}{40.0 \times N_{\text{base}} - 20.0 \times 0.1} \right)$$

Equating the values of  $\text{p}K_b$  from these two expressions, we get

$$3.96 - \log \left( \frac{0.5}{40.0 \times N_{\text{base}} - 0.5} \right) = 4.86 - \log \left( \frac{2.0}{40.0 \times N_{\text{base}} - 2.0} \right)$$

$$\text{or } \log \left( \frac{2.0}{40.0 \times N_{\text{base}} - 2.0} \times \frac{40.0 \times N_{\text{base}} - 0.5}{0.5} \right) = 0.9$$

$$\text{or } \left( \frac{4(40.0 \times N_{\text{base}} - 0.5)}{40.0 \times N_{\text{base}} - 2.0} \right) = 7.943$$

Solving for  $N_{\text{base}}$ , we get

$$N_{\text{base}} = \frac{2.0(7.943/4) - 0.5}{40.0(7.943/4) - 40.0} = \frac{3.472}{39.44} = 0.088$$

Substituting the above value in Eq. (1), we get

$$3.96 = pK_b + \log \left( \frac{0.5}{40.0 \times 0.088 - 0.5} \right)$$

$$\text{or } pK_b = 3.96 - \log (0.166) = 3.96 - (-0.78) = 4.74$$

$$\text{This gives } K_b = 1.83 \times 10^{-5}.$$

12. The total volume of the solution would become 1 L. Hence, the concentration of NaOH would become half, i.e. 0.2 M. Hence,

$$[\text{Ca}^{2+}] = \frac{K_{\text{sp}}(\text{Ca(OH)}_2)}{[\text{OH}^-]^2} = \frac{4.42 \times 10^{-5} \text{ M}^3}{(0.2 \text{ M})^2} = 1.105 \times 10^{-3} \text{ M}$$

To start with, the concentration of  $\text{Ca}^{2+}$  were

$$[\text{Ca}^{2+}] = \left( \frac{K_{\text{sp}}(\text{Ca(OH)}_2)}{4} \right)^{1/3} = \left( \frac{4.42 \times 10^{-5} \text{ M}^3}{4} \right)^{1/3} = 0.0223 \text{ M}$$

In 500 mL of the solution,

$$\text{Amount of } \text{Ca}^{2+} \text{ was } \frac{1}{2} \times 0.0223 \text{ mol, i.e. } 0.01115 \text{ mol.}$$

Of this, the remaining  $\text{Ca}^{2+}$  ions after the addition of NaOH is 0.001105 mol. Hence,

$$\text{Amount of } \text{Ca}^{2+} \text{ ions precipitated} = (0.01115 - 0.001105) \text{ mol} = 0.010045 \text{ mol}$$

$$\text{Mass of } \text{Ca(OH)}_2 \text{ precipitated} = 0.010045 \times 74 \text{ g} = 0.74333 \text{ g} = 743.33 \text{ mg.}$$

13. Let  $V$  be the required volume of 5 M  $\text{NaHCO}_3$  solution. Total volume of the system becomes  $V + 10 \text{ mL}$ . Now in the solution

$$[\text{HCO}_3^-] = (5 \text{ M}) \left( \frac{V}{V + 10 \text{ mL}} \right); \quad [\text{H}_2\text{CO}_3] = (2 \text{ M}) \left( \frac{10 \text{ mL}}{V + 10 \text{ mL}} \right)$$

Using the expression

$$\text{pH} = pK_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$\text{we get } 7.4 = -\log (7.8 \times 10^{-7}) + \log \frac{(5 \text{ M})V}{(2 \text{ M})(10 \text{ mL})} = 6.108 + \log \left( \frac{1}{4} \right) + \log (V / \text{mL})$$

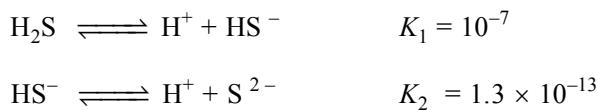
$$\text{or } \log (V/\text{mL}) = 7.4 - 6.108 + 0.062 = 1.894$$

$$\text{Hence, } V = 78.34 \text{ mL.}$$

- 14.** The concentration of  $S^{2-}$  ions needed to precipitate MS is

$$[S^{2-}] = \frac{K_{sp}}{[M^{2+}]} = \frac{6.0 \times 10^{-21} \text{ M}^2}{0.05 \text{ M}} = 1.2 \times 10^{-19} \text{ M}$$

In the solution,  $H_2S$  ionizes as



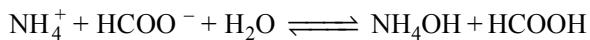
Hence,  $K_1 K_2 = \left( \frac{[H^+]^2 [S^{2-}]}{[H_2S]} \right)$

This gives  $[H^+] = \left( \frac{K_1 K_2 [H_2S]}{[S^{2-}]} \right)^{1/2} = \left( \frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{1.2 \times 10^{-19}} \right)^{1/2} = 0.104 \text{ M}$

Hence, the minimum pH at which MS will precipitate is

$$pH = -\log(0.104) = 0.98$$

- 15.** Ammonium formate undergoes hydrolysis as



$$K_h = \frac{[NH_4OH][HCOOH]}{[NH_4^+][HCOO^-]} \quad (1)$$

Using the expressions

$$\text{Formic acid, } K_a = \frac{[HCOO^-][H^+]}{[HCOOH]} \quad (2)$$

$$\text{Ammonium hydroxide, } K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad (3)$$

$$\text{we get } K_h = \frac{[OH^-]}{K_b} \frac{[H^+]}{K_a} = \frac{K_w}{K_a K_b} \quad (4)$$

where  $K_w$  is ionic product of water. Moreover, in the solution, we will have

$$[NH_4OH] = [HCOOH] \quad \text{and} \quad [NH_4^+] = [HCOO^-]$$

With these Eq. (1) becomes

$$K_h = \frac{[HCOOH]^2}{[HCOO^-]^2}$$

Using Eqs. (2) and (4), we get

$$\frac{K_w}{K_a K_b} = \frac{[H^+]^2}{K_a^2} \quad \text{or} \quad [H^+]^2 = \frac{K_w K_a}{K_b}$$

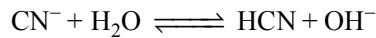
Taking logarithm and multiplying by  $-1$  throughout, we get

$$2(-\log [H^+]) = (-\log K_w) + (-\log K_a) - (-\log K_b)$$

$$\text{i.e.} \quad 2pH = pK_w + pK_a - pK_b$$

$$\text{or} \quad pH = \frac{1}{2} [pK_w + pK_a - pK_b] = \frac{1}{2} [14 + 3.8 - 4.8] = 6.5.$$

**16.** The  $CN^-$  ions undergo hydrolysis as



$$\text{Hence,} \quad K_b = \frac{[HCN][OH^-]}{[CN^-]} \approx \frac{[OH^-]^2}{[CN]_0}$$

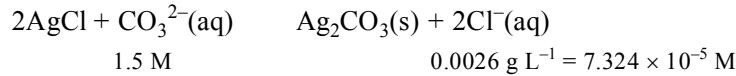
$$\text{or} \quad -\log K_b = -2 \log [OH^-] + \log [CN]_0$$

$$4.70 = 2 pOH + \log (0.50)$$

$$\text{or} \quad pOH = \frac{4.70 + 0.30}{2} = 2.5$$

$$pH = 14 - pOH = 14 - 2.5 = 11.5$$

**17.** The involved reaction is



Assuming  $[CO_3^{2-}] \approx 1.5 \text{ M}$  as very small quantity ( $= 3.662 \times 10^{-5} \text{ M}$ ) of  $CO_3^{2-}$  combines, we get

$$[Ag^+] = \left( \frac{K_{sp}(Ag_2CO_3)}{[CO_3^{2-}]} \right)^{1/2} = \left( \frac{8.2 \times 10^{-12} \text{ M}^3}{1.5 \text{ M}} \right)^{1/2} = 2.338 \times 10^{-6} \text{ M}$$

$$\text{Hence, } K_{sp}(AgCl) = [Ag^+] [Cl^-] = (2.338 \times 10^{-6} \text{ M}) (7.324 \times 10^{-5} \text{ M}) = 1.71 \times 10^{-10} \text{ M}^2$$

**18.** Using the Henderson's equation  $pH = pK_a + \log \{[In^-]/[HIn]\}$ , we get

$$pH_1 = -\log (1.0 \times 10^{-5}) + \log (1/10) = 5 - 1 = 4$$

$$pH_2 = -\log (1.0 \times 10^{-5}) + \log (10/1) = 5 + 1 = 6$$

The pH of the solution should change from 4 to 6.

**19.** We have  $K_{sp}(AgCl) = [Ag^+] [Cl^-] = 1.8 \times 10^{-10} \text{ M}^2$

$$K_c = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.2 \times 10^{-8} \text{ M}^2 \quad (2)$$

The charge-balance expression in the solution is



Making use of Eqs (1) and (2), we get

$$\frac{(6.2 \times 10^{-8} \text{ M}^2)[\text{Ag}(\text{NH}_3)_2^+]}{[\text{NH}_3]^2} + [\text{Ag}(\text{NH}_3)_2^+] = \frac{1.8 \times 10^{-10} \text{ M}^2}{[\text{Ag}^+]} = \frac{(1.8 \times 10^{-10} \text{ M}^2)[\text{NH}_3]^2}{(6.2 \times 10^{-8} \text{ M}^2)[\text{Ag}(\text{NH}_3)_2^+]}$$

For 1.0 M ammonia solution, we get

$$(6.2 \times 10^{-8})[\text{Ag}(\text{NH}_3)_2^+] + [\text{Ag}(\text{NH}_3)_2^+] = \frac{(1.8 \times 10^{-10} \text{ M}^2)}{(6.2 \times 10^{-8})[\text{Ag}(\text{NH}_3)_2^+]}$$

or  $[\text{Ag}(\text{NH}_3)_2^+] = \frac{1.8 \times 10^{-10} \text{ M}^2}{(6.2 \times 10^{-8})[\text{Ag}(\text{NH}_3)_2^+]}$

or  $[\text{Ag}(\text{NH}_3)_2^+] = \left( \frac{1.8 \times 10^{-10} \text{ M}^2}{6.2 \times 10^{-8}} \right)^{1/2} = 0.054 \text{ M}$

**20.** We are given the following solutions.

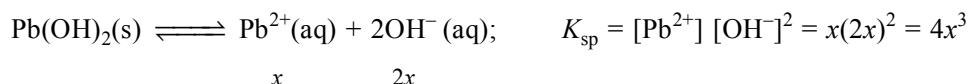
200 mL of  $10^{-2}$  M ( $\text{pH} = 2.0$ ) of HCl and 300 mL of  $10^{-2}$  M ( $\text{pH} = 12.0$ ) of NaOH

On mixing, 100 mL of  $10^{-2}$  M NaOH will be left unneutralised. Since the total volume of the solution would be 500 mL, the concentration of  $\text{OH}^-$  in the solution would be  $(1/5)(10^{-2} \text{ M}) = 2.0 \times 10^{-3} \text{ M}$

Hence,  $\text{pOH} = -\log [\text{OH}^-] = -\log (2.0 \times 10^{-3}) = 2.70$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.70 = 11.30$$

**21.** If  $x$  is the solubility of  $\text{Pb}(\text{OH})_2$  in water, we will have



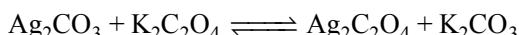
It is given that  $x = 6.7 \times 10^{-6} \text{ M}$ . Hence

$$K_{\text{sp}} = 4(6.7 \times 10^{-6} \text{ M})^3 = 1.20 \times 10^{-15} \text{ M}^3$$

The solubility of  $\text{Pb}(\text{OH})_2$  in a buffer solution of  $\text{pH} = 8$  (i.e.  $[\text{H}^+] = 10^{-8} \text{ M}$  or  $[\text{OH}^-] = 10^{-6} \text{ M}$ ) will be

$$[\text{Pb}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{1.20 \times 10^{-15} \text{ M}^3}{(10^{-6} \text{ M})^2} = 1.20 \times 10^{-3} \text{ M}$$

**22.** We have



Initial amount	0.152 mol	0
Final amount	$(0.152 - 0.0358)$ mol	0.0358 mol
	= 0.1162 mol	

Concentrations	$2 \times 0.1162 \text{ M}$	$2 \times 0.0358 \text{ M}$
----------------	-----------------------------	-----------------------------

In the solution, the concentration of  $\text{Ag}^+$  as dictated by solubility products is

$$\left\{ \frac{K_{\text{sp}}(\text{Ag}_2\text{CO}_3)}{[\text{CO}_3^{2-}]} \right\}^{1/2} = \left\{ \frac{K_{\text{sp}}(\text{Ag}_2\text{C}_2\text{O}_4)}{[\text{C}_2\text{O}_4^{2-}]} \right\}^{1/2}$$

This gives  $K_{\text{sp}}(\text{Ag}_2\text{CO}_3) = K_{\text{sp}}(\text{Ag}_2\text{C}_2\text{O}_4) \left( \frac{[\text{CO}_3^{2-}]}{[\text{C}_2\text{O}_4^{2-}]} \right)$

Since, the degrees of dissociation of  $\text{K}_2\text{C}_2\text{O}_4$  and  $\text{K}_2\text{CO}_3$  are equal, we will have

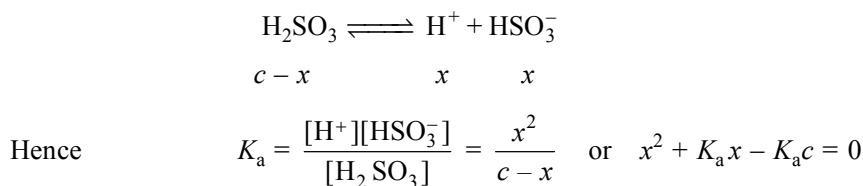
$$\begin{aligned} K_{\text{sp}}(\text{Ag}_2\text{CO}_3) &= K_{\text{sp}}(\text{Ag}_2\text{C}_2\text{O}_4) \left( \frac{[\text{K}_2\text{CO}_3]}{[\text{K}_2\text{C}_2\text{O}_4]} \right) \\ &= (1.29 \times 10^{-11} \text{ M}^3) \left( \frac{2 \times 0.0358 \text{ M}}{2 \times 0.1162 \text{ M}} \right) \\ &= 3.97 \times 10^{-12} \text{ M}^3 \end{aligned}$$

23. For 10 ppm of  $\text{SO}_2$  in the atmosphere, the partial molar volume of  $\text{SO}_2$  in a total volume of  $10^6 \text{ dm}^3$  of the atmospheric air will be equal to  $10 \text{ dm}^3$ . Its molar concentration in air would be

$$\begin{aligned} c &= \frac{(10 \text{ dm}^3) / \{(22.144 \text{ dm}^3 \text{ mol}^{-1})(298 \text{ K}) / (273 \text{ K})\}}{10^6 \text{ dm}^3} \\ &= 4.087 \times 10^{-7} \text{ mol dm}^{-3}. \end{aligned}$$

This concentration is very much less than the given solubility of  $\text{SO}_2$  in water. Hence, it may be assumed that the entire  $\text{SO}_2$  in air will dissolve in rain water.

If the concentration  $x$  of dissolved  $\text{SO}_2$  is present in the ionized form, we will have



$$\text{i.e. } x = \frac{-K_a + \sqrt{K_a^2 + 4K_a c}}{2} \quad (1)$$

It is given that  $K_a^\circ = 10^{-1.92} = 0.012$

Substituting  $K_a$  and  $c$  in Eq. (1), we get

$$\begin{aligned} x &= \frac{(-0.012 \text{ M}) + \sqrt{(0.012 \text{ M})^2 + 4(0.012 \text{ M})(4.087 \times 10^{-7} \text{ M})}}{2} \\ &= 4.08 \times 10^{-7} \text{ M} \end{aligned}$$

that is, almost whole of dissolved  $\text{SO}_2$  is present in the ionized form  $\text{H}^+$  and  $\text{HSO}_3^-$ . This is to be expected since the concentration of dissolved  $\text{SO}_2$  is very small (Ostwald dilution law).

For this small concentration of  $\text{H}^+$  from the dissolved  $\text{SO}_2$ , the contribution coming from the dissociation of water may not be negligible. Hence, in solution we will have

$$\begin{aligned} [\text{H}^+]_{\text{total}} &= [\text{H}^+]_{\text{acid}} + [\text{H}^+]_{\text{water}} = [\text{H}^+]_{\text{acid}} + [\text{OH}^-]_{\text{water}} \\ &= [\text{H}^+]_{\text{acid}} + \frac{K_w}{[\text{H}^+]_{\text{total}}} \end{aligned}$$

$$\text{or } [\text{H}^+]_{\text{total}}^2 - [\text{H}^+]_{\text{acid}} [\text{H}^+]_{\text{total}} - K_w = 0$$

Solving for  $[\text{H}^+]_{\text{total}}$ , we get

$$\begin{aligned} [\text{H}^+]_{\text{total}} &= \frac{[\text{H}^+]_{\text{acid}} + \sqrt{[\text{H}^+]_{\text{acid}}^2 + 4K_w}}{2} \\ &= \frac{(4.08 \times 10^{-7} \text{ M}) + \sqrt{(4.08 \times 10^{-7} \text{ M})^2 + 4(1 \times 10^{-14} \text{ M}^2)}}{2} \\ &= 4.31 \times 10^{-7} \text{ M} \end{aligned}$$

$$\text{Hence, } \text{pH} = -\log \{[\text{H}^+]/\text{M}\} = -\log (4.31 \times 10^{-7}) = 6.37$$

24. On mixing 500 mL of 0.2 M acetic acid with 500 mL of 0.2 M HCl, the volume of solution becomes 1000 mL and thus the molarity of each acid becomes half, i.e.

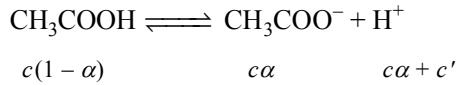
$$\text{Molarity of acetic acid, } c = 0.1 \text{ M}$$

$$\text{Molarity of HCl, } c' = 0.1 \text{ M}$$

Since HCl is completely ionized, we will have

$$[\text{H}^+]_{\text{HCl}} = c' = 0.1 \text{ M}$$

If  $\alpha$  is the degree of dissociation of  $\text{HC}_3\text{COOH}$ , then



$$\text{and } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(c\alpha)(c\alpha + c')}{c(1-\alpha)}$$

Assuming  $\alpha \ll 1$ , we get

$$K_a = \frac{\alpha(c\alpha + c')}{1}$$

Substituting the values of  $c$ ,  $c'$  and  $K_a$ , we get

$$1.75 \times 10^{-5} \text{ M} = \alpha \{(0.1 \text{ M}) \alpha + (0.1 \text{ M})\}$$

$$\text{or } \alpha^2 + \alpha - 1.75 \times 10^{-4} = 0$$

Solving for  $\alpha$ , we get

$$\alpha = \frac{-1 + \sqrt{1 + 4 \times 1.75 \times 10^{-4}}}{2} = 1.75 \times 10^{-4}$$

The concentration of  $\text{H}^+$  in the solution is

$$[\text{H}^+] = c\alpha + c' = (0.1 \text{ M}) (1.75 \times 10^{-4} + 1) \approx 0.1 \text{ M}$$

$$\text{pH} = -\log \{[\text{H}^+]/\text{M}\} = -\log (0.1) = 1$$

$$(ii) \text{ Amount of NaOH added} = 6 \text{ g}/40 \text{ g mol}^{-1} = 0.15 \text{ mol}$$

$$\text{Molarity of NaOH in solution} = 0.15 \text{ mol}/1 \text{ L} = 0.15 \text{ M}$$

The added NaOH will combine firstly with strong acid and then with weak acid. Hence, whole of HCl (0.1 M) and 0.05 M of acetic acid will be neutralized. The resultant solution will contain 0.05 M of acetic acid and 0.05 M CH<sub>3</sub>COONa. In solution, we will have



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(c\alpha + 0.05\text{M})(c\alpha)}{c(1 - \alpha)} = \frac{c(\alpha + 1)\alpha}{1 - \alpha}$$

Assuming  $\alpha \ll 1$ , we get

$$\alpha = \sqrt{\frac{K_a}{c}} = \left( \frac{1.75 \times 10^{-5} \text{ M}}{0.05 \text{ M}} \right)^{1/2} = 3.5 \times 10^{-4}$$

$$[\text{H}^+] = c\alpha = (0.05 \text{ M}) (3.5 \times 10^{-4}) = 1.75 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log \{[\text{H}^+]/\text{M}\} = -\log (1.75 \times 10^{-5}) = 4.76$$

(alternatively, one can use the expression pH = pK<sub>a</sub> + log {[salt]/[acid]})

Since [salt]= [acid], we get pH = pK<sub>a</sub>.)



# ELECTROLYTIC AND GALVANIC CELLS

8

## **SECTION-I ELECTROLYTIC CELLS**

## **Straight Objective Type**

1. Molten sodium chloride conducts electricity due to the presence of  
(a) free electrons (b) free ions  
(c) free molecules (d) atoms of sodium and chlorine (1981)

2. Faraday's law of electrolysis are related to the  
(a) atomic number of the cation (b) atomic number of the anion  
(c) equivalent mass of the electrolyte (d) speed of the cation (1983)

3. A solution of sodium sulphate in water is electrolysed using inert electrodes. The product at the cathode and anode are respectively.  
(a) H<sub>2</sub>, O<sub>2</sub> (b) O<sub>2</sub>, H<sub>2</sub> (c) O<sub>2</sub>, Na (d) O<sub>2</sub>, SO<sub>2</sub> (1987)

4. A dilute aqueous solution of Na<sub>2</sub>SO<sub>4</sub> is electrolysed using platinum electrodes. The products at the anode and cathode are  
(a) O<sub>2</sub>, H<sub>2</sub> (b) S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, Na (c) O<sub>2</sub>, Na (d) S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, H<sub>2</sub> (1996)

5. The electric charge for electrode deposition of one equivalent of the substance is  
(a) one ampere per second (b) 96500 C per second  
(c) one ampere per hour (d) charge on 1 mol of electrons (1984)

6. When a lead storage battery is discharged  
(a) SO<sub>2</sub> is evolved (b) lead sulphate is consumed  
(c) lead is formed (d) sulphuric acid is consumed (1987)

7. Which of the following statements is correct for an electrolytic cells?  
(a) Electrons flow from cathode to anode through the external battery  
(b) Electrons flow from cathode to anode within the electrolytic solution  
(c) Migration of ions along with oxidation reaction at cathode and reduction reaction at anode  
(d) Migration of ions along with reduction reaction at cathode and oxidation reaction at anode (2003)

8. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milliampere current. The time required to liberate 0.01 mol of H<sub>2</sub> gas at the cathode is (1 Faraday constant = 96500 C mol<sup>-1</sup>)  
(a)  $9.65 \times 10^4$  s (b)  $19.3 \times 10^4$  s  
(c)  $28.95 \times 10^4$  s (d)  $38.6 \times 10^4$  s (2008)

## **Multiple Correct-Choice Type**

1. Of the following, the metal that cannot be obtained by electrolysis of the aqueous solution of their salts are  
(a) Ag                    (b) Mg                    (c) Cu                    (d) Al                    (e) Cr      (1990)

### **Fill-in-the-Blanks Type**

1. Dilute sulphuric acid on electrolysis liberates \_\_\_\_\_ at the anode. (1985)
  2. The electrical conductivity of a solution of acetic acid will be \_\_\_\_\_ if a solution of sodium hydroxide is added. (1987)
  3. The electrolysis of molten sodium hydride liberates \_\_\_\_\_ gas at the \_\_\_\_\_. (1989)
  4. When an aqueous solution of sodium fluoride is electrolysed, the gas liberated at the anode is \_\_\_\_\_. (1997)

## **True/False Type**

- 1.** In the electrolysis of molten potassium chloride, chlorine is liberated at the cathode. (1978)  
**2.** Copper undergoes oxidation more readily than iron. (1978)

## **Linked Comprehension Type**

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately  $6.022 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implication in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reactions, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (relative atomic mass: Na = 23, Hg = 200; 1 Faraday constant = 96500 C mol<sup>-1</sup>).

1. The total number of moles of chlorine gas evolved is  
(a) 0.5              (b) 1.0              (c) 2.0              (d) 3.0

2. If the cathode is a Hg electrode, the maximum mass of amalgam formed from this solution is  
(a) 200 g              (b) 225 g              (c) 400 g              (d) 446 g

3. The total charge required for complete electrolysis is  
(a) 24125 C              (b) 48250 C              (c) 96500 C              (d) 193000 C              (2007)

## **Subjective Type**

1. A current of 3.7 amperes is passed for 6 hours between nickel electrodes in 0.5 L of a 2 M solution of  $\text{Ni}(\text{NO}_3)_2$ . What will be the molarity of the solution at the end of electrolysis? (1978)
  2. Silver is electrodeposited on a metallic vessel of surface area  $800 \text{ cm}^2$  by passing a current of 0.20 ampere for 3 hours. Calculate the thickness of silver deposited, given its density as  $10.47 \text{ g cm}^{-3}$ . (1978)
  3. The density of copper is  $8.94 \text{ g/mL}$ . Find out the number of coulombs needed to plate an area  $10 \text{ cm} \times 10 \text{ cm}$  to a thickness of  $10^{-2} \text{ cm}$  using  $\text{CuSO}_4$  solution as electrolyte. (1979)
  4. Nineteen grams of molten  $\text{SnCl}_2$  is electrolysed for some time using inert electrodes until 0.119 g of Sn is deposited at the cathode. No substance is lost during the electrolysis. Find the ratio of the masses of  $\text{SnCl}_2$  and  $\text{SnCl}_4$  after electrolysis. (1980)

5. A hot solution of NaCl in water is electrolysed. Iron electrodes are used. Diaphragm cell is not used. Give equations for all the chemical reactions that take place during electrolysis. (1980)
6. Find the charge in coulombs of 1 g of N<sup>3-</sup>. (1980)
7. In an electrolysis experiment current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the mass of copper deposited on the cathode of the second cell. Also calculate the current passed through the experiment. (1983)
8. How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm<sup>2</sup> with a 0.005 mm thick layer? Density of silver is 10.5 g cm<sup>-3</sup>. (1985)
9. During the discharge of a lead storage battery, the density of sulphuric acid fell from 1.294 to 1.139 g mL<sup>-1</sup>. Sulphuric acid of density 1.294 g mL<sup>-1</sup> is 39% H<sub>2</sub>SO<sub>4</sub> by mass and that of density 1.139 g mL<sup>-1</sup> is 20% H<sub>2</sub>SO<sub>4</sub> by mass. The battery holds 3.5 L of the acid and the volume remained practically constant during the discharge. Calculate the number of ampere-hour for which the battery must have been used. The charging and discharging reactions are



10. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for 10 hours? (1987)
11. In a fuel cell, hydrogen and oxygen react to produce electricity. In the process, hydrogen gas is oxidised at the anode and oxygen is reduced at the cathode. If 67.2 L of H<sub>2</sub> at STP reacts in 15 minutes, what is the average current produced? If the entire current is used for electrodeposition of copper from copper(II) solution, what mass of copper will be deposited?



12. An acidic solution of Cu<sup>2+</sup> salt containing 0.4 g of Cu<sup>2+</sup> is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 mL and the current at 1.2 amperes. Calculate the volume of gases evolved at STP during the entire electrolysis. (1989)
13. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 per cent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed? (1990)
14. A current of 1.70 A is passed through 300.0 mL of 0.160 M solution of ZnSO<sub>4</sub> for 230 s with a current efficiency of 90 per cent. Find out the molarity of Zn<sup>2+</sup> after the deposition of Zn. Assume the volume of the solution to remain constant during the electrolysis. (1991)
15. An aqueous solution of NaCl on electrolysis gives H<sub>2</sub>(g), Cl<sub>2</sub>(g) and NaOH according to the reaction



A direct current of 25 amperes with current efficiency of 62% is passed through 20 litres of NaCl solution (20% by mass). Write down the reactions taking place at the anode and cathode. How long will it take place to produce 1 kg of Cl<sub>2</sub>? What will be the molarity of the solution with respect to hydroxide ion? Assume there is no loss due to evaporation. (1992)

16. Electrolysis of solution of MnSO<sub>4</sub> in aqueous sulphuric acid is a method for the preparation of MnO<sub>2</sub> as per the reaction



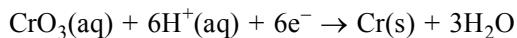
Passing a current of 27 A for 24 hours gives one kg of MnO<sub>2</sub>. What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. (1997)

17. What mass of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8 hours at a current of 8.46 amperes? What is the area of tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm<sup>3</sup>. (1997)
18. Copper sulphate (250 mL) was electrolysed using a platinum anode and copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the

solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

(2000)

19. Chromium metal can be plated out from an acidic solution containing  $\text{CrO}_3$  according to the following equation



Calculate (a) the mass of chromium plated out by 24,000 C and (b) how long will it take to plate out 1.5 g of chromium by using 12.5 A current?

(1993)

## ANSWERS

### Straight Objective Type

1. (b)      2. (c)      3. (a)      4. (a)      5. (d)      6. (d)      7. (d)  
 8. (b)

### Multiple Correct-Choice Type

1. (b), (d)

### Fill-in-the-Blanks Type

1. oxygen      2. increased      3.  $\text{H}_2$ , cathode      4.  $\text{O}_2$

### True/False Type

1. False      2. False

### Linked Comprehension Type

1. (b)      2. (d)      3. (d)

### Subjective Type

- |  |  |
|--|--|
| 1. $1.172 \text{ mol L}^{-1}$  | 2. $2.88 \times 10^{-4} \text{ cm}$  |
| 3. 27172 C   | 4. 71.62 : 1   |
| 5. Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$<br>Anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ | 6. 20679 C   |
| 7. 4.7625 g; 0.8042 A  | 8. 125.09 s  |
| 9. 265.05  | 10. 19.06 g  |
| 11. 643.33 A; 190.5 g  | 12. 158.2 mL if the salt is $\text{CuSO}_4$ ;<br>228.7 mL of salt is $\text{CuCl}_2$ |
| 13. 115800 C; 347.4 kJ   | 14. 0.154 M  |
| 15. 48.69 h; $1.408 \text{ mol L}^{-1}$  | 16. 95.185%  |
| 17. 272.18 g; $10204.7 \text{ cm}^2$   | 18. $7.96 \times 10^{-5} \text{ mol L}^{-1}$   |
| 19. 2.155 g; 22.27 min   |  |

## HINTS AND SOLUTIONS

### Straight Objective Type

1. Molten sodium chloride conducts electricity due to the presence of free ions.
2. Faraday's law of electrolysis are related to the equivalent mass of the electrolyte.
3. Electrolysis of a solution of sodium sulphate yields H<sub>2</sub> and O<sub>2</sub>.
4. The products are O<sub>2</sub> and H<sub>2</sub>.
6. The overall reaction taking place on discharging a lead storage battery is



8. Hydrogen is produced due to the reaction  $2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{H}_2\text{(g)} + 2\text{OH}^-(\text{aq})$

Since  $m = (Q/F) (M/v_e)$ , we get

$$n = \frac{m}{M} = \frac{Q}{F} \frac{1}{v_e} = \frac{It}{F} \frac{1}{v_e} \Rightarrow t = \frac{nFv_e}{I}$$

Substituting the given data, we get

$$t = \frac{(0.01 \text{ mol})(96500 \text{ C mol}^{-1})(2)}{(10 \times 10^{-3} \text{ A})} = 19.3 \times 10^4 \text{ s}$$

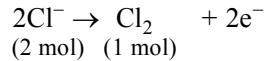
### Multiple Correct-Choice Type

1. Electropositive elements Mg and Al.

### Linked Comprehension Type

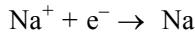
1. Amount of Na<sup>+</sup> or Cl<sup>-</sup> ion in solution undergoing electrolysis  
 $= (4.0 \text{ mol L}^{-1})(0.5 \text{ L}) = 2.0 \text{ mol}$

Chlorine is formed due to the reaction



Hence, from 2 mol of Cl<sup>-</sup> ions, 1 mol of Cl<sub>2</sub> is formed.

2. At cathode, the reaction occurring is



For 2 mol of Na<sup>+</sup> ions, 2 mol of Na is formed and the amalgam, Na(Hg), formed will also be 2 mol. Hence, the total mass of amalgam will be  $2(23 \text{ g} + 200 \text{ g}) = 446 \text{ g}$ .

3. For complete electrolysis, 2 mol of electrons are required. Total charge carried by these electrons is  $(2 \text{ mol})(96.500 \text{ C mol}^{-1}) = 193\,000 \text{ C}$ .

### Subjective Type

1. Amount of electricity passed  $= \frac{It}{F} = \frac{(3.7 \text{ A})(6 \times 60 \times 60 \text{ s})}{(96500 \text{ C mol}^{-1})} = 0.828 \text{ mol}$

Amount of Ni deposited based on the reaction  $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$  is given by

$$n_1 = \frac{0.828}{2} \text{ mol} = 0.414 \text{ mol}$$

Amount of  $\text{Ni}^{2+}$  ions to start with

$$n_2 = VM = (0.5 \text{ L}) (2 \text{ mol L}^{-1}) = 1.0 \text{ mol}$$

Amount of  $\text{Ni}^{2+}$  ions remaining in the solution after electrolysis

$$n_3 = n_2 - n_1 = (1.0 - 0.414) \text{ mol} = 0.586 \text{ mol}$$

Molarity of solution after electrolysis is

$$M = \frac{n_3}{V} = \frac{0.586 \text{ mol}}{0.5 \text{ L}} = 1.172 \text{ mol L}^{-1}$$

## 2. Amount of electricity passed

$$\frac{It}{F} = \frac{(0.2 \text{ A})(3 \times 60 \times 60 \text{ s})}{(96500 \text{ C mol}^{-1})} = 0.0224 \text{ mol}$$

Amount of silver deposited as per the reaction  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$  is

$$n = 0.0224 \text{ mol}$$

Mass of silver deposited

$$m = nM = (0.0224 \text{ mol}) (107.9 \text{ g mol}^{-1}) = 2.415 \text{ g}$$

If  $x$  is the thickness of silver deposited, then the mass of silver deposited is also given by

$$m = (Ax) \rho = (800 \text{ cm}^2) (x) (10.47 \text{ g cm}^{-3})$$

Equating the two masses and solving for  $x$ , we get

$$x = \frac{2.415}{800 \times 10.47} \text{ cm} = 2.88 \times 10^{-4} \text{ cm}$$

## 3. Area to be plated = $(10 \text{ cm}) (10 \text{ cm}) (10^{-2} \text{ cm}) = 1 \text{ cm}^3$

$$\text{Mass of Cu to be plated} = \rho V = (8.94 \text{ g cm}^{-3}) (1 \text{ cm}^3) = 8.94 \text{ g}$$

$$\text{Amount of Cu to be plated} = \frac{m}{M} = \frac{8.94 \text{ g}}{63.5 \text{ g mol}^{-1}} = 0.1408 \text{ mol}$$

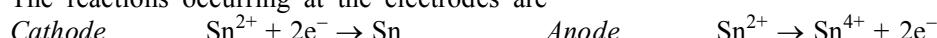
Amount of electricity required as per equation  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  is

$$n_Q = 2 \times 0.1408 \text{ mol} = 0.2816 \text{ mol}$$

Since  $n_Q = It/F = Q/F$ , we have

$$Q = n_Q F = (0.2816 \text{ mol}) (96500 \text{ C mol}^{-1}) = 27172 \text{ C}$$

## 4. The reactions occurring at the electrodes are



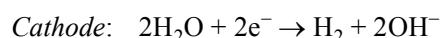
If 0.119 g of Sn is deposited at cathode, then 0.119 g of  $\text{Sn}^{4+}$  will be formed at the anode. Thus, a total of  $2 \times 0.119$  g of  $\text{Sn}^{2+}$  is lost from the solution. Hence,

$$\begin{aligned} \text{Mass of remaining } \text{SnCl}_2 &= 19 \text{ g} - \frac{M_{\text{SnCl}_2}}{M_{\text{Sn}}} \times m_{\text{Sn}} = 19 \text{ g} - \frac{189.6}{119} \times 2 \times 0.119 \text{ g} \\ &= (19 - 0.379) \text{ g} = 18.621 \text{ g} \end{aligned}$$

$$\text{Mass of } \text{SnCl}_4 \text{ formed} = \frac{M_{\text{SnCl}_4}}{M_{\text{Sn}}} \times m_{\text{Sn}} = \frac{260.2}{119} \times 0.119 \text{ g} = 0.26 \text{ g}$$

$$\text{Now } \frac{m(\text{SnCl}_2)}{m(\text{SnCl}_4)} = \frac{18.621}{0.260} = \frac{71.62}{1}$$

## 5. The basic reactions are





The liberated  $\text{Cl}_2$  reacts with  $\text{NaOH}$  formed during electrolysis as shown in the following.



6. Amount of charge in 1 g  $\text{N}^{3-}$  is

$$n_Q = 3 \left( \frac{1\text{g}}{14\text{ g mol}^{-1}} \right) = \frac{3}{14} \text{ mol}$$

Charge in coulomb is

$$Q = n_Q F = \left( \frac{3}{14} \text{ mol} \right) (96\,500 \text{ C mol}^{-1}) = 20\,679 \text{ C}$$

7. We have

$$\text{Amount of gold deposited} = \frac{9.85 \text{ g}}{197 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

Based on the reaction  $\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$ , it may be concluded that

$$\text{Amount of electrons passed} = 3 \times 0.05 \text{ mol} = 0.15 \text{ mol}$$

Now, the same quantity of electricity is passed through  $\text{CuSO}_4$  solution causing the reaction  $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$  at cathode. We will have

$$\text{Amount of Cu deposited} = \frac{0.15 \text{ mol}}{2} = 0.075 \text{ mol}$$

$$\text{Mass of Cu deposited} = (0.075 \text{ mol}) (63.5 \text{ g mol}^{-1}) = 4.7625 \text{ g}$$

$$\text{Quantity of electricity passed} = (0.15 \text{ mol}) (96\,500 \text{ C mol}^{-1}) = 14\,475 \text{ C}$$

$$\text{Quantity of current passed} = \frac{Q}{t} = \frac{14\,475 \text{ C}}{5 \times 60 \times 60 \text{ s}} = 0.8042 \text{ A.}$$

8. We have

$$\text{Volume of metal deposited} = (80 \text{ cm}^2) (0.0005 \text{ cm}) = 0.04 \text{ cm}^3$$

$$\text{Mass of metal deposited} = \rho V = (10.5 \text{ g cm}^{-3}) (0.04 \text{ cm}^3) = 0.42 \text{ g}$$

$$\text{Amount of silver deposited} = \frac{0.42 \text{ g}}{108 \text{ g mol}^{-1}} = 3.889 \times 10^{-3} \text{ mol}$$

$$\text{Quantity of electricity passed} = (3.889 \times 10^{-3} \text{ mol}) (96\,500 \text{ C mol}^{-1}) = 375.27 \text{ C}$$

$$\text{Time for which 3A current is passed} = \frac{375.27 \text{ C}}{3 \text{ A}} = 125.09 \text{ s}$$

9. We have

$$\text{Mass of H}_2\text{SO}_4 \text{ solution to start with, } \rho V = (1.294 \text{ g mL}^{-1}) (3.5 \times 10^3 \text{ mL}) = 4\,529 \text{ g}$$

$$\text{Actual mass of H}_2\text{SO}_4 \text{ in this solution} = \left( \frac{39}{100} \right) (4\,529 \text{ g}) = 1766.3 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ solution at the end} = (1.139 \text{ g mL}^{-1}) (3.5 \times 10^3 \text{ mL}) = 3\,986.5 \text{ g}$$

$$\text{Actual mass of H}_2\text{SO}_4 \text{ in this solution} = \left( \frac{200}{1000} \right) (3\,986.5 \text{ g}) = 797.3 \text{ g}$$

$$\text{Mass of H}_2\text{SO}_4 \text{ consumed} = (1766.3 - 91.3) \text{ g} = 969.0 \text{ g}$$

$$\text{Amount of H}_2\text{SO}_4 \text{ consumed} = \frac{969 \text{ g}}{98 \text{ g mol}^{-1}} = 9.888 \text{ mol}$$

Amount of  $\text{H}^+$  consumed =  $2 \times 9.888 \text{ mol}$

Since 4 mol of  $\text{H}^+$  are consumed per 2 mol of electrons during discharge, we have

$$\text{Amount of electrons discharged} = \left( \frac{2 \text{ mol}}{4 \text{ mol}} \right) (2 \times 9.888 \text{ mol}) = 9.888 \text{ mol}$$

$$\text{Quantity of electricity discharged} = (9.888 \text{ mol})(96500 \text{ C mol}^{-1}) = 954192 \text{ C}$$

$$\text{Number of ampere-hour for which the battery has been used} = \frac{954192}{60 \times 60} = 265.05.$$

10. Since  $W = VI$ , we have

$$I = \frac{100 \text{ W}}{110 \text{ V}} = \frac{10}{11} \text{ A}$$

$$Q = It = \left( \frac{10}{11} \text{ A} \right) (10 \times 60 \times 60 \text{ s}) = 32727.3 \text{ C}$$

$$\begin{aligned} \text{Mass of Cd deposited } (\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}) &= \left( \frac{M_{\text{Cd}}}{2F} \right) Q = \left( \frac{112.4 \text{ g mol}^{-1}}{2 \times 96500 \text{ C mol}^{-1}} \right) (32727.3 \text{ C}) \\ &= 19.06 \text{ g.} \end{aligned}$$

11. Amount of hydrogen oxidised =  $\frac{67.2 \text{ L}}{22.4 \text{ L mol}^{-1}} = 3 \text{ mol}$

$$\text{Amount of electrons produced} = 2 \times 3 \text{ mol}$$

$$\text{Quantity of electricity produced} = 2 \times 3 \times 96500 \text{ C}$$

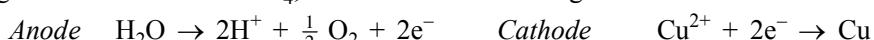
$$\text{Current produced} = \frac{2 \times 3 \times 96500 \text{ C}}{15 \times 60 \text{ s}} = 643.33 \text{ A}$$

Since 1 mol of Cu is deposited by the absorption of 2 mol electrons, we will have

$$\text{Amount of Cu deposited} = 3 \text{ mol}$$

$$\text{Mass of Cu deposited} = (3 \text{ mol}) (63.5 \text{ mol}^{-1}) = 190.5 \text{ g.}$$

12. Assuming  $\text{Cu}^{2+}$  salt to be  $\text{CuSO}_4$ , the reactions occurring at the electrodes would be



After the complete deposition of copper, the reactions would be



$$\text{Now, Amount of Cu deposited} = \frac{0.4 \text{ g}}{63.6 \text{ g mol}^{-1}} = 0.00629 \text{ mol}$$

$$\text{Amount of oxygen liberated} = \frac{1}{2} \times 0.00629 \text{ mol} = 0.003145 \text{ mol}$$

$$\begin{aligned} \text{Quantity of electricity passed in seven minutes after the deposition of the entire copper} \\ = (1.2 \text{ A}) (7 \times 60 \text{ s}) = 504 \text{ C} \end{aligned}$$

$$\text{Amount of electrons carrying this much of electricity} = \frac{504 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.00522 \text{ mol}$$

From the electrode reactions which occur after the deposition of copper, we have

$$\text{Amount of oxygen liberated} = \frac{1}{4} \times 0.00522 \text{ mol} = 0.001305 \text{ mol}$$

$$\text{Amount of hydrogen liberated} = \frac{1}{2} \times 0.00522 \text{ mol} = 0.00261 \text{ mol}$$

Total amount of gases liberated in the entire electrolysis

$$= (0.003145 + 0.001305 + 0.00261) \text{ mol} = 0.00706 \text{ mol}$$

volume of the gases evolved at STP during the entire electrolysis

$$= (0.007\ 06 \text{ mol}) (22\ 414 \text{ mL mol}^{-1}) = 158.2 \text{ mL}$$

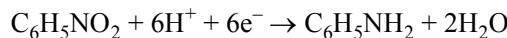
If the salt of  $\text{Cu}^{2+}$  ions is  $\text{CuCl}_2$ , then the anodic reaction during the deposition of copper would be  
 $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$

In this case,

$$\begin{aligned}\text{Total amount of gases liberated would be} &= (0.006\ 29 + 0.001\ 305 + 0.002\ 61) \text{ mol} \\ &= 0.010\ 205 \text{ mol}\end{aligned}$$

$$\begin{aligned}\text{Volume of the gases evolved would be} &= (0.010\ 205 \text{ mol}) (22\ 414 \text{ mL mol}^{-1}) \\ &= 228.7 \text{ mL.}\end{aligned}$$

13. The reduction reaction is



Mass of  $\text{C}_6\text{H}_5\text{NO}_2$  to be reduced = 12.3 g

$$\text{Amount of } \text{C}_6\text{H}_5\text{NO}_2 \text{ to be reduced} = \frac{12.3 \text{ g}}{M(\text{C}_6\text{H}_5\text{NO}_2)} = \frac{12.3 \text{ g}}{123 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

To reduce 0.1 mol of  $\text{C}_6\text{H}_5\text{NO}_2$ , 0.6 mol of electrons would be required. But the current efficiency is 50%.

Hence, the amount of electrons required would be 1.2 mol. Now

$$\text{Electricity carried by 1.2 mol electrons} = (1.2 \text{ mol}) (96\ 500 \text{ C mol}^{-1}) = 115\ 800 \text{ C}$$

$$\text{Energy consumed} = (115\ 800 \text{ C}) (3.0 \text{ V}) = 347\ 400 \text{ J} = 347.4 \text{ kJ.}$$

14. Amount of electrons passed =  $\frac{It}{F} = \frac{(1.70 \text{ A})(230 \text{ s})}{(96\ 500 \text{ C mol}^{-1})} = 0.004\ 05 \text{ mol}$

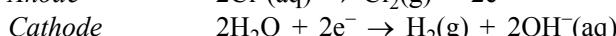
Amount of electrons actually used in the reduction of  $\text{Zn}^{2+}$

$$= (0.004\ 05) \left( \frac{90}{100} \right) = 0.003\ 65 \text{ mol}$$

$$\text{Amount of } \text{Zn}^{2+} \text{ ions reduced} = \frac{1}{2} \times 0.003\ 65 \text{ mol} = 0.0018\ 25 \text{ mol}$$

$$\text{Molarity of } \text{Zn}^{2+} \text{ after the deposition of Zn} = 0.160 \text{ M} - \left( 0.001825 \times \frac{1000}{300} \right) \text{ M} = 0.154 \text{ M}$$

15. The reactions occurring at the electrodes are



$$\text{Amount of } \text{Cl}_2 \text{ to be produced} = \frac{10^3 \text{ g}}{71 \text{ g mol}^{-1}} = 14.08 \text{ mol}$$

$$\text{Amount of electrons needed to carry out electrolysis} = 2 \times 14.08 \text{ mol}$$

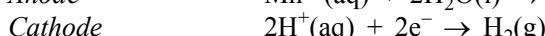
$$\text{Quantity of electricity carried by these electrons} = 2 \times 14.08 \times 96\ 500 \text{ C}$$

$$\begin{aligned}\text{Time required to carry out electrolysis } t &= \frac{Q}{I} = \frac{2 \times 14.08 \times 96500 \text{ C}}{(25 \text{ A})(62/100)} = 175\ 300 \text{ s} \\ &\equiv (175300/60 \times 60) \text{ h} = 48.69 \text{ h}\end{aligned}$$

$$\text{Amount of } \text{OH}^- \text{ ions released in the electrolysis} = 2 \times 14.08 \text{ mol}$$

$$\text{Molarity of } \text{OH}^- \text{ ions} = \frac{2 \times 14.08 \text{ mol}}{20 \text{ L}} = 1.408 \text{ mol L}^{-1}.$$

16. The electrode reactions are



The actual current needed to deposit 1 kg  $\text{MnO}_2$  is given by the expression

$$I = m \left( \frac{F}{t} \right) \left( \frac{z}{M} \right) = (1\ 000 \text{ g}) \left( \frac{96\ 500 \text{ C mol}^{-1}}{24 \times 60 \times 60 \text{ s}} \right) \left[ \frac{2}{(54.9 + 2 \times 16) \text{ g mol}^{-1}} \right] = 25.70 \text{ A}$$

$$\text{The current efficiency} = \left( \frac{25.70 \text{ A}}{27 \text{ A}} \right) (100) = 95.185\%$$

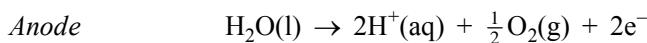
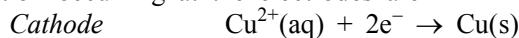
17. Using the expression  $m = \frac{It}{F} \frac{M}{|v_e|}$  we get

$$m = \frac{(8.46 \text{ A})(80 \times 60 \times 60 \text{ s})(107.8 \text{ g mol}^{-1})}{(96\ 500 \text{ C mol}^{-1}) (1)} = 272.18 \text{ g} \quad (1)$$

$$\text{Volume of silver plated out, } V = \frac{m}{\rho} = \frac{272.18 \text{ g}}{10.5 \text{ g cm}^{-3}} = 25.92 \text{ cm}^3$$

$$\text{Area of the tray plated} = \frac{25.92 \text{ cm}^3}{0.002\ 54 \text{ cm}} = 10\ 204.7 \text{ cm}^2$$

18. The reaction occurring at the electrodes are



The concentration of  $\text{Cu}^{2+}$  ions decreases during the electrolysis of copper sulphate solution. The amount of  $\text{Cu}^{2+}$  deposited when a current of 2 mA is passed for 16 min, will be

$$\Delta n \equiv \frac{\Delta m}{M_{\text{Cu}}} = \frac{It}{F} \frac{1}{z} = \frac{(2 \times 10^{-3} \text{ A})(16 \times 60 \text{ s})}{(96\ 500 \text{ C mol}^{-1})} \frac{1}{2} = 9.948 \times 10^{-6} \text{ mol}$$

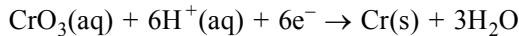
Since the absorbance (which is directly proportional to the  $\text{Cu}^{2+}$  concentration in the solution) after the electrolysis is half of its value in the original solution, the amount of  $\text{Cu}^{2+}$  ions in the original solution will be

$$n_i = 2 \times 9.948 \times 10^{-6} \text{ mol}$$

Since the volume of solution is 250 mL (the volume of water decomposed during electrolysis is negligible), the concentration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the original solution would be

$$c_i = \frac{n_i}{V} = \frac{2 \times 9.948 \times 10^{-6} \text{ mol}}{0.250 \text{ L}} = 7.96 \times 10^{-5} \text{ mol L}^{-1}$$

19. The given equation is



- (a) Using the expression  $m = \frac{Q}{F} \frac{M}{z}$  we get (1)

$$m = \left( \frac{24\ 000 \text{ C}}{96\ 500 \text{ C mol}^{-1}} \right) \left( \frac{52 \text{ mol}^{-1}}{6} \right) = 2.155 \text{ g}$$

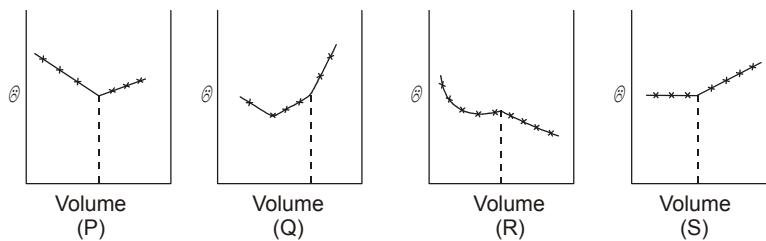
- (b) Since  $Q = It$ , Eq. (1) gives

$$t = m \left( \frac{F}{I} \right) \left( \frac{z}{M} \right) = (1.5 \text{ g}) \left( \frac{96\ 500 \text{ C mol}^{-1}}{12.5 \text{ A}} \right) \left( \frac{6}{52 \text{ g mol}^{-1}} \right)$$

$$= 1336.15 \text{ s} \equiv 22.27 \text{ min}$$

## **SECTION-II ELECTROLYTIC CONDUCTION**

## **Straight Objective Type**



## **Integer Answer Type**

1. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If  $\lambda_X^\infty \approx \lambda_Y^\infty$ , the difference in their  $pK_a$  values,  $pK_a(\text{HX}) - pK_a(\text{HY})$ , is \_\_\_\_\_. (Consider degree of ionization of both acids to be  $\ll 1$ ) (2015)

## **Matching Type**

1. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists.

List I	List II
P $(C_2H_5)_3N + CH_3COOH$ (X)              (Y)	1.    Conductivity decreases and then increases
Q $KI(0.1 \text{ M}) + AgNO_3(0.1 \text{ M})$ (X)              (Y)	2.    Conductivity decreases and then does not change much
R $CH_3COOH + KOH$ (X)              (Y)	3.    Conductivity increases and then does not change much
S $NaOH + HI$ (X)              (Y)	4.    Conductivity does not change much and then increases

## Codes:

	P	Q	R	S
(a)	3	4	2	1
(b)	4	3	2	1
(c)	2	3	4	1
(d)	1	4	3	2

(2013)

### Subjective Type

1. A saturated solution of silver bromide is made  $10^{-7}$  M in silver nitrate. Calculate the conductivity of the solution. Given:

$$K_{\text{sp}}^{\circ}(\text{AgBr}) = 3.0 \times 10^{-13}, \lambda_m^{\infty}(\text{Ag}^+) = 6 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1},$$

$$\lambda_m^{\infty}(\text{NO}_3^-) = 7 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}, \lambda_m^{\infty}(\text{Br}^-) = 8 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1},$$

and  $\kappa(\text{water}) = 7.5 \times 10^{-6} \text{ S m}^{-1}$ . (2006)

### ANSWERS

### Straight Objective Type

1. (b)      2. (d)

### Integer Answer Type

1. 3

### Matching Type

1. (a) (P)  $\leftrightarrow$  3; (Q)  $\leftrightarrow$  4; (R)  $\leftrightarrow$  2 and (S)  $\leftrightarrow$  1.

### Subjective Type

1.  $158 \times 10^{-7} \text{ S m}^{-1}$

### HINTS AND SOLUTIONS

### Straight Objective Type

1. The sizes of hydrated ions in solution follow the order.  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$   
The conductivity of these ions follow the reverse order.

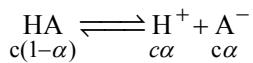
2. The reaction is



In the titrating solution,  $\text{Cl}^-(\text{aq})$  is replaced by  $\text{NO}_3^-(\text{aq})$ . The molar conductivities of  $\text{Cl}^-$  and  $\text{NO}_3^-$  are 76.34 and 71.44  $\text{S cm}^2 \text{ mol}^{-1}$ , respectively. Thus, molar conductivity decreases upto the equivalence point. Beyond the equivalence point, the addition of extra  $\text{AgNO}_3$  causes the increase in molar conductivity due to increase in the ionic concentrations of  $\text{Ag}^+$  and  $\text{NO}_3^-$  ions.

### Integer Answer Type

1. For a weak acid HA, we have



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\alpha][\alpha]}{\text{c}(1-\alpha)} \approx \text{c} \alpha^2 \quad (\text{Since } \alpha \ll 1)$$

Also,  $\alpha = A_{\text{HA}} / A_{\text{HA}}^\infty = A_{\text{HA}} / (\lambda_{\text{H}^+}^\infty + \lambda_{\text{A}^-}^\infty)$

Hence,  $K_a = c A_{\text{HA}}^2 / (\lambda_{\text{H}^+}^\infty + \lambda_{\text{A}^-}^\infty)^2$

Since  $\lambda_{\text{X}^-}^\infty \approx \lambda_{\text{Y}^-}^\infty$ , for the given two acids, we have

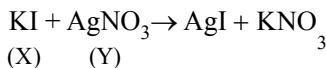
$$\frac{K_a(\text{HX})}{K_a(\text{HY})} = \frac{c_{\text{HX}}}{c_{\text{HY}}} \left( \frac{A_{\text{HX}}}{A_{\text{HY}}} \right)^2 = \left( \frac{0.01\text{M}}{0.1\text{M}} \right) \left( \frac{1}{10} \right)^2 = 10^{-3}$$

Hence  $pK_a(\text{HX}) - pK_a(\text{HY}) = 3$

### Matching Type

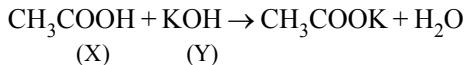
1. In the choice P of List I, a weak base is added to a weak acid. There will be salt formation till whole of acid is neutralized. This will cause an increase in conductivity. Beyond this point, the conductivity will not change much as the compound X is a weak base. The behaviour is given by the choice 3 of List II.

In the choice of Q of List I, we have



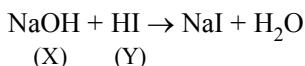
Effectively,  $\text{Ag}^+$  ions are replaced by  $\text{K}^+$  ions. Since their conductivities are more or less same, the conductivity of the solution does not change much. After the complete precipitation of  $\text{AgI}$ , the solution will contain an increasing concentration of KI, hence, its conductivity will increase. This behaviour is given by the choice 4 of List II.

In the choice R of List I, we have



Effectively KOH is replaced by  $\text{CH}_3\text{COOK}$ . Since conductivity of  $\text{OH}^-$  ions is much larger than that of  $\text{CH}_3\text{COO}^-$ , the conductivity of the solution will decrease. After the complete neutralization of KOH, the solution will contain a fixed amount of  $\text{CH}_3\text{COOK}$  and increasing amount of  $\text{CH}_3\text{COOH}$ , a weak acid. Thus, its conductivity will not change much. This behaviour is given by the choice 2 of List II.

In the choice S of List I, we have



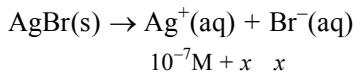
Effectively,  $\text{H}^+$  is replaced by  $\text{Na}^+$ . This will cause a decrease in conductivity after the complete neutralization of HI, the solution will contain fixed amount of NaI and increasing amount of NaOH. This will cause an increase in conductivity. This behaviour is given by the choice 1 of List II.

Hence, the correct matching (choice a) are as follows

(P)  $\leftrightarrow$  3; (Q)  $\leftrightarrow$  4; (R)  $\leftrightarrow$  2 and (S)  $\leftrightarrow$  1.

### Subjective Type

1. Let  $x$  be the solubility of  $\text{AgBr}$  in  $10^{-7}\text{ M AgNO}_3$  solution. We will have



Since  $K_{sp} = [\text{Ag}^+] [\text{Br}^-]$ , we have

$$(10^{-7} \text{ M} + x) (x) = 3.0 \times 10^{-13} \text{ M}^2$$

$$\text{or } x^2 + (10^{-7} \text{ M})x - 30 \times 10^{-14} \text{ M}^2 = 0$$

$$\text{This gives } x = 5 \times 10^{-7} \text{ M}$$

$$\begin{aligned} \lambda_m^\infty(\text{AgNO}_3) &= \lambda_m^\infty(\text{Ag}^+) + \lambda_m^\infty(\text{NO}_3^-) \\ &= (6 + 7) \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} = 13 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \lambda_m^\infty(\text{AgBr}) &= \lambda_m^\infty(\text{Ag}^+) + \lambda_m^\infty(\text{Br}^-) \\ &= (6 + 8) \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} = 14 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \kappa(\text{AgNO}_3) &= [\lambda_m^\infty(\text{AgNO}_3)]c \\ &= (13 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) (10^{-7} \text{ M}) = (13 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) (10^{-4} \text{ mol m}^{-3}) \\ &= 13 \times 10^{-7} \text{ S m}^{-1} \end{aligned}$$

$$\begin{aligned} \kappa(\text{AgBr}) &= \{\lambda_m^\infty(\text{AgBr})\}c = (14 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) (5 \times 10^{-7} \text{ M}) \\ &= (14 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) (5 \times 10^{-4} \text{ mol m}^{-3}) \\ &= 70 \times 10^{-7} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \kappa(\text{soln}) &= \kappa(\text{AgNO}_3) + \kappa(\text{AgBr}) + \kappa(\text{water}) \\ &= (13 \times 10^{-7} + 70 \times 10^{-7} + 75 \times 10^{-7}) \text{ S m}^{-1} \\ &= 158 \times 10^{-7} \text{ S m}^{-1} \end{aligned}$$

### SECTION-III GALVANIC CELLS

#### Straight Objective Type

1. The standard potentials at 298 K for the following half reactions are given against each:



Which is the strongest reducing agent?

- (a) Zn(s)      (b) Cr(s)      (c) H<sub>2</sub>(g)      (d) Fe<sup>2+</sup>(aq)      (1981)

2. The reaction  $\frac{1}{2} \text{H}_2(\text{g}) + \text{AgCl(s)} = \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(s)}$  occurs in the galvanic cell

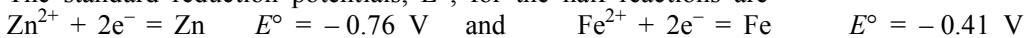
- (a) Ag | AgCl(s) | KCl(aq) || AgNO<sub>3</sub>(aq) | Ag

- (b) Pt | H<sub>2</sub>(g) | HCl(aq) || AgNO<sub>3</sub>(aq) | Ag

- (c) Pt | H<sub>2</sub>(g) | HCl(aq) | AgCl(s) | Ag

- (d) Pt | H<sub>2</sub>(g) | KCl (aq) | AgCl(s) | Ag      (1985)

3. The standard reduction potentials,  $E^\circ$ , for the half reactions are

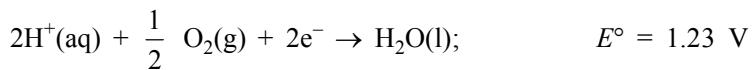


The emf of the cell involving the reaction  $\text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe}$  is

- (a) -0.35 V      (b) +1.17 V      (c) +0.35 V      (d) -1.17 V      (1988)

4. The standard reduction potentials of  $\text{Cu}^{2+}|\text{Cu}$  and  $\text{Cu}^{2+}|\text{Cu}^+$  are 0.337 V and 0.153 V, respectively. The standard electrode potential of  $\text{Cu}^+|\text{Cu}$  half cell is  
 (a) 0.184 V      (b) 0.827 V      (c) 0.521 V      (d) 0.490 V      (1997)
5. A standard hydrogen electrode has zero electrode potential because  
 (a) hydrogen is easiest to oxidise  
 (b) this electrode potential is assumed to be zero  
 (c) hydrogen atom has only one electron  
 (d) hydrogen is the lightest element      (1997)
6. The standard reduction potential values of three metallic cations, X, Y, Z are 0.52, -3.03 and -1.18 V, respectively. The order of reducing power of the corresponding metals is  
 (a)  $\text{Y} > \text{Z} > \text{X}$       (b)  $\text{X} > \text{Y} > \text{Z}$       (c)  $\text{Z} > \text{Y} > \text{X}$       (d)  $\text{Z} > \text{X} > \text{Y}$       (1998)
7. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25 °C. If the reduction potential of  $\text{Z} > \text{Y} > \text{X}$ , then  
 (a) Y will oxidise X and not Z      (b) Y will oxidise Z and not X  
 (c) Y will oxidise both X and Z      (d) Y will reduce both X and Z      (1999)
8. For the electrochemical cell,  $\text{M} | \text{M}^+ \parallel \text{X}^- | \text{X}$ ,  $E^\circ(\text{M}^+|\text{M}) = 0.44$  V and  $E^\circ(\text{X}|\text{X}^-) = 0.33$  V. From this data one can deduce that  
 (a)  $\text{M} + \text{X} \rightarrow \text{M}^+ + \text{X}^-$  is the spontaneous reaction  
 (b)  $\text{M}^+ + \text{X}^- \rightarrow \text{M} + \text{X}$  is the spontaneous reaction  
 (c)  $E_{\text{cell}} = 0.77$  V  
 (d)  $E_{\text{cell}} = -0.77$  V      (2000)
9. A solution containing one mole per litre of each,  $\text{Cu}(\text{NO}_3)_2$ ;  $\text{AgNO}_3$ ;  $\text{Hg}_2(\text{NO}_3)_2$ ;  $\text{Mg}(\text{NO}_3)_2$ , is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are  $\text{Ag}^+|\text{Ag} = 0.80$ ,  $\text{Hg}_2^{2+}|\text{Hg} = 0.79$ ,  $\text{Cu}^{2+}|\text{Cu} = 0.34$  and  $\text{Mg}^{2+}|\text{Mg} = -2.37$ . With increasing voltage, the sequence of deposition of metals on the cathode will be  
 (a) Ag, Hg, Cu, Mg      (b) Mg, Cu, Hg, Ag  
 (c) Ag, Hg, Mg, Cu      (d) Cu, Hg, Ag, Mg      (1984)
10. Saturated solution of  $\text{KNO}_3$  is used to make 'salt-bridge' because  
 (a) velocity of  $\text{K}^+$  is greater than that of  $\text{NO}_3^-$   
 (b) velocity of  $\text{NO}_3^-$  is greater than that of  $\text{K}^+$   
 (c) velocities of both  $\text{K}^+$  and  $\text{NO}_3^-$  are nearly the same  
 (d)  $\text{KNO}_3$  is highly soluble in water      (2001)
11. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:
- |   |                    |
|---|--------------------|
| $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(l)}$               | $E^\circ = 1.51$ V |
| $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$ | $E^\circ = 1.38$ V |
| $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$  | $E^\circ = 0.77$ V |
| $\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$   | $E^\circ = 1.40$ V |
- Identify the only *incorrect* statement regarding the quantitative estimation of aqueous  $\text{Fe}(\text{NO}_3)_2$ .
- (a)  $\text{MnO}_4^-$  can be used in aqueous HCl      (b)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous HCl  
 (c)  $\text{MnO}_4^-$  can be used in aqueous  $\text{H}_2\text{SO}_4$       (d)  $\text{Cr}_2\text{O}_7^{2-}$  can be used in aqueous  $\text{H}_2\text{SO}_4$       (2002)
12. The emf of the cell  $\text{Zn} | \text{Zn}^{2+} (0.001 \text{ M}) \parallel \text{Fe}^{2+} (0.01 \text{ M}) | \text{Fe}$  at 298 K is 0.3495 V. The value of equilibrium constant for the cell reaction is  
 (a)  $\exp(0.32/0.0295)$       (b)  $\exp(0.3495/0.0295)$   
 (c)  $10^{(0.32/0.0295)}$       (d)  $10^{(-0.32/0.0295)}$       (2004)

13. From the following data

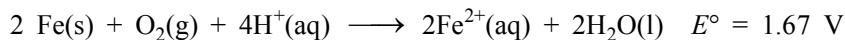


show that  $\Delta G^\circ$  for  $2\text{Fe}(\text{s}) + 4\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$  is

- (a)  $-322.3 \text{ kJ mol}^{-1}$       (b)  $-483.5 \text{ kJ mol}^{-1}$   
 (c)  $-644.6 \text{ kJ mol}^{-1}$       (d)  $644.6 \text{ kJ mol}^{-1}$

(2005)

14. Consider the following cell reaction.



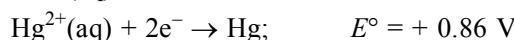
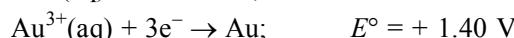
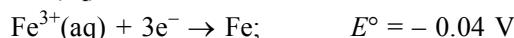
At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $p(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^\circ\text{C}$  is

- (a) 1.47 V      (b) 1.77 V      (c) 1.87 V      (d) 1.57 V

(2011)

### Multiple Correct-Choice Type

1. For the reduction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\circ = 0.96 \text{ V}$ . The values of  $E^\circ$  for some metal ions are as follows.



The pair(s) of metals that is(are) oxidised by  $\text{NO}_3^-$  in aqueous medium is(are)

- (a) V and Hg      (b) Hg and Fe      (c) Fe and Au      (d) Fe and V

(2009)

2. In a galvanic cell, the salt bridge

- (a) does not participate chemically in the cell reaction  
 (b) stops the diffusion of ions from one electrode to another  
 (c) is necessary for the occurrence of the cell reaction  
 (d) ensures mixing of the two electrolytic solutions

(2014)

### Fill-in-the-Blanks Type

1. The more negative the standard potential, the \_\_\_\_\_ is its ability to displace hydrogen from acids.  
 (1986)

### True/False Type

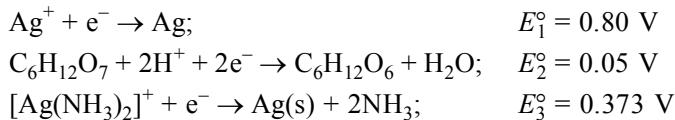
1. Copper metal can reduce  $\text{Fe}^{2+}$  in acidic medium.      (1982)  
 2. The dependence of electrode potential for the electrode  $\text{M}^{n+} \mid \text{M}$  with concentration under STP conditions is given by the expression:

$$E = E^\circ + \frac{0.0591 \text{ V}}{n} \log_{10} [\text{M}^{n+}] \quad (1993)$$

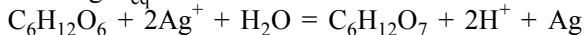
## Linked Comprehension Type

### Passage-1

Tollens reagent (ammoniacal solution of silver nitrate) is used to test aldehydes. The following data are available.



1. The value of  $\log K_{\text{eq}}^\circ$  for the reaction



is

- (a) 12.7 (b) 25.4 (c) 29.27 (d) 58.54

2. The use of  $\text{NH}_3$  makes the pH of solution equal to 11. This causes

- (a) decrease in the value of  $E_2$  (b) increase in the value of  $E_2$   
 (c) increase in the value of  $E_1$  (d) increase in the value of  $E_1^\circ$

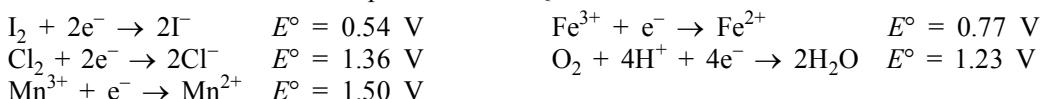
3. Ammonia is used in this reaction rather than any other base. This is due to the fact that

- (a)  $[\text{Ag}(\text{NH}_3)_2]^+$  is a weaker oxidising agent than  $\text{Ag}^+$   
 (b) Ammonia prevents the decomposition of gluconic acid  
 (c) silver precipitates gluconic acid as its silver salt  
 (d) the standard reduction potential of  $[\text{Ag}(\text{NH}_3)_2]^+$  is changed.

(2006)

### Passage-2

Redox reactions play a pivot role in chemistry and biology. The values of standard redox potential ( $E^\circ$ ) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their  $E^\circ$  (with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 1-3.



1. Among the following, identify the correct statement.

- (a) Chloride ion is oxidised by  $\text{O}_2$  (b)  $\text{Fe}^{2+}$  is oxidised by iodine  
 (c) Iodide ion is oxidised by chlorine (d)  $\text{Mn}^{2+}$  is oxidised by chlorine

2. While  $\text{Fe}^{3+}$  is stable,  $\text{Mn}^{3+}$  is not stable in acid solution because

- (a)  $\text{O}_2$  oxidises  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$   
 (b)  $\text{O}_2$  oxidises both  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$   
 (c)  $\text{Fe}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$   
 (d)  $\text{Mn}^{3+}$  oxidises  $\text{H}_2\text{O}$  to  $\text{O}_2$

3. Sodium fusion extract, obtained from aniline, on treatment with iron(II) sulphate and  $\text{H}_2\text{SO}_4$  in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

- (a)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  (b)  $\text{Fe}_3[\text{Fe}(\text{FCN})_6]_2$   
 (c)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$  (d)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$

(2007)

### Passage-3

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:



For the above electrolytic cell the magnitude of the cell potential  $|E_{\text{cell}}| = 70 \text{ mV}$ .

1. For the above cell
 

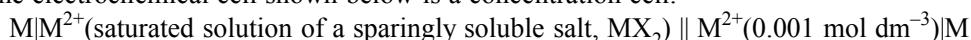
(a) $E_{\text{cell}} < 0; \Delta G > 0$	(b) $E_{\text{cell}} > 0; \Delta G < 0$
(c) $E_{\text{cell}} < 0; \Delta G^\circ > 0$	(d) $E_{\text{cell}} > 0; \Delta G^\circ < 0$
2. If the 0.05 molar solution of  $M^+$  is replaced by a 0.0025 molar  $M^+$  solution, then the magnitude of the cell potential would be
 

(a) 35 mV	(b) 70 mV
(c) 140 mV	(d) 700 mV

(2010)

#### Passage-4

The electrochemical cell shown below is a concentration cell.



The emf of the cell depends on the difference in concentration of  $M^{2+}$  ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

1. The solubility product ( $K_{\text{sp}}$ ) of  $MX_2$  at 298 K based on the information available for the given concentration cell (take  $2.303 RT/F = 0.059 \text{ V}$  at 298 K) is
 

(a) $1 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$	(b) $4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$
(c) $1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$	(d) $4 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$
2. The value of  $\Delta G$  for the given cell reaction (take  $1F = 96500 \text{ C mol}^{-1}$ ) is
 

(a) $-5.7 \text{ kJ mol}^{-1}$	(b) $5.7 \text{ kJ mol}^{-1}$	(c) $11.4 \text{ kJ mol}^{-1}$	(d) $-11.4 \text{ kJ mol}^{-1}$
--------------------------------	-------------------------------	--------------------------------	---------------------------------

(2012)

#### Matching Type

1. The standard reduction potential data at 25 °C is given below.

$$E^\circ(Fe^{3+}, Fe^{2+}) = +0.77 \text{ V}; E^\circ(Fe^{2+}, Fe) = -0.44 \text{ V}$$

$$E^\circ(Cu^{2+}, Cu) = +0.34 \text{ V}; E^\circ(Cu^+, Cu) = +0.52 \text{ V}$$

$$E^\circ(O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O) = +1.23 \text{ V}$$

$$E^\circ(O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-) = +0.40 \text{ V}$$

$$E^\circ(Cr^{3+}, Cr) = -0.74 \text{ V}; E^\circ(Cr^{2+}, Cr) = -0.91 \text{ V}$$

Match  $E^\circ$  of the redox pair in List I with the values given in List II and select the correct answer using the code given below the list:

##### List I

- |  |                      |
|--|----------------------|
| P $E^\circ(Fe^{3+}, Fe)$                           | 1. $-0.18 \text{ V}$ |
| Q $E^\circ(4H_2O \rightleftharpoons 4H^+ + 4OH^-)$ | 2. $-0.4 \text{ V}$  |
| R $E^\circ(Cu^{2+} + Cu \rightarrow 2Cu^+)$        | 3. $-0.04 \text{ V}$ |
| S $E^\circ(Cr^{3+}, Cr^{2+})$                      | 4. $-0.83 \text{ V}$ |

##### List II

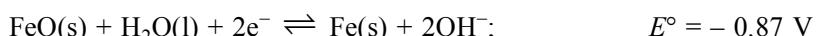
- |                               |                      |
|-------------------------------|----------------------|
| P      Q      R      S        | 1.    2.    3.    4. |
| (a)    4      1      2      3 | 1.    2.    3.    4. |
| (b)    2      3      4      1 | 1.    2.    3.    4. |
| (c)    1      2      3      4 | 1.    2.    3.    4. |
| (d)    3      4      1      2 | 1.    2.    3.    4. |

(2013)

##### Codes:

## Subjective Type

- Consider the cell  $Zn \mid Zn^{2+}(aq, 1.0\text{ M}) \parallel Cu^{2+}(aq, 1.0\text{ M}) \mid Cu$ . The standard reduction potentials are 0.350 V for  $Cu^{2+}(aq) + 2e^- \rightarrow Cu$  and -0.763 V for  $Zn^{2+}(aq) + 2e^- \rightarrow Zn$ .  
 (i) Write down the cell reaction. (ii) Calculate the emf of the cell. (iii) Is the cell reaction spontaneous or not? (1982)
- The emf of a cell corresponding to the reaction  $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(0.1\text{ M}) + H_2(g, 1\text{ bar})$  is 0.28 V at 25°C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.  
 Given:  $E_{Zn^{2+}|Zn}^\circ = -0.763\text{ V}$ . (1986)
- A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of  $10^{-6}\text{ M}$  hydrogen ions. The emf of the cell is 0.118 V at 25 °C. Calculate the concentration of hydrogen ions at the positive electrode. (1988)
- The standard reduction potential at 25 °C of the reaction  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$  is -0.8277 V. Calculate standard equilibrium constant for the reaction  $2H_2O \rightarrow H_3O^+ + OH^-$  at 25 °C. (1989)
- The standard reduction potential of  $Cu^{2+} \mid Cu$  and  $Ag^+ \mid Ag$  electrodes are 0.337 V and 0.799 V, respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of  $Ag^+$  will the emf of the cell be zero at 25 °C if the concentration of  $Cu^{2+}$  ions is 0.01 M? (1990)
- Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until equilibrium is reached. If the standard reduction potential of  $Zn^{2+} \mid Zn$  and  $Ni^{2+} \mid Ni$  are -0.75 V and -0.24 V, respectively, calculate the concentrations of  $Ni^{2+}$  in solution at equilibrium. (1991)
- For the galvanic cell  $Ag \mid AgCl(s) \mid KCl(0.2\text{ M}) \parallel KBr(0.001\text{ M}) \mid AgBr(s) \mid Ag$ . Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell at 25 °C. Given:  $K_{sp}(AgCl) = 2.8 \times 10^{-10}$  and  $K_{sp}(AgBr) = 3.3 \times 10^{-13}$ . (1992)
- The standard reduction potential for the half-cell  $NO_3^-(aq) + 2H^+(aq) + e^- \rightarrow NO_2(g) + H_2O$  is 0.78 V  
 (a) Calculate the reduction potential at 8 M  $H^+$ .  
 (b) What will be the reduction potential of the half-cell in a neutral solution? Assume all other species to be at unit concentration. (1993)
- The standard reduction potential of the  $Ag^+ \mid Ag$  electrode at 298 K is 0.799 V. Given that for  $AgI$ ,  $K_{sp} = 8.7 \times 10^{-17}$ , evaluate the potential of the  $Ag^+ \mid Ag$  electrode in a saturated solution of  $AgI$ . Also calculate the standard reduction potential of the  $I^- \mid AgI \mid Ag$  electrode. (1994)
- The standard reduction potential for  $Cu^{2+} \mid Cu$  is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple in a saturated solution of cupric hydroxide.  $K_{sp}$  of  $Cu(OH)_2$  is  $1.0 \times 10^{-19}$ . (1996)
- Calculate the equilibrium constant for the reaction  $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$ .  
 (given:  $E_{Ce^{4+}|Ce^{4+}}^\circ = 1.44\text{ V}$  and  $E_{Fe^{3+}|Fe^{2+}}^\circ = 0.68\text{ V}$ ). (1997)
- Calculate the equilibrium constant for the reaction  $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$ . The standard reduction potentials in acidic conditions are 0.77 V and 0.54 V respectively for  $Fe^{3+} \mid Fe^{2+}$  and  $I_3^- \mid I^-$  couples. (1998)
- Find the solubility product of a saturated solution of  $Ag_2CrO_4$  in water at 298 K if the emf of the cell  $Ag \mid Ag^+ \text{ (satd. } Ag_2CrO_4 \text{ soln)} \parallel Ag^+(0.1\text{ M}) \mid Ag$  is 0.164 V at 298 K. (1998)
- A cell,  $Ag \mid Ag^+ \parallel Cu^{2+} \mid Cu$ , initially contains 1 M  $Ag^+$  and 1 M  $Cu^{2+}$  ions. Calculate the change in the cell potential after the passage of 9.65 A of current for 1 h. (1999)
- The following electrochemical cell has been set up.  
 $Pt(1) \mid Fe^{3+}, Fe^{2+} (a = 1) \parallel Ce^{4+}, Ce^{3+} (a = 1) \mid Pt(2)$   
 Given that  $E^\circ(Fe^{3+}, Fe^{2+}) = 0.77\text{ V}$  and  $E^\circ(Ce^{4+}, Ce^{3+}) = 1.61\text{ V}$   
 If an ammeter is connected between two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? (2000)
- The Edison storage cell is represented as  $Fe(s) \mid FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid Ni(s)$   
 The half-cell reactions are

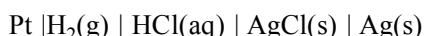


- (i) What is the cell reaction ?  
(ii) What is the cell emf? How does it depend on the concentration of KOH ?  
(iii) What is the maximum amount of electrical energy that can be obtained from one mole of  $\text{Ni}_2\text{O}_3$ ?  
(1994)

17. An excess of liquid mercury is added to an acidified solution of  $1.0 \times 10^{-3}$  M  $\text{Fe}^{3+}$ . It is found that 5% of  $\text{Fe}^{3+}$  remains at equilibrium at  $25^\circ\text{C}$ . Calculate  $E_{\text{Hg}_2^{2+}|\text{Hg}}^\circ$ , assuming that the only reaction that occurs is  $2 \text{Hg} + 2 \text{Fe}^{3+} \rightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+}$ .

(Given  $E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^\circ = 0.77 \text{ V}$ ).(1995)

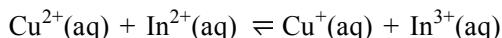
18. The standard potential of the following cell is 0.23 V at  $15^\circ\text{C}$  and 0.21 V at  $35^\circ\text{C}$ .



- (i) Write the cell reaction.  
(ii) Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range  $15^\circ\text{C}$  to  $35^\circ\text{C}$ .  
(iii) Calculate the solubility of AgCl at  $25^\circ\text{C}$ . Given: The standard reduction potential of the  $\text{Ag}^+(\text{aq})|\text{Ag}(\text{s})$  couple is 0.80 V at  $25^\circ\text{C}$ .(2001)

19. Two Daniell cells contain the same solution of  $\text{ZnSO}_4$  but differ in the  $\text{CuSO}_4$  solution. The emf of the cell containing 0.5 M  $\text{CuSO}_4$  is higher than the other cell by 0.06 V. Calculate the concentration of  $\text{CuSO}_4$  in the other cell.(2003)

20. Determine the standard equilibrium constant at 298 K for the reaction



Given that  $E^\circ(\text{Cu}^{2+} \mid \text{Cu}) = 0.335 \text{ V}$ ,  $E^\circ(\text{Cu}^+ \mid \text{Cu}) = 0.52 \text{ V}$ ,  $E^\circ(\text{In}^{3+}, \text{In}^+ \mid \text{Pt}) = - 0.42 \text{ V}$  and  $E^\circ(\text{In}^{2+}, \text{In}^+ \mid \text{Pt}) = - 0.40 \text{ V}$ .(2004)

## ANSWERS

### Straight Objective Type

- |        |        |         |         |         |         |         |
|--------|--------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (c)  | 4. (c)  | 5. (b)  | 6. (a)  | 7. (a)  |
| 8. (b) | 9. (b) | 10. (c) | 11. (a) | 12. (c) | 13. (c) | 14. (d) |

### Multiple Correct-Choice Type

1. (a), (b), (d)      2. (a), (c)

### Fill-in-the-Blanks Type

1. greater

### True/False Type

1. False      2. False

## Linked Comprehension Type

### Passage 1

1. (b)      2. (a)      3. (a)

### Passage 2

1. (c)      2. (d)      3. (a)

### Passage 3

1. (b)      2. (c)

### Passage 4

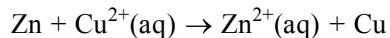
1. (b)      2. (d)

## Matching Type

1. (d)

## Subjective Type

1. (i) Cell reaction



- (ii) 1.113 V

- (iii) spontaneous

6.  $5.6 \times 10^{-18}$  M

8. 0.887 V; - 0.046 V

9. 0.324 V; 0.151 V

11.  $7.14 \times 10^{12}$

13.  $2.29 \times 10^{-12}$  M<sup>3</sup>

15. Current from Pt(1) to Pt(2);  $E_{\text{cell}}$  decreases with the passage of time.

17. 0.792 V

18. (i)  $2 \text{AgCl}(\text{s}) + \text{H}_2(\text{g}) \rightarrow 2\text{Ag}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$

- (ii)  $\Delta H^\circ = -99974 \text{ J mol}^{-1}$ ;

$$\Delta S^\circ = 193 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (iii)  $1.25 \times 10^{-5}$  M

2. pH = 8.67

3.  $10^{-4}$  M

4.  $1.1 \times 10^{-14}$

5.  $1.523 \times 10^{-9}$  M

7. - 0.0371 V; Ag as cathode;  
Br<sup>-</sup> | AgBr | Ag as anode.

10. - 0.22 V

12.  $5.98 \times 10^7$

14. - 0.010 V

16. (i)  $\text{Fe}(\text{s}) + \text{Ni}_2\text{O}_3(\text{s}) = \text{FeO}(\text{s}) + 2\text{NiO}(\text{s})$

- (ii) 1.27 V

- (iii) - 245.11 kJ mol<sup>-1</sup>

19. 0.005 M

20.  $10^{10}$

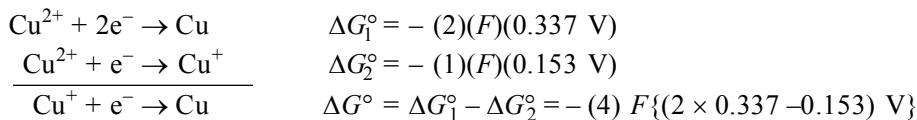
## HINTS AND SOLUTIONS

## Straight Objective Type

- More negative the standard potential, least the reduction tendency of the ion. The corresponding atom has largest oxidation tendency and thus is a strong reducing agent. In the present case, Zn is the strongest reducing agent.
- In the given reaction H<sub>2</sub> is oxidised to H<sup>+</sup> and AgCl is reduced to Ag. Hence, the cell with these reactions is Pt | H<sub>2</sub>(g) | HCl (aq) | AgCl (s) | Ag
- In the given reaction Zn is oxidised to Zn<sup>2+</sup> and Fe<sup>2+</sup> is reduced to Fe. Hence,

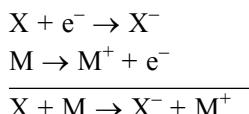
$$E_{\text{cell}} = E^\circ_{\text{Fe}^{2+}|\text{Fe}} - E^\circ_{\text{Zn}^{2+}|\text{Zn}} = -0.41 \text{ V} - (-0.76 \text{ V}) = 0.35 \text{ V.}$$

4. Since  $\Delta G^\circ = -nFE^\circ$ , we have



$$E_{\text{Cu}^+|\text{Cu}} = 2 \times 0.337 \text{ V} - 0.153 \text{ V} = 0.521 \text{ V}$$

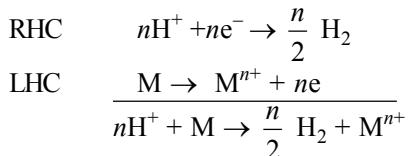
5. The standard potential of hydrogen electrode is assumed to be zero at all temperatures.  
 6. More negative the standard potential, least the tendency of the cation to be reduced. The corresponding atom has larger tendency for oxidation and hence larger reducing power.  
 7. The order of reduction tendencies is  $Z > Y > X$ . Hence, Y can oxidise X and not Z.  
 8. For the given cell, the reaction is



The cell potential is  $E = E^\circ(\text{X}|\text{X}^-) - E^\circ(\text{M}^+|\text{M}) = 0.33 \text{ V} - 0.44 \text{ V} = -0.11 \text{ V}$

Since the cell potential is negative, the cell reaction is not spontaneous.

9. The cell reaction of  $\text{M}|\text{M}^{n+} \text{ (aq)} \parallel \text{H}^+ (\alpha = 1)|\text{H}_2 \text{ (1atm)} \mid \text{Pt}$  is



with  $E_{\text{cell}} = E_{\text{RHC}} - E_{\text{LHC}} = -E_{\text{M}^{n+}|\text{M}}$

If  $E_{\text{ext}}$  is greater than  $|E_{\text{cell}}|$ , the above reaction is reversed causing  $\text{M}^{n+}$  to reduce to M. Thus, for reducing

$\text{Ag}^+$  to  $\text{Ag}$   $E_{\text{ext}} > |-0.80 \text{ V}|$ , say  $0.81 \text{ V}$

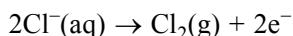
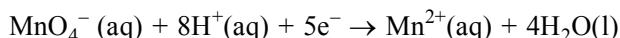
$\text{Hg}_2^{2+}$  to  $\text{Hg}$   $E_{\text{ext}} > |-0.79 \text{ V}|$ , say  $0.80 \text{ V}$

$\text{Cu}^{2+}$  to  $\text{Cu}$   $E_{\text{ext}} > |-0.34 \text{ V}|$ , say  $0.35 \text{ V}$

$\text{Mg}^{2+}$  to  $\text{Mg}$   $E_{\text{ext}} > 2.37 \text{ V}$ , say  $-2.38$

Hence, the order of reduction with increase in external potential will be  $\text{Mg}^{2+}, \text{Cu}^{2+}, \text{Hg}_2^{2+}$  and  $\text{Ag}^+$ .

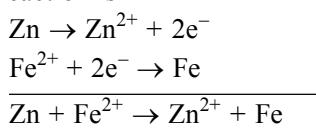
11. The statement is incorrect as  $\text{MnO}_4^-$  in aqueous HCl also oxidises  $\text{Cl}^-$  to  $\text{Cl}_2$ .



The standard emf of the cell producing above two reactions is

$$\begin{aligned} E_{\text{cell}}^\circ &= E_R^\circ - E_L^\circ = E_{\text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+|\text{Pt}}^\circ - E_{\text{Cl}^-|\text{Cl}_2|\text{Pt}}^\circ \\ &= 1.51 \text{ V} - 1.40 \text{ V} = 0.11 \text{ V} \end{aligned}$$

12. The cell reaction is



The cell emf is given by  $E = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]}$

Substituting the given data, we get  $0.349\text{ V} = E^\circ - \frac{(0.059\text{ V})}{2} \log \left( \frac{0.001}{0.01} \right)$

This gives  $E^\circ = 0.349\text{ V} - 0.029\text{ V} = 0.32\text{ V}$

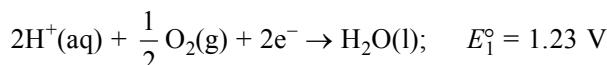
Since  $\Delta G^\circ = -nFE^\circ = -RT \ln K_{\text{eq}}^\circ$ , we get

$$\ln K_{\text{eq}}^\circ = \frac{nF}{RT} E^\circ$$

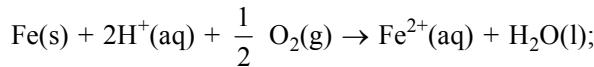
At 25 °C, we have  $\log K_{\text{eq}}^\circ = \left( \frac{1}{0.0295\text{ V}} \right) (0.32\text{ V}) = \frac{0.32}{0.0295}$

Hence,  $K_{\text{eq}}^\circ = 10^{(0.32/0.0295)}$

- 13.** From the given data, we have



Subtract \_\_\_\_\_



$$E^\circ = E_1^\circ - E_2^\circ = (1.23 + 0.44)\text{ V} = 1.67\text{ V}$$

The given reaction is obtained by multiplying the above reaction by 2. Hence, in the given reaction, the number of electrons involved is 4. Thus

$$\Delta G^\circ = -nFE^\circ = -(4)(96\,500\text{ C mol}^{-1})(1.67\text{ V})$$

$$= -644\,620\text{ J mol}^{-1} = -644.62\text{ kJ mol}^{-1}$$

- 14.** The Nernst equation for the given reaction is

$$E = E^\circ - \frac{RT}{4F} \ln \frac{\left( [\text{Fe}^{2+}] / c^\circ \right)^2}{\left( p_{\text{O}_2} / p^\circ \right) \left( [\text{H}^+] / c^\circ \right)^4}$$

where  $p^\circ = 1\text{ atm}$  and  $c^\circ = 1\text{ M}$ . Substituting the given values, we get

$$E = 1.67\text{ V} - \left( \frac{0.059\text{ V}}{4} \right) \log \frac{(10^{-3})^2}{(0.1)(10^{-3})^4}$$

$$= 1.67\text{ V} - \left( \frac{0.059\text{ V}}{4} \right) \log (10^7)$$

$$= (1.67 - 0.059 \cdot 7/4)\text{ V}$$

$$= (1.67 - 0.103)\text{ V} = 1.57\text{ V}$$

### Multiple Correct-Choice Type

- 1.** Since the metal is to be oxidised by the  $\text{NO}_3^-$  ion in an aqueous solution, the left half cell will be that of metal-metal ion and right half cell will be that of  $\text{NO}_3^-$  ion. The emf of the overall cell will be

$$E_{\text{cell}}^\circ = E_{\text{RHC}}^\circ - E_{\text{LHC}}^\circ = 0.96\text{ V} - E_{\text{LHC}}^\circ$$

In order that the oxidation of metal is feasible, we must have  $E_{\text{cell}}^\circ$  positive, for that we must have  $E_{\text{LHC}}^\circ < 0.96\text{ V}$ . The choices (a), (b) and (d) satisfy this condition.

2. The salt bridge is used to connect the two half-cells of a galvanic cells. It does not participate chemically in the cell reaction.

The two half-cells are not in direct touch with each other. Thus, salt bridge does not stop the diffusion of ions from one electrode to another.

There are many galvanic cells which do not require the use of salt bridge. One of the examples is lead accumulator. However, a galvanic cell which requires the use of a salt bridge, the cell reaction will not occur without the salt bridge.

### True/False Type

- It is Fe which can reduce  $\text{Cu}^{2+}$  to Cu.
- The factor of value 0.0591 appears when the temperature is 298 K and not 273 K.

### Linked Comprehension Type

#### Passage 1

- The value of  $E_{\text{cell}}^{\circ}$  producing the given reaction is

$$E^{\circ} = E_1^{\circ} - E_2^{\circ} = 0.80 \text{ V} - 0.05 \text{ V} = 0.75 \text{ V}$$

$$\text{Thus } \log K_{\text{eq}}^{\circ} = \frac{nFE^{\circ}}{2.303 RT} = \frac{nE^{\circ}}{2.303 RT/F} = \frac{2(0.75 \text{ V})}{(0.059 \text{ V})} = 25.4$$

- The expression of  $E_2$  is

$$E_2 = E_2^{\circ} - \frac{RT}{2F} \ln \frac{[\text{C}_6\text{H}_{12}\text{O}_6]}{[\text{C}_6\text{H}_{12}\text{O}_7][\text{H}^+]^2}$$

The addition of  $\text{NH}_3$  causes increase in pH, i.e. decrease in  $[\text{H}^+]$ . This makes  $E_2$  more negative. The expression of  $E_1$  is

$$E_1 = E_1^{\circ} - \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]}$$

The addition of  $\text{NH}_3$  forms the complex with  $\text{Ag}^+$ , decreasing its concentration and thus making  $E_1$  more negative.

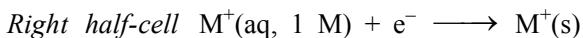
- The value  $E_3^{\circ} < E_1^{\circ}$ . This implies that  $[\text{Ag}(\text{NH}_3)_2]^+$  is a weaker oxidising agent than  $\text{Ag}^+$ .

#### Passage 2

- Larger value of reduction potential implies larger reduction tendency hence larger oxidising ability. The reduction potential  $\text{Cl}_2 | \text{Cl}^- | \text{Pt}$  is larger than  $\text{I}_2 | \text{I}^- | \text{Pt}$ . Hence,  $\text{Cl}_2$  can oxidise  $\text{I}^-$  to  $\text{I}_2$ .
- The reduction potential of  $\text{Mn}^{3+}, \text{Mn}^{2+} | \text{Pt}$  is larger than  $\text{H}_3\text{O}^+ | \text{O}_2 | \text{Pt}$ . Hence,  $\text{Mn}^{3+}$  can oxidise  $\text{H}_2\text{O}$  to  $\text{O}_2$ .
- The blue coloration is due to the formation of ferric ferrocyanide,  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

#### Passage 3

- For the cell  $\text{M(s)} | \text{M}^+(\text{aq}, 0.05 \text{ M}) \parallel \text{M}^+(\text{aq}, 1 \text{ M}) | \text{M(s)}$ , we have



The emf of the cell is  $E = -\frac{RT}{F} \ln \frac{(0.05 \text{ M})}{(1 \text{ M})}$

At 25 °C, we have  $E = + (0.059 \text{ V}) \log (20) = 0.0768 \text{ V}$

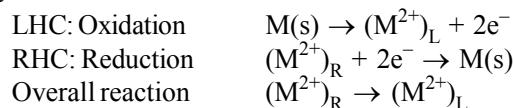
Since  $E = +\text{ve}$ ,  $\Delta G (= -nFE)$  will be less than zero.

2. We have  $E = -\frac{RT}{F} \ln \frac{(0.0025 \text{ M})}{(1 \text{ M})}$

At 25 °C, we have  $E = (0.059 \text{ V}) \log (400) = 0.154 \text{ V} = 154 \text{ mV}$

#### Passage-4

1., 2. The cell reaction may be obtained as follows.



The cell potential is

$$E = \frac{RT}{2F} - \ln \left\{ \frac{[\text{M}^{2+}]_{\text{L}} / \text{mol dm}^{-3}}{[\text{M}^{2+}]_{\text{R}} / \text{mol dm}^{-3}} \right\} \text{ i.e., } 0.059 \text{ V} = - \left( \frac{0.059 \text{ V}}{2} \right) \log \left\{ \frac{[\text{M}^{2+}]_{\text{L}} / \text{mol dm}^{-3}}{0.001} \right\}$$

This gives  $\log ([\text{M}^{2+}]_{\text{L}}/\text{mol dm}^{-3}) = -2 + \log (0.001) = -2 - 3 = -5$  i.e.,  $[\text{M}^{2+}]_{\text{L}} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$

From the reaction



$$K_{\text{sp}} = [\text{M}^{2+}][\text{X}^2] = (\text{s})(2\text{s})^2 = 4\text{s}^3 = 4 (1.0 \times 10^{-5} \text{ mol dm}^{-3})^3 = 4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$$

The  $\Delta G$  of the cell reaction is

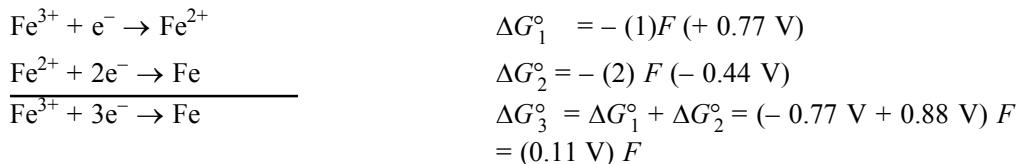
$$\Delta G = -nFE = - (2) (96500 \text{ C mol}^{-1}) (0.059 \text{ V}) = -11387 \text{ J mol}^{-1} = -11.4 \text{ kJ mol}^{-1}$$

Hence, we have

1. The choice (b) is correct.
2. The choice (d) is correct.

#### Matching Type

1. For the choice P of List I, we have

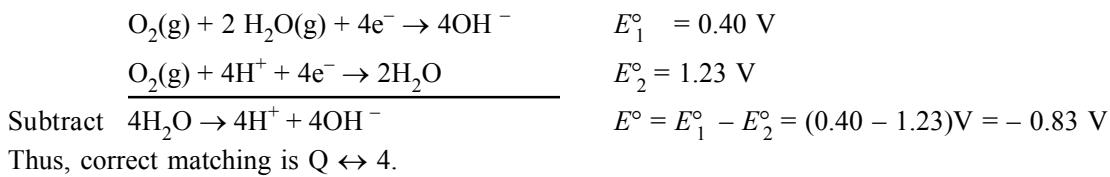


$$E_3^\circ = \Delta G_3^\circ / (-3F) = -0.04 \text{ V}$$

Since this value appears in the choice 3 of List II, we will have the matching (P)  $\leftrightarrow$  3. With this matching alone, one can say that the choice (d) of the given codes is correct.

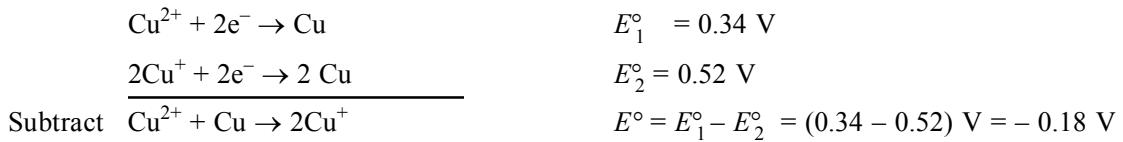
However, we may proceed to prove the remaining matching of the choice (d).

For the choice Q of List I, we have

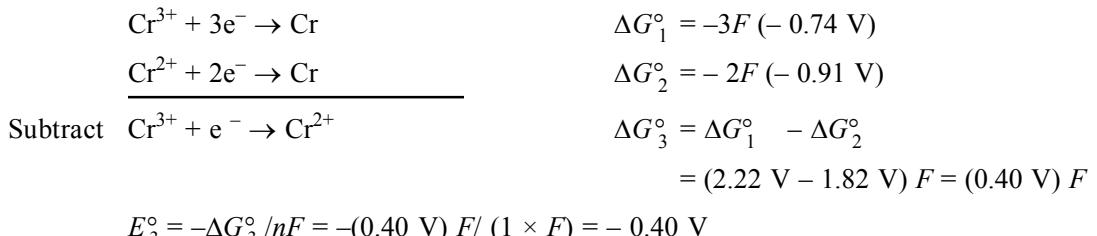


Thus, correct matching is Q  $\leftrightarrow$  4.

For the choice R of List I, we have



For the choice S of List I, we have

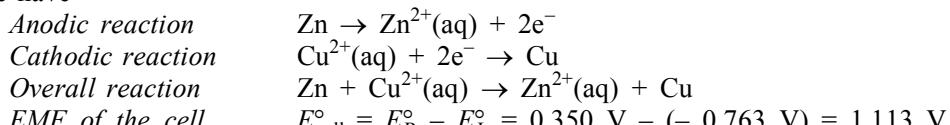


The correct matching is S  $\leftrightarrow$  2.

Therefore, the choice (d) of the given code is correct.

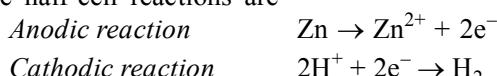
## Subjective Type

1. We have



Since  $E_{\text{cell}}^\circ$  is positive, the cell reaction is spontaneous.

2. The half-cell reactions are



The Nernst equation for the cell reaction is

$$E = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]p(\text{H}_2)}{[\text{H}^+]^2}$$

$$\text{where } E^\circ = E_{\text{H}_2|\text{Pt}}^\circ - E_{\text{Zn}^{2+}|\text{Zn}}^\circ = 0 - (-0.763 \text{ V}) = 0.763 \text{ V}$$

Substituting the given data in Nernst equation, we get

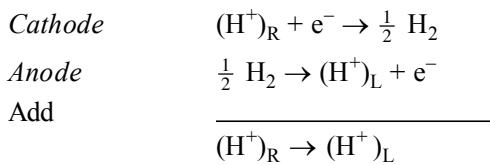
$$0.28 \text{ V} = 0.763 \text{ V} - \frac{0.05915 \text{ V}}{2} \log \frac{(0.1)(1)}{([\text{H}^+]/\text{mol dm}^{-3})^2}$$

$$\begin{aligned}
 \text{This gives } -\log ([\text{H}^+]/\text{mol dm}^{-3}) &= \frac{1}{2} \left[ \frac{2(0.763 \text{ V} - 0.28 \text{ V})}{(0.05915 \text{ V})} - \log(0.1) \right] \\
 &= \frac{1}{2} [16.33 + 1] = 8.67
 \end{aligned}$$

Thus, the pH of the solution is 8.67.

3. The given cell is Pt | H<sub>2</sub>(1 bar) | H<sup>+</sup>(10<sup>-6</sup>M) || H<sup>+</sup>(?) | H<sub>2</sub>(1 bar) | Pt

The cell reactions are



The cell potential is given as

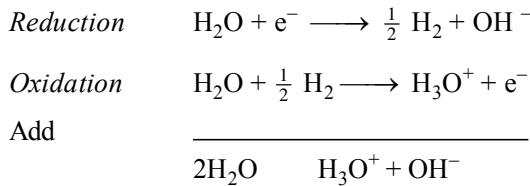
$$E_{\text{cell}} = -\frac{RT}{F} \ln \frac{[\text{H}^+]_L}{[\text{H}^+]_R}$$

$$\text{which gives } 0.118 \text{ V} = -(0.05915 \text{ V}) \log \frac{10^{-6}}{[\text{H}^+]_R / \text{M}}$$

$$\text{or } \log ([\text{H}^+]_R / \text{M}) = (\log 10^{-6}) + 2 = -6 + 2 = -4$$

$$\text{i.e. } [\text{H}^+]_R = 10^{-4} \text{ M.}$$

4. The reaction  $2\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$  may be obtained by the addition of the following two half reactions.



The standard emf of the cell, producing the above reactions is

$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = -0.8277 \text{ V} - 0 \text{ V} = -0.8277 \text{ V}$$

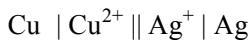
$$\text{Now } \log K^\circ = \frac{nFE^\circ}{2303RT} = \frac{(1)(96500 \text{ C mol}^{-1})(-0.8277 \text{ V})}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = -13.9985$$

$$\text{i.e. } K^\circ = 1.1 \times 10^{-14}.$$

5. We have



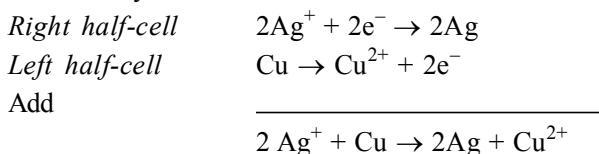
Since  $E_{\text{Ag}^+|\text{Ag}}^\circ$  is greater than  $E_{\text{Cu}^{2+}|\text{Cu}}^\circ$ , the half cell  $\text{Ag}^+|\text{Ag}$  will constitute the cathode of the galvanic cell. Hence, the required cell is



Its standard emf is

$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = 0.799 \text{ V} - 0.337 \text{ V} = 0.462 \text{ V}$$

The cell reaction may be obtained as follows.



Its Nernst equation is

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

For  $E = 0$ , we will have

$$0 = 0.462 \text{ V} - \left( \frac{0.05915 \text{ V}}{2} \right) \log \frac{0.01}{([\text{Ag}^+]/\text{M})^2}$$

$$\text{or } \log \frac{0.01}{([\text{Ag}^+]/\text{M})^2} = \frac{2 \times 0.462}{0.05915} = 15.6345$$

$$\text{or } 2 \log ([\text{Ag}^+]/\text{M}) = \log 0.01 - 15.6345$$

$$\text{or } \log ([\text{Ag}^+]/\text{M}) = \frac{-2 - 15.6345}{2} = -8.8173$$

$$\text{or } [\text{Ag}^+] = 1.523 \times 10^{-9} \text{ M.}$$

6. The reaction to be considered is



The cell producing this reaction would be



with standard cell potential as

$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = -0.24 \text{ V} - (-0.75 \text{ V}) = 0.51 \text{ V}$$

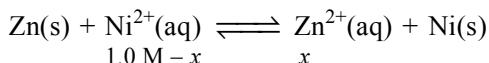
The equilibrium constant of the reaction would be given as

$$\log K_{\text{eq}} = \frac{nFE^\circ}{2.303RT} = \frac{(2)(96500 \text{ C mol}^{-1})(0.51 \text{ V})}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 17.25$$

$$\text{Hence } K_{\text{eq}} = 1.78 \times 10^{17}$$

Let  $x$  be the concentration of  $\text{Ni}^{2+}$  ions that have been reduced to Ni at equilibrium.

We will have



$$\text{Thus } K_{\text{eq}} = \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = \frac{x}{1.0 \text{ M} - x}$$

Solving for  $x$ , we would get

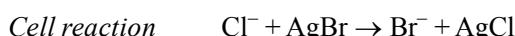
$$x \approx \frac{K_{\text{eq}} \times 1.0 \text{ M}}{1 + K_{\text{eq}}} \approx 1.0 \text{ M}$$

$$\text{Now } [\text{Ni}^{2+}] = \frac{[\text{Zn}^{2+}]}{K_{\text{eq}}} = \frac{1.0 \text{ M}}{1.78 \times 10^{17}} = 5.6 \times 10^{-18} \text{ M.}$$

7. The cell reaction and its potential may be determined as follows.

<i>Half-cell</i>	<i>Reduction reaction</i>	<i>Reduction potential</i>
(i) LHC	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	$E_{\text{Cl}^- \text{AgCl} \text{Ag}} = E_{\text{Cl}^- \text{AgCl} \text{Ag}}^\circ - \frac{RT}{F} \ln [\text{Cl}^-]$
(ii) RHC	$\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$	$E_{\text{Br}^- \text{AgBr} \text{Ag}} = E_{\text{Br}^- \text{AgBr} \text{Ag}}^\circ - \frac{RT}{F} \ln [\text{Br}^-]$

Subtracting Eq. (i) from Eq. (ii), we get



$$\text{Cell potential} \quad E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{F} \ln \frac{[\text{Br}^-]}{[\text{Cl}^-]} \quad (1)$$

$$\text{where} \quad E_{\text{cell}}^{\circ} = E_{\text{Br}^-|\text{AgBr}|\text{Ag}}^{\circ} - E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ}$$

The expression of  $E_{\text{Br}^-|\text{AgBr}|\text{Ag}}^{\circ}$  (or  $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ}$ ) may be derived in terms of  $E_{\text{Ag}^+|\text{Ag}}^{\circ}$  and the corresponding solubility product constant of AgBr (or AgCl).

In the assembly  $\text{Br}^-|\text{AgBr}|\text{Ag}$ , some AgBr will dissolve in KBr solution whose solubility will be dictated through solubility product constant. The half-cell  $\text{Br}^-|\text{AgBr}|\text{Ag}$  may be equivalently taken as  $\text{Ag}^+|\text{Ag}$ . The potential of half-cell computed through  $\text{Br}^-|\text{AgBr}|\text{Ag}$  and  $\text{Ag}^+|\text{Ag}$  will be identical, i.e.

$$E_{\text{Br}^-|\text{AgBr}|\text{Ag}} = E_{\text{Ag}^+|\text{Ag}}$$

$$\text{or} \quad E_{\text{Br}^-|\text{AgBr}|\text{Ag}}^{\circ} - \frac{RT}{F} \ln [\text{Br}^-] = E_{\text{Ag}^+|\text{Ag}}^{\circ} - \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]}$$

$$\text{or} \quad E_{\text{Br}^-|\text{AgBr}|\text{Ag}}^{\circ} = E_{\text{Ag}^+|\text{Ag}}^{\circ} + \frac{RT}{F} \ln [\text{Ag}^+] [\text{Br}^-] = E_{\text{Ag}^+|\text{Ag}}^{\circ} + \frac{RT}{F} \ln K_{\text{sp}}(\text{AgBr})$$

$$\text{Similarly, } E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ} = E_{\text{Ag}^+|\text{Ag}}^{\circ} + \frac{RT}{F} \ln K_{\text{sp}}(\text{AgCl})$$

$$\text{Thus} \quad E_{\text{cell}}^{\circ} = E_{\text{Br}^-|\text{AgBr}|\text{Ag}}^{\circ} - E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^{\circ} = \frac{RT}{F} \ln \frac{K_{\text{sp}}(\text{AgBr})}{K_{\text{sp}}(\text{AgCl})}$$

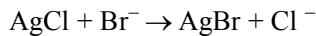
Substituting the values, we get

$$E_{\text{cell}}^{\circ} = (0.059 \text{ V}) \log \left( \frac{3.3 \times 10^{-13}}{2.8 \times 10^{-10}} \right) = -0.173 \text{ V}$$

With this, Eq. (1) becomes

$$E_{\text{cell}}^{\circ} = (-0.173 \text{ V}) - (0.059 \text{ V}) \log \left( \frac{0.001}{0.2} \right) = -0.037 \text{ V}$$

Since the cell potential comes out to be negative, the cell reaction will be nonspontaneous. The spontaneous reaction will be



with  $\text{Cl}^-|\text{AgCl}|\text{Ag}$  serving as cathode (positive terminal) and  $\text{Br}^-|\text{AgBr}|\text{Ag}$  serving as anode (negative terminal). The spontaneity is due to the fact that AgBr is less soluble than AgCl.

[Alternatively, the given cell may be written as



with the cell reaction as  $(\text{Ag}^+)_{\text{R}} \rightarrow (\text{Ag}^+)_{\text{L}}$

$$\text{and cell potential as} \quad E_{\text{cell}} = -\frac{RT}{F} \ln \frac{[\text{Ag}^+]_{\text{L}}}{[\text{Ag}^+]_{\text{R}}}$$

Now  $[\text{Ag}^+]_{\text{L}}$  and  $[\text{Ag}^+]_{\text{R}}$  may be computed through solubility product expressions. Hence, we have

$$E_{\text{cell}} = -\frac{RT}{F} \ln \left( \frac{K_{\text{sp}}(\text{AgCl})/[\text{Cl}^-]}{K_{\text{sp}}(\text{AgBr})/[\text{Br}^-]} \right) = -(0.059 \text{ V}) \log \left( \frac{2.8 \times 10^{-10}/0.2}{3.3 \times 10^{-13}/0.001} \right) = -0.037 \text{ V.}$$

8. For the half-cell reaction  $\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ , the Nernst equation is

$$E = E^{\circ} - \frac{RT}{F} \ln \frac{P_{\text{NO}_2}}{[\text{NO}_3^-][\text{H}^+]^2}$$

(a) In 8 M H<sup>+</sup>, we have

$$\begin{aligned} E &= (0.78 \text{ V}) - (0.059 15 \text{ V}) \log \frac{1}{8^2} = 0.78 + (0.059 15) (2) \log 8 \\ &= 0.78 + (0.059 15) (2) (0.903) = 0.887 \text{ V} \end{aligned}$$

(b) For a neutral solution at 25 °C, [H<sup>+</sup>] = 10<sup>-7</sup> M.

$$\begin{aligned} \text{Hence, } E &= 0.78 \text{ V} - (0.059 15 \text{ V}) \log \frac{1}{(10^{-7})^2} = 0.78 \text{ V} + (0.059 15 \text{ V}) (2) (-7) \\ &= -0.046 \text{ V.} \end{aligned}$$

**9.** The concentration of Ag<sup>+</sup> in the saturated solution of AgI is

$$s = \sqrt{K_{\text{sp}}} = \sqrt{8.7 \times 10^{-17} \text{ M}^2} = 9.33 \times 10^{-9} \text{ M}$$

For the cell reaction Ag<sup>+</sup>(aq) + e<sup>-</sup> → Ag(s), the Nernst equation is

$$E = E^\circ - \frac{RT}{F} \ln \frac{1}{[\text{Ag}^+]}$$

$$\begin{aligned} \text{Hence, } E &= 0.799 \text{ V} - (0.059 15 \text{ V}) \log \left( \frac{1}{9.33 \times 10^{-9}} \right) \\ &= 0.799 \text{ V} - (0.059 15 \text{ V}) (8.030) = 0.799 \text{ V} - 0.475 \text{ V} = 0.324 \text{ V} \end{aligned}$$

The expression relating E<sub>I<sup>-</sup> | AgI | Ag</sub><sup>o</sup> and E<sub>Ag<sup>+</sup> | Ag</sub><sup>o</sup> is

$$\begin{aligned} E_{\text{I}^- \mid \text{AgI} \mid \text{Ag}}^\circ &= E_{\text{Ag}^+ \mid \text{Ag}}^\circ + \frac{RT}{F} \ln K_{\text{sp}}(\text{AgI}) = 0.799 \text{ V} + (0.059 15 \text{ V}) \log (8.7 \times 10^{-17}) \\ &= 0.799 \text{ V} - (0.059 15 \times 16.060 5) \text{ V} = 0.799 \text{ V} - 0.950 \text{ V} = 0.151 \text{ V.} \end{aligned}$$

**10.** For the reaction Cu<sup>2+</sup>(aq) + 2e<sup>-</sup> → Cu(s); the reduction potential is

$$E = E^\circ - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]}$$

From the given data pH = 14 and K<sub>sp</sub>(Cu(OH)<sub>2</sub>) = 1.0 × 10<sup>-19</sup>, we get

$$[\text{H}^+] = 10^{-14} \text{ M}, \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14} \text{ M}^2}{10^{-14} \text{ M}} = 1 \text{ M}$$

$$[\text{Cu}^{2+}] = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} = \frac{1.0 \times 10^{-19} \text{ M}^2}{1 \text{ M}} = 1.0 \times 10^{-19} \text{ M}$$

$$\begin{aligned} \text{Hence, } E &= 0.34 \text{ V} - \left( \frac{0.059 \text{ V}}{2} \right) \log \frac{1}{(1.0 \times 10^{-19})} = 0.34 \text{ V} - \frac{0.059 \times 19 \text{ V}}{2} \\ &= 0.34 \text{ V} - 0.56 \text{ V} \\ &= -0.22 \text{ V} \end{aligned}$$

**11.** The cell producing the reaction Fe<sup>2+</sup> + Ce<sup>4+</sup> ⇌ Fe<sup>3+</sup> + Ce<sup>3+</sup> is  
Pt|Fe<sup>2+</sup>, Fe<sup>3+</sup>||Ce<sup>4+</sup>, Ce<sup>3+</sup>| Pt

The standard cell potential is

$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = 1.44 \text{ V} - 0.68 \text{ V} = 0.76 \text{ V}$$

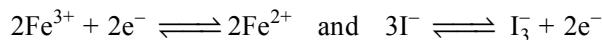
Since ΔG<sup>o</sup> = -nFE<sup>o</sup> and ΔG<sup>o</sup> = -RT ln K<sub>eq</sub><sup>o</sup>, we get

$$\log K_{\text{eq}}^\circ = \frac{nFE^\circ}{2.303 RT} = \frac{(1)(96500 \text{ C mol}^{-1})(0.76 \text{ V})}{(2.303)(8.314 \text{ J K}^{-1}\text{mol}^{-1})(298 \text{ K})} = 12.85$$

$$\text{Hence } K_{\text{eq}}^\circ = 7.14 \times 10^{12}$$

12. The given reaction is  $2\text{Fe}^{3+} + 3\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_3^-$

Its partial reactions are



The standard emf of the cell producing these reactions is

$$E_{\text{cell}}^\circ = E_{\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}}^\circ - E_{\text{I}^-, \text{I}_3^- | \text{Pt}}^\circ = 0.77 \text{ V} - 0.54 \text{ V} = 0.23 \text{ V}$$

Now, using the expression

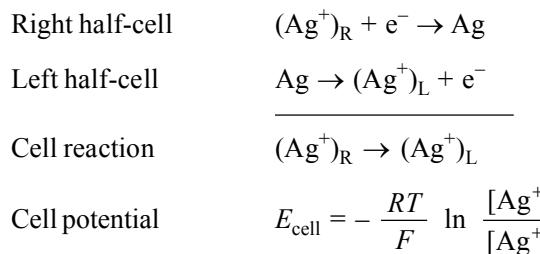
$$\log K^\circ = \frac{nE^\circ}{2.303 RT/F}$$

at 298 K, we get

$$\log K^\circ = \frac{(2)(0.23 \text{ V})}{(0.05915 \text{ V})} = 7.777 \quad \text{or} \quad K^\circ = 5.98 \times 10^7$$

13. The given cell is  $\text{Ag} | \text{Ag}^+(\text{saturated Ag}_2\text{CrO}_4 \text{ soln.}) || \text{Ag}^+(0.1 \text{ M}) | \text{Ag}$

*Cell Reaction*



In the left half-cell, the concentration of  $\text{Ag}^+$  will be related to the solubility product of  $\text{Ag}_2\text{CrO}_4$  as shown in the following.



If  $x$  is the solubility of  $\text{Ag}_2\text{CrO}_4$  in solution, then

$$\begin{aligned} [\text{Ag}^+] &= 2x \quad \text{and} \quad [\text{CrO}_4^{2-}] = x \\ \text{and} \quad K_{\text{sp}} &= [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2x)^2 (x) \quad \text{or} \quad 2x = (K_{\text{sp}}/4)^{1/3} \\ \Rightarrow [\text{Ag}^+]_{\text{L}} &= 2x = 2(K_{\text{sp}}/4)^{1/3} = (2K_{\text{sp}})^{1/3} \end{aligned}$$

With its, the cell potential becomes

$$E_{\text{cell}} = -\frac{RT}{F} \ln \frac{(2K_{\text{sp}})^{1/3}}{[\text{Ag}^+]_{\text{R}}}$$

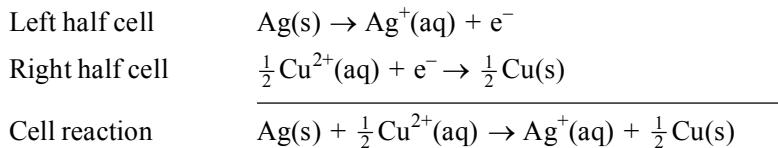
Substituting the given data, we get

$$\begin{aligned} 0.164 \text{ V} &= - (0.059 \text{ V}) \log \frac{(2K_{\text{sp}})^{1/3}}{(0.1 \text{ M})} \\ \text{or} \quad \log (2K_{\text{sp}}/M^3)^{1/3} &= -\frac{0.164}{0.059} + \log 0.1 = -3.78 \\ \text{or} \quad 2K_{\text{sp}}/M^3 &= \text{antilog} (-3 \times 3.78) = 4.57 \times 10^{-12} \\ \text{or} \quad K_{\text{sp}} &= 2.29 \times 10^{-12} \text{ M}^3 \end{aligned}$$

14. Quantity of electricity passed is  $Q = It = (9.65 \text{ A}) (60 \times 60 \text{ s})$

$$\text{Amount of electrons passed is } n = \frac{Q}{F} = \frac{(9.65 \text{ A})(60 \times 60 \text{ s})}{(96500 \text{ C mol}^{-1})} = 0.36 \text{ mol}$$

The cell reaction is



The given data are

Ag(s)	+	$\frac{1}{2}\text{Cu}^{2+}(\text{aq})$	$\rightarrow$	$\text{Ag}^+(\text{aq}) + \frac{1}{2}\text{Cu(s)}$
$t = 0$		1 M		1 M
After passing the current		$(1 - 0.36/2) \text{ M}$		$(1 + 0.36) \text{ M}$

The Nernst equation is

$$E = E^\circ - \frac{RT}{F} \ln \frac{[\text{Ag}^+]}{[\text{Cu}^{2+}]^{1/2}}$$

Substituting the given data, we get

$$E_1 = E^\circ - (0.059 \text{ V}) \log \frac{1}{(1)^{1/2}} = E^\circ$$

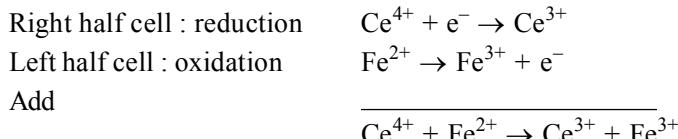
$$E_2 = E^\circ - (0.059 \text{ V}) \log \frac{1.36}{\sqrt{0.82}} = E^\circ - 0.010 \text{ V}$$

$$\Delta E = E_2 - E_1 = -0.010 \text{ V}$$

### 15. For the electrochemical cell



the cell reactions are



The net cell potential is

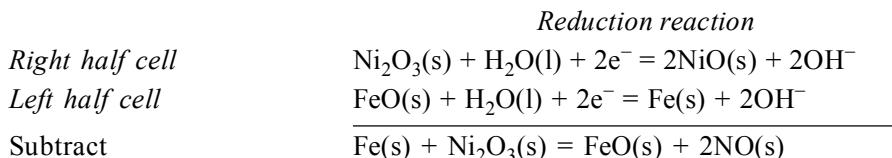
$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = 1.61 \text{ V} - 0.77 \text{ V} = 0.84 \text{ V}$$

Since  $E_{\text{cell}}^\circ$  is positive, the cell reaction is spontaneous. The current in the external circuit will flow from Pt(1) (which serves as anode) to Pt(2), which serves as cathode.

With the passage of time,  $E_{\text{cell}}$  will decrease and so is the current in the external circuit.

### 16. (i) The Edison storage cell is $\text{Fe(s)} | \text{FeO(s)} | \text{KOH(aq)} | \text{Ni}_2\text{O}_3(\text{s}) | \text{Ni}$

The cell reaction is obtained by subtracting reduction reaction of left half-cell from that of right half-cell.



(ii) The cell emf is given as

$$E_{\text{cell}} = E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = 0.40 \text{ V} - (-0.87 \text{ V}) = 1.27 \text{ V}$$

The cell emf is independent of concentration of KOH as no  $\text{OH}^-$  appears in the cell reaction.

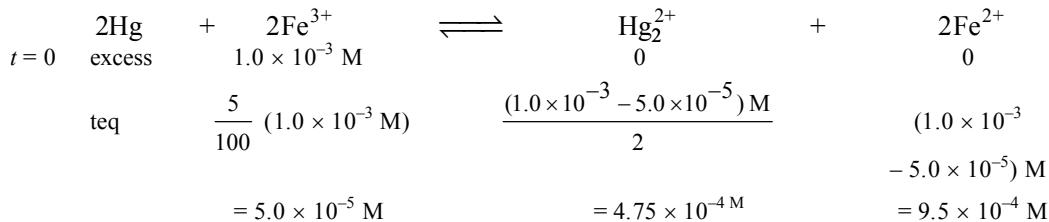
(iii) The maximum electrical energy obtained per mole of  $\text{Ni}_2\text{O}_3$  (in the cell reaction, stoichiometric number of  $\text{Ni}_2\text{O}_3$  is also one) would be

$$\Delta G = -nEF$$

$$= -(2)(96500 \text{ C mol}^{-1})(1.27 \text{ V}) = -2.4511 \times 10^5 \text{ J mol}^{-1}$$

$$= -245.11 \text{ kJ mol}^{-1}$$

17. The reaction occurring is



$$K_{\text{eq}} = \frac{[\text{Hg}_2^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} = \frac{(4.75 \times 10^{-4} \text{ M})(9.5 \times 10^{-4} \text{ M})^2}{(5.0 \times 10^{-5} \text{ M})^2}$$

$$= 0.1715 \text{ M}$$

The cell producing this chemical reaction is



$$\text{with } E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = E_{\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}}^\circ - E_{\text{Hg}_2^{2+} \mid \text{Hg}}^\circ \quad (1)$$

The standard cell potential,  $E_{\text{cell}}^\circ$ , is related to  $K_{\text{eq}}$  by the expression

$$E_{\text{cell}}^\circ = \frac{RT/F}{n} \ln K_{\text{eq}}^\circ$$

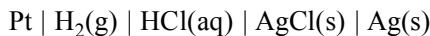
For the given reaction  $n = 2$ . At 298 K, we will have

$$E_{\text{cell}}^\circ = \frac{(0.05916 \text{ V})}{2} \log (0.1715) = -0.02265 \text{ V} \quad (2)$$

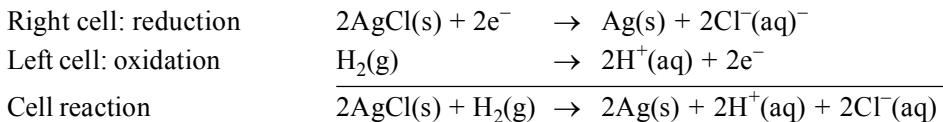
Equating Eqs (1) and (2), we get

$$\begin{aligned} E_{\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}}^\circ - E_{\text{Hg}_2^{2+} \mid \text{Hg}}^\circ &= -0.02265 \text{ V} \\ \text{or } E_{\text{Hg}_2^{2+} \mid \text{Hg}}^\circ &= E_{\text{Fe}^{3+}, \text{Fe}^{2+} \mid \text{Pt}}^\circ + 0.02265 \text{ V} \\ &= 0.77 \text{ V} + 0.02265 \text{ V} \\ &= 0.792 \text{ V} \end{aligned}$$

18. The given cell is



(i) The cell reaction may be obtained as follows.



$$(ii) \Delta G_{15^\circ\text{C}}^\circ = -nFE^\circ = -(2)(96500 \text{ C mol}^{-1})(0.23 \text{ V}) = -44390 \text{ J mol}^{-1}$$

$$\Delta G_{35^\circ\text{C}}^\circ = -nFE^\circ = -(2)(96500 \text{ C mol}^{-1})(0.21 \text{ V}) = -40530 \text{ J mol}^{-1}$$

$$\text{Now } \Delta G_{15^\circ\text{C}}^\circ = \Delta H^\circ - (288 \text{ K}) \Delta S^\circ = -44390 \text{ J mol}^{-1}$$

$$\Delta G_{35^\circ\text{C}}^\circ = \Delta H^\circ - (308 \text{ K}) \Delta S^\circ = -40530 \text{ J mol}^{-1}$$

Solving for  $\Delta H^\circ$  and  $\Delta S^\circ$ , we get

$$\Delta H^\circ = -99974 \text{ J mol}^{-1} \quad \text{and} \quad \Delta S^\circ = -193 \text{ J K}^{-1} \text{ mol}^{-1}$$

(iii) The value of  $\Delta G^\circ$  at 25 °C will be

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - (298 \text{ K}) \Delta S^\circ = -99974 \text{ J mol}^{-1} - (298 \text{ K})(293 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -42460 \text{ J mol}^{-1}\end{aligned}$$

The value of  $E_{\text{Cl}^-|\text{AgCl}|\text{Ag}}^\circ$  at 25 °C will be

$$E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{(-42460 \text{ J mol}^{-1})}{(2)(96500 \text{ C mol}^{-1})} = 0.22 \text{ V}$$

Now using the expression

$$E_{\text{Cl}^-|\text{Ag Cl}|\text{Ag}}^\circ = E_{\text{Ag}^+|\text{Ag}}^\circ + \frac{RT}{F} \ln K_{\text{sp}}^\circ$$

$$\text{we get } 0.22 \text{ V} = 0.80 \text{ V} + (0.05915 \text{ V}) \log K_{\text{sp}}^\circ$$

$$\text{or } \log K_{\text{sp}}^\circ = \frac{(0.22 - 0.80) \text{ V}}{(0.05915 \text{ V})} = -9.806$$

$$\text{Hence } K_{\text{sp}}^\circ = 1.56 \times 10^{-10}$$

$$\text{Solubility of AgCl} = \sqrt{K_{\text{sp}}} = 1.25 \times 10^{-5} \text{ M}$$

**19.** The reaction occurring in a Daniell cell is



$$\text{Its cell emf is given by } E = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

For the two cells, we have

$$E_1 = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]_1} \quad \text{and} \quad E_2 = E^\circ - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]_2}$$

$$\text{Hence, } E_2 - E_1 = \frac{RT}{2F} \ln \frac{[\text{Cu}^{2+}]_2}{[\text{Cu}^{2+}]_1}$$

If  $E_2 > E_1$ , then  $[\text{Cu}^{2+}]_2 > [\text{Cu}^{2+}]_1$ . Hence, we will have

$$0.06 \text{ V} = \left( \frac{0.059 \text{ V}}{2} \right) \log \left( \frac{0.5 \text{ M}}{[\text{Cu}^{2+}]_1} \right)$$

$$\text{Hence } [\text{Cu}^{2+}]_1 = (0.5 \text{ M}) \text{ antilog} \left( -\frac{2 \times 0.06}{0.059} \right) = (0.5 \text{ M}) (0.01) = 0.005 \text{ M}$$

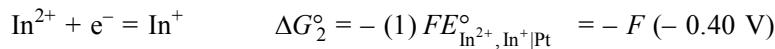
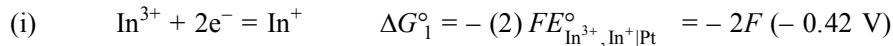
**20.** In the given reaction  $\text{In}^{2+}$  is oxidised to  $\text{In}^{3+}$  and  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$ . The cell producing this reaction is



Its standard cell potential is given by

$$E_{\text{cell}}^\circ = E_R^\circ - E_L^\circ = E_{\text{Cu}^{2+}, \text{Cu}^+|\text{Pt}}^\circ - E_{\text{In}^{3+}, \text{In}^+|\text{Pt}}^\circ$$

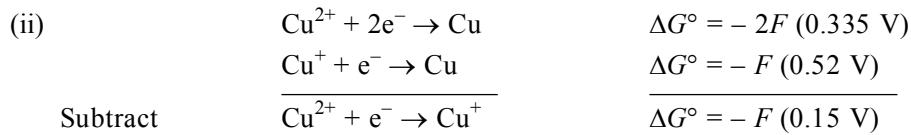
From the given data, we write



From these reactions, we get

$$\begin{aligned} \text{In}^{3+} + \text{e}^- &= \text{In}^{2+} & \Delta G^\circ &= \Delta G_1^\circ - \Delta G_2^\circ = - F (- 0.84 \text{ V} + 0.40 \text{ V}) \\ &&&= - F (- 0.44 \text{ V}) \end{aligned}$$

For this reaction,  $\Delta G^\circ = - F E_{\text{In}^{2+}, \text{In}^+|\text{Pt}}^\circ$ . Hence  $E_{\text{In}^{2+}, \text{In}^+|\text{Pt}}^\circ = - 0.44 \text{ V}$



Hence,  $E_{\text{Cu}^{2+}, \text{Cu}^+|\text{Pt}}^\circ = 0.15 \text{ V}$

Thus, for the given reaction

$$E_{\text{cell}}^\circ = E_{\text{Cu}^{2+}, \text{Cu}^+|\text{Pt}}^\circ - E_{\text{In}^{3+}, \text{In}^{2+}|\text{Pt}}^\circ = 0.15 \text{ V} - (- 0.44 \text{ V}) = 0.59 \text{ V}$$

Finally, from the expression  $\Delta_r G^\circ = - nFE^\circ = - RT \ln K^\circ$

$$\text{we get } \log K^\circ = \frac{n}{(2.303 RT / F)} E^\circ = \frac{1}{(0.059 \text{ V})} (0.59 \text{ V})$$

$$\text{Hence, } K^\circ = 10^{10}$$



# SOLUTIONS

9

## Straight Objective Type

1. An azeotropic solution of two liquids has a boiling point lower than either of them when it
  - (a) shows negative deviation from Raoult's law
  - (b) shows no deviation from Raoult's law
  - (c) shows positive deviation from Raoult's law
  - (d) is saturated

(1981)
2. For a dilute solution, Raoult's law states that
  - (a) the lowering of vapour pressure is equal to the mole fraction of solute
  - (b) the relative lowering of vapour pressure is equal to the mole fraction of solute
  - (c) the relative lowering of vapour pressure is proportional to the amount of solute in the solution
  - (d) the vapour pressure of the solution is equal to the mole fraction of solvent

(1985)
3. A molal solution is one that contains one mole of a solute in
  - (a) 1000 g of the solvent
  - (b) one litre of the solvent
  - (c) one litre of the solution
  - (d) 22.4 litres of the solution

(1986)
4. When mercuric iodide is added to an aqueous solution of potassium iodide the
  - (a) freezing point is raised
  - (b) freezing point is lowered
  - (c) freezing point does not change
  - (d) boiling point does not change

(1987)
5. In which mode of expression the concentration of a solution remains independent of temperature?
  - (a) Molarity
  - (b) Normality
  - (c) Formality
  - (d) Molality

(1988)
6. Which of the following 0.1 M aqueous solutions will have the lowest freezing point?
  - (a) Potassium sulphate
  - (b) Sodium chloride
  - (c) Urea
  - (d) Glucose

(1989)
7. The freezing point of equimolal aqueous solutions will be highest for
  - (a)  $C_6H_5NH_3Cl$ (anilinium chloride)
  - (b)  $Ca(NO_3)_2$
  - (c)  $La(NO_3)_3$
  - (d)  $C_6H_{12}O_6$ (glucose)

(1990)
8. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to
  - (a) ionization of benzoic acid
  - (b) dimerization of benzoic acid
  - (c) trimerization of benzoic acid
  - (d) solvation of benzoic acid

(1996)

9. A 0.004 M solution of  $K_2SO_4$  is isotonic with a 0.010 M solution of glucose at the same temperature. The apparent per cent degree of dissociation of  $K_2SO_4$  is  
 (a) 25%      (b) 50%      (c) 75%      (d) 100%      (2004)
10. The elevation in boiling point when 20.16 g of freshly prepared  $CuCl_2$  (relative molar mass: 134.4) is dissolved in 1 kg of water ( $K_b = 0.52 \text{ kg K mol}^{-1}$ ) is  
 (a) 0.075 °C      (b) 0.150 °C      (c) 0.234 °C      (d) 0.468 °C      (2005)
11. When 20 g of naphthoic acid ( $C_{11}H_8O_2$ ) is dissolved in 50 g of benzene ( $K_f = 1.72 \text{ K kg mol}^{-1}$ ), a freezing point depression of 2 K is observed. The van't Hoff factor ( $i$ ) is  
 (a) 0.5      (b) 1      (c) 2      (d) 3      (2007)
12. The Henry's law constant for the solubility of  $N_2$  gas in water is  $1.0 \times 10^5 \text{ atm}$ . The mole fraction of  $N_2$  in air is 0.8. The amount of  $N_2$  from air dissolved in 10 mol of water at 298 K and 5 atm pressure is  
 (a)  $4.0 \times 10^{-4} \text{ mol}$       (b)  $4.0 \times 10^{-5} \text{ mol}$       (c)  $5.0 \times 10^{-4} \text{ mol}$       (d)  $4.0 \times 10^{-6} \text{ mol}$       (2009)
13. Dissolving 120 g of urea (relative molar mass 60) in 1000 g of water gave a solution of density 1.15 g  $\text{mL}^{-1}$ . The molarity of the solution is  
 (a) 1.78 M      (b) 2.00 M      (c) 2.05 M      (d) 2.22 M      (2011)
14. The freezing point (in °C) of a solution containing 0.1 g of  $K_3[Fe(CN)_6]$  (relative molar mass: 329) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is  
 (a)  $-2.3 \times 10^{-2}$       (b)  $-5.7 \times 10^{-2}$       (c)  $-5.7 \times 10^{-3}$       (d)  $-1.2 \times 10^{-2}$       (2011)
15. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation of boiling point at 1 atm pressure is 2 °C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure of the solution (take  $K_b = 0.76 \text{ K kg mol}^{-1}$ ) is  
 (a) 724 mmHg      (b) 740 mmHg      (c) 736 mmHg      (d) 718 mmHg      (2012)

### Multiple Correct-Choice Type

1. In the depression of freezing point experiment, it is found that the  
 (a) vapour pressure of the solution is less than that of pure solvent  
 (b) vapour pressure of the solution is more than that of pure solvent  
 (c) only solute molecules solidify at the freezing point  
 (d) only solvent molecules solidify at the freezing point      (1999)
2. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are)  
 (a)  $\Delta G$  is positive      (b)  $\Delta S_{\text{system}}$  is positive  
 (c)  $\Delta S_{\text{surroundings}} = 0$       (d)  $\Delta H = 0$       (2013)

### Fill-in-the-Blanks Type

1. 3 g of a salt of molar mass 30 g  $\text{mol}^{-1}$  is dissolved in 250 g of water. The molality of the solution is \_\_\_\_\_.      (1983)
2. Given that  $\Delta T_f$  is the depression in freezing point of the solvent in a solution of a nonvolatile solute of molality,  $m$ , the quantity  $\lim_{m \rightarrow 0} (\Delta T_f / m)$  is equal to \_\_\_\_\_.      (1994)

### Integer Answer Type

- A compound  $H_2X$  with molar mass of  $80 \text{ g mol}^{-1}$  is dissolved in a solvent having density  $0.4 \text{ g mL}^{-1}$ . Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is \_\_\_\_\_ mol  $\text{kg}^{-1}$ . (2014)
- $MX_2$  dissociates into  $M^{2+}$  and  $X^-$  ions in an aqueous solution, with a degree of dissociation ( $\alpha$ ) is 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is \_\_\_\_\_. (2014)
- If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is  $-0.0558 \text{ }^\circ\text{C}$ , the number of chloride(s) in the coordination sphere of the complex is \_\_\_\_\_.  
[ $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$ ] (2015)

### Linked Comprehension Type

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given:

Freezing point depression constant of water ( $K_f^{\text{water}}$ ) =  $1.86 \text{ K kg mol}^{-1}$

Standard boiling point of water =  $373 \text{ K}$

Freezing point depression constant of ethanol ( $K_f^{\text{ethanol}}$ ) =  $2.0 \text{ K kg mol}^{-1}$

Standard boiling point of ethanol =  $351.5 \text{ K}$

Boiling point elevation constant of water ( $K_b^{\text{water}}$ ) =  $0.52 \text{ K kg mol}^{-1}$

Vapour pressure of pure water =  $32.8 \text{ mmHg}$

Boiling point elevation constant of ethanol ( $K_b^{\text{ethanol}}$ ) =  $1.2 \text{ K kg mol}^{-1}$

Vapour pressure of pure ethanol =  $40 \text{ mmHg}$

Standard freezing point of water =  $273 \text{ K}$

Molar mass of water =  $18 \text{ g mol}^{-1}$

Standard freezing point of ethanol =  $155.7 \text{ K}$

Molar mass of ethanol =  $46 \text{ g mol}^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

- The freezing point of the solution **M** is

(a)  $268.7 \text{ K}$       (b)  $268.5 \text{ K}$       (c)  $234.2 \text{ K}$       (d)  $150.9 \text{ K}$

- The vapour pressure of the solution **M** is

(a)  $39.3 \text{ mmHg}$       (b)  $36.0 \text{ mmHg}$       (c)  $29.5 \text{ mmHg}$       (d)  $28.8 \text{ mmHg}$

- Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

(a)  $380.4 \text{ K}$       (b)  $376.2 \text{ K}$       (c)  $375.5 \text{ K}$       (d)  $354.7 \text{ K}$  (2008)

### Subjective Type

- The vapour pressure of pure benzene at  $25 \text{ }^\circ\text{C}$  is  $639.7 \text{ mmHg}$  and the vapour pressure of a solution of a solute in benzene at the same temperature is  $631.9 \text{ mmHg}$ . Calculate the molality of the solution. (1981)
- Two liquids A and B form ideal solutions. At  $300 \text{ K}$ , the vapour pressure of solution containing 1 mol of A and 3 mol of B is  $550 \text{ mmHg}$ . At the same temperature, if one more mole of B is added to this solution, the

vapour pressure of the solution increases by 10 mmHg. Determine the vapour pressures of A and B in their pure states. (1982)

3. The density of a 3 molal sodium thiosulphate solution is  $1.25 \text{ g cm}^{-3}$ . Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate, and (iii) molarities of  $\text{Na}^+$  and  $\text{S}_2\text{O}_3^{2-}$  ions. (1983)
4. The vapour pressures of ethanol and methanol are 44.5 mmHg and 88.7 mmHg, respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol and 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986)
5. A sugar syrup of mass 214.2 g contains 34.2 g of sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). Calculate (i) molality, and (ii) mole fraction of sugar in the syrup. (1988)
6. The vapour pressure of a dilute aqueous solution of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is 750 mmHg at 373 K. Calculate (i) molality and (ii) mole fraction of the solution. (1989)
7. Calculate the molality of a 1 litre solution of 93%  $\text{H}_2\text{SO}_4$  (mass/volume). The density of the solution is  $1.84 \text{ g mL}^{-1}$ . (1990)
8. The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A nonvolatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molar mass of the solid substance? (1990)
9. Addition of 0.643 g of a compound to 50 mL of benzene (density:  $0.879 \text{ g mL}^{-1}$ ) lowers the freezing point from  $5.51^\circ\text{C}$  to  $5.03^\circ\text{C}$ . If  $K_f$  for benzene is  $5.12 \text{ K kg mol}^{-1}$ , calculate the molar mass of the compound. (1992)
10. What mass of the non-volatile solute urea ( $\text{NH}_2\text{CONH}_2$ ) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993)
11. The molar volume of liquid benzene (density =  $0.877 \text{ g mL}^{-1}$ ) increases by a factor of 2750 as it vaporises at  $20^\circ\text{C}$  and that of liquid toluene (density =  $0.867 \text{ g mL}^{-1}$ ) increases by a factor of 7720 at  $20^\circ\text{C}$ . A solution of benzene and toluene at  $20^\circ\text{C}$  has vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. (1996)
12. A very small amount of a nonvolatile solute (that does not dissociate) is dissolved in  $56.8 \text{ cm}^3$  of benzene (density  $0.889 \text{ g cm}^{-3}$ ). At room temperature, vapour pressure of this solution is 98.88 mmHg while that of benzene is 100 mmHg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree Celsius lower than that of benzene, what is the value of molal freezing point depression constant of benzene. (1997)
13. A solution of a non-volatile solute in water freezes at  $-30^\circ\text{C}$ . The vapour pressure of pure water at 298 K is 23.51 mmHg and  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ . Calculate the vapour pressure of this solution at 298 K. (1998)
14. To  $500 \text{ cm}^3$  of water,  $3.0 \times 10^{-3} \text{ kg}$  of acetic acid is added. If 2.3% of acetic acid is dissociated, what will be the depression of freezing point?  $K_f$  and density of water are  $1.86 \text{ K kg mol}^{-1}$  and  $0.997 \text{ g cm}^{-3}$ , respectively. (2000)
15. The degree of dissociation of  $\text{Ca}(\text{NO}_3)_2$  in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at  $100^\circ\text{C}$  is 70 per cent. If the vapour pressure of water at  $100^\circ\text{C}$  is 760 mmHg, calculate the vapour pressure of the solution. (1991)
16. Match the following if the molar mass of X, Y and Z are the same

Solvent	$t_b/\text{ }^\circ\text{C}$	$K_b/\text{kg K mol}^{-1}$
X	127	0.73
Y	27	0.53
Z	253	0.98

(2003)

17. 12.2 g of benzoic acid is dissolved in (i) 1 kg acetone ( $K_b = 1.7 \text{ K kg mol}^{-1}$ ) and (ii) 1 kg benzene ( $K_b = 2.6 \text{ K kg mol}^{-1}$ ). The elevation of boiling points are  $0.17^\circ\text{C}$  and  $0.13^\circ\text{C}$ , respectively.
- What are the molar masses of benzoic acid in the two solutions?
  - What are the structures of benzoic acid in the two solutions? (2004)
18. In 1 kg of a solvent ( $K_f = 14 \text{ K kg}^{-1} \text{ mol}$ ), 75.2 g of phenol was dissolved. The depression in freezing point of the solvent was found to be 7 K. Determine the degree of dimerization of phenol. (2006)

## ANSWERS

### Straight Objective Type

- |         |        |         |         |         |         |         |
|---------|--------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (b) | 3. (a)  | 4. (a)  | 5. (d)  | 6. (a)  | 7. (d)  |
| 8. (b)  | 9. (c) | 10. (c) | 11. (a) | 12. (a) | 13. (c) | 14. (a) |
| 15. (a) |        |         |         |         |         |         |

### Multiple Correct-Choice Type

1. (a), (d)    2. (b), (c), (d)

### Fill-in-the-Blanks Type

1.  $0.4 \text{ mol kg}^{-1}$   
2.  $K_f$

### Integer Answer Type

1. (8)                          2. (2)                          3. (1)

### Linked Comprehension Type

#### Passage-1

1. (d)                          2. (b)  
3. (b)

### Subjective Type

1.  $0.156 \text{ mol kg}^{-1}$   
2.  $p_A^* = 400 \text{ mmHg}; p_B^* = 600 \text{ mmHg}$   
3. (i) 4.27%; 0.051; 4.30 M of  $\text{Na}^+$ ; 2.15 M of  $\text{S}_2\text{O}_3^{2-}$   
4. 66.11 mmHg; 0.656  
5.  $0.556 \text{ mol kg}^{-1}$ ; 0.0099  
6.  $0.732 \text{ mol kg}^{-1}$ ; 0.013
7.  $10.43 \text{ mol kg}^{-1}$   
8.  $69.6 \text{ g mol}^{-1}$   
9.  $156.06 \text{ g mol}^{-1}$   
10.  $(1000/9)\text{g}; (500/27) \text{ mol kg}^{-1}$   
11. 0.735  
12.  $5.028 \text{ K kg mol}^{-1}$   
13. 23.44 mmHg  
14. 0.23 K  
15. 746.3 mmHg  
16.  $K_b(\text{X}) = 0.73 \text{ kg K mol}^{-1}$ ;  
 $K_b(\text{Y}) = 0.53 \text{ kg K mol}^{-1}$ ;  
 $K_b(\text{Z}) = 0.98 \text{ kg K mol}^{-1}$   
17. (a) 122 g mol<sup>-1</sup> in acetone; 244 g mol<sup>-1</sup> in benzene (b) Dimer  
18. 0.75

## HINTS AND SOLUTIONS

### Straight Objective Type

1. Positive deviation from Raoult's law implies higher vapour pressure and thus lower boiling point.

2. Relative lowering of vapour pressure,

$$-\Delta p/p^* = -(p - p^*)/p^* = 1 - p/p^* = 1 - x_1 = x_2$$

3. Molality involves 1000 g of solvent.

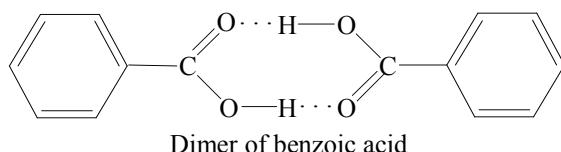
4. The reaction is  $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4$ . Hence,  $2\text{K}^+$  and  $2\text{I}^-$  are replaced by  $2\text{K}^+$  and  $\text{HgI}_4^{2-}$ . There is a decrease in the number of species in the solution. The value of  $-\Delta T_f$  decreases, hence, freezing point is raised.

5. Molality involved a fixed mass of solvent. Hence, this is independent of temperature.

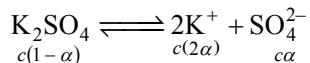
6. Potassium sulphate produces larger number of species and hence larger value of  $-\Delta T_f$ .

7. Glucose being nonelectrolyte produces lesser value of  $-\Delta T_f$  and hence higher freezing point.

8. Benzoic acid exists as dimer in benzene.



9. The dissociation of  $\text{K}_2\text{SO}_4$  may be written as



The concentration of species in the solution is  $c(1 - \alpha) + c(2\alpha) + c\alpha = c(1 + 2\alpha)$  (where  $c = 0.004 \text{ M}$ ). Hence,  $c(1 + 2\alpha) = 0.01 \text{ M}$

$$\text{or } \alpha = \frac{1}{2} \left( \frac{0.01}{0.004} - 1 \right) = 0.75$$

The percent of dissociation is  $0.75 \times 100$ , i.e. 75%.

10. Molality of given solution is

$$m = \frac{n_2}{m_1} = \frac{m_2 / M_2}{m_1} = \frac{(20.16 \text{ g}) / (134.4 \text{ g mol}^{-1})}{(1 \text{ kg})} = 0.15 \text{ mol kg}^{-1}$$

Molality of ions in solution is 3 m, i.e.  $0.45 \text{ mol kg}^{-1}$ .

$$\Delta T_b = K_b m = (0.52 \text{ kg K mol}^{-1})(0.45 \text{ mol kg}^{-1}) = 0.234 \text{ K} \equiv 0.234 \text{ }^\circ\text{C}$$

$$11. \text{ Amount of naphthoic acid} = \frac{20 \text{ g}}{172 \text{ g mol}^{-1}} = \frac{20}{172} \text{ mol}$$

$$\text{Molality of naphthoic acid} = \frac{(20/172) \text{ mol}}{(0.05 \text{ kg})} = \frac{400}{172} \text{ mol kg}^{-1}$$

Using the expression  $(-\Delta T_f) = i K_f m$ , we get

$$i = \frac{(-\Delta T_f)}{K_f m} = \frac{(2 \text{ K})}{(1.72 \text{ K kg mol}^{-1}) \{(400/172) \text{ mol kg}^{-1}\}}$$

$$= 0.5$$

12. Partial pressure of  $N_2$  in 5 atmospheric pressure,  $p_{N_2} = (0.8) (5 \text{ atm}) = 4 \text{ atm}$

By definition, Henry's law is  $p_{N_2} = K_H x_{N_2}$

$$\text{This gives } x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{4 \text{ atm}}{1.0 \times 10^5 \text{ atm}} = 4.0 \times 10^{-5}$$

Since  $x_{N_2} = n_{N_2}/(n_{N_2} + n_{H_2O})$ , in 10 mol of water, the amount of  $N_2$  will be given by the expression

$$4.0 \times 10^{-5} = \frac{n_{N_2}}{n_{N_2} + (10 \text{ mol})}$$

$$\text{Solving for } n_{N_2}, \text{ we get } n_{N_2} = \frac{4.0 \times 10^{-5} (10 \text{ mol})}{1 - 4.0 \times 10^{-5}} = 4.0 \times 10^{-4} \text{ mol}$$

13. Total mass of solution,  $m = 1000 \text{ g} + 120 \text{ g} = 1120 \text{ g}$

$$\text{Volume of the solution, } V = \frac{m}{\rho} = \frac{1120 \text{ g}}{1.15 \text{ g mL}^{-1}}$$

$$= (1120/1.15) \text{ mL} = (1.120/1.15) \text{ L}$$

$$\text{Amount of urea, } n = \frac{m_2}{M_2} = \frac{120 \text{ g}}{60 \text{ g mol}^{-1}} = 2 \text{ mol}$$

$$\text{Molarity of the solution} = \frac{n}{V} = \frac{2 \text{ mol}}{(1.120/1.15) \text{ L}} = 2.05 \text{ mol L}^{-1}$$

14. Amount of  $K_3[Fe(CN)_6]$ ,  $n = \frac{m}{M} = \frac{0.1 \text{ g}}{329 \text{ g mol}^{-1}}$   
 $= (0.1/329) \text{ mol}$

$$\text{Molality of solution, } m = \frac{n}{m_l} = \frac{(0.1/329) \text{ mol}}{0.1 \text{ kg}} \\ = (1/329) \text{ mol kg}^{-1}$$

For an electrolytic solution,

$$-\Delta T_f = i K_f m$$

where  $i$  is the van't Hoff factor. For  $K_3[Fe(CN)_6]$ ,  $i = 4$  as it will give four species in solution. Thus

$$-\Delta T_f = (4) (1.86 \text{ K kg mol}^{-1}) \{(1/329) \text{ mol kg}^{-1}\} \\ \simeq 2.3 \times 10^{-2} \text{ K} \cdot 2.3 \times 10^{-2} \text{ °C}$$

Thus

$$\Delta T_f = -2.3 \times 10^{-2} \text{ °C}$$

or

$$t_f - t_f^* = -2.3 \times 10^{-2} \text{ °C}$$

or

$$t_f = -2.3 \times 10^{-2} \text{ °C} \text{ as } t_f^* = 0 \text{ °C.}$$

15. From the expression  $\Delta T_b = K_b m$ , we find that the molality of solute ( $m$ ) in the solution is

$$m = \frac{\Delta T_b}{K_b} = \frac{2 \text{ K}}{0.76 \text{ K kg mol}^{-1}} = \frac{2}{0.76} \text{ mol kg}^{-1}$$

Since  $m = n_2/m_1$  (where  $n_2$  is the amount of solute and  $m_1$  is the mass of solvent expressed in kg), we get

$$n_2 = mm_1 = \left( \frac{2}{0.76} \text{ mol kg}^{-1} \right) (0.1 \text{ kg}) = \frac{2}{7.6} \text{ mol}$$

From the expression  $-\Delta p = x_2 p_1^*$  of the relative lowering of vapour pressure of solvent (whose vapour pressure is 1 atm as the solute is non-volatile), we find that

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{m_1 / M_1} = \frac{(2 / 7.6) \text{ mol}}{(100 \text{ g} / 18 \text{ g mol}^{-1})} = \frac{36}{76}$$

$$\text{Hence } -\Delta p = \left( \frac{36}{760} \right) (760 \text{ mmHg}) = 36 \text{ mmHg}$$

$$p = p_1^* + \Delta p = 760 \text{ mmHg} - 36 \text{ mmHg} = 724 \text{ mmHg}$$

Therefore, the **choice (a)** is correct.

### Multiple Correct-Choice Type

2. In the formation of an ideal solution,  $\Delta H = 0$ ,  $\Delta G = -ve$  and  $\Delta S_{\text{system}} = +ve$ .

Also, since  $q = 0$ ,  $\Delta S_{\text{surroundings}} = 0$ .

Therefore, the **choices (b), (c) and (d)** are correct.

### Integer Answer Type

1. In 3.2 molar solution, we have

Amount of solute = 3.2 mol

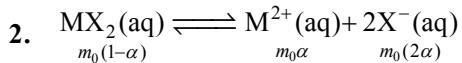
Volume of solution = 1.0 L

Since there occurs no change in volume on dissolving solute, we will have

Volume of solvent = 1.0 L

$$\begin{aligned} \text{Mass of solvent} &= (1.0 \text{ L}) (0.4 \text{ g mL}^{-1}) \\ &= (10^3 \text{ mL}) (0.4 \text{ g mL}^{-1}) \\ &= 400 \text{ g} \equiv 0.4 \text{ kg}. \end{aligned}$$

$$\text{Molality of the solution} = \frac{3.2 \text{ mol}}{0.4 \text{ kg}} = 8 \text{ mol kg}^{-1}$$



$$\begin{aligned} \text{Total molality of solution} &= m_0(1 + 2\alpha) \\ &= m_0(1 + 2 \times 0.5) = 2m_0 \end{aligned}$$

$$\text{Hence } \frac{(-\Delta T_f)_{\text{observed}}}{(-\Delta T_f)_{\text{undissociated}}} = \frac{2m_0}{m_0} = 2$$

3. For an electrolyte, the van't Hoff factor is defined as

$$i = i - \frac{\Delta T_f}{K_f m} = \frac{0.0558 \text{ K}}{(1.86 \text{ K kg mol}^{-1})(0.01 \text{ mol kg}^{-1})} = 3$$

From this, it follows that the complex is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  as it gives three species in the solution. Hence, the number of chloride within the coordination sphere is 1.

## Linked Comprehension Type

1. In solution M, water acts as solute and ethanol as a solvent. Consider a solution with 0.9 mol of ethanol and 0.1 mol of water. In this solution,  
we have

$$\text{Amount of water, } n_2 = 0.1 \text{ mol}$$

$$\text{Mass of ethanol, } m_1 = n_1 M_1 = (0.9 \text{ mol}) (46 \text{ g mol}^{-1}) = 41.4 \text{ g} = 0.0414 \text{ kg}$$

$$\text{Molality of water, } m = \frac{n_2}{m_1} = \frac{0.1 \text{ mol}}{0.0414 \text{ kg}}$$

$$-\Delta T_f = K_f^{\text{ethanol}} m = (2 \text{ K kg mol}^{-1}) \left( \frac{0.1 \text{ mol}}{0.0414 \text{ kg}} \right) = 4.83 \text{ K}$$

$$T_f = T_f^* + \Delta T_f = 155.7 \text{ K} - 4.83 \text{ K} = 150.9 \text{ K}$$

2. Since the solute is considered to be nonvolatile,

$$p_{\text{solution}} = p_1^* x_1 = (40 \text{ mmHg}) (0.9) = 36 \text{ mmHg}.$$

3. Amount of water = 0.9 mol

$$\text{Mass of water, } m_1 = (0.9 \text{ mol}) (18 \text{ g mol}^{-1}) = 16.2 \text{ g} = 0.0162 \text{ kg}$$

$$\text{Molality of ethanol, } m = \frac{0.1 \text{ mol}}{0.0162 \text{ kg}}$$

$$\Delta T_b = K_b^{\text{water}} m = (0.52 \text{ K kg mol}^{-1}) \left( \frac{0.1 \text{ mol}}{0.0162 \text{ kg}} \right) = 3.2 \text{ K}$$

$$T_b = T_b^* + \Delta T_b = 373 \text{ K} + 3.2 \text{ K} = 376.2 \text{ K}$$

## Subjective Type

1. Using Raoult's law ( $p_1 = x_1 p_1^*$ ), we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{631.9 \text{ mmHg}}{639.7 \text{ mmHg}} = 0.988$$

Now molality of the solution is given as

$$m = \frac{n_2}{n_1 M_1} = \frac{x_2}{x_1} \frac{1}{M_1} = \frac{0.012}{0.988} \times \frac{1}{0.078 \text{ kg mol}^{-1}} = 0.156 \text{ mol kg}^{-1}.$$

2. Since  $p = x_A p_A^* + x_B p_B^*$ , we have

$$\left( \frac{1}{1+3} \right) p_A^* + \left( \frac{3}{1+3} \right) p_B^* = 550 \text{ mmHg}$$

$$\text{and } \left( \frac{1}{1+4} \right) p_A^* + \left( \frac{4}{1+4} \right) p_B^* = 560 \text{ mmHg}$$

$$\text{That is, } 0.25 p_A^* + 0.75 p_B^* = 550 \text{ mmHg}$$

$$\text{and } 0.20 p_A^* + 0.8 p_B^* = 560 \text{ mmHg}$$

Solving for  $p_A^*$  and  $p_B^*$ , we get

$$p_A^* = 400 \text{ mmHg} \quad \text{and} \quad p_B^* = 600 \text{ mmHg}.$$

- 3.** For a 3 molal solution, we will have

$$\text{Amount of sodium thiosulphate} = 3 \text{ mol}$$

$$\text{Mass of sodium thiosulphate} = 3 \times 248 \text{ g} = 744 \text{ g}$$

$$\text{Amount of water} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.56 \text{ mol}$$

$$\text{Total mass of solution} = (1000 + 744) \text{ g} = 1744 \text{ g}$$

$$\text{Volume of } 1744 \text{ g of solution} = \frac{1744 \text{ g}}{1.25 \text{ g cm}^{-3}} = 1395.2 \text{ cm}^3$$

$$\text{Mass per cent of sodium thiosulphate} = \frac{744 \text{ g}}{1744 \text{ g}} \times 100 = 42.7$$

$$\text{Mole fraction of sodium thiosulphate} = \frac{3}{3 + 55.56} = 0.051$$

$$\text{Molarity of Na}^+ = \frac{2 \times 3 \text{ mol}}{1.395 \text{ dm}^3} = 4.30 \text{ mol dm}^{-3}$$

$$\text{Molarity of S}_2\text{O}_3^{2-} = \frac{3 \text{ mol}}{1.395 \text{ dm}^3} = 2.15 \text{ mol dm}^{-3}$$

- 4.** Let A be ethanol and B be methanol.

$$\text{Amount of A} = \frac{60 \text{ g}}{46 \text{ g mol}^{-1}} = 1.304 \text{ mol}$$

$$\text{Amount of B} = \frac{40 \text{ g}}{32 \text{ g mol}^{-1}} = 1.25 \text{ mol}$$

$$\text{Mole fraction of A in solution}, x_A = \frac{1.304}{1.304 + 1.25} = 0.511$$

$$\text{Mole fraction of B in solution}, x_B = 1 - x_A = 1 - 0.511 = 0.489$$

$$\text{Partial pressure of A}, p_A = x_A p_A^* = (0.511)(44.5 \text{ mmHg}) = 22.74 \text{ mmHg}$$

$$\text{Partial pressure of B}, p_B = x_B p_B^* = (0.489)(88.7 \text{ mmHg}) = 43.37 \text{ mmHg}$$

$$\text{Total vapour pressure}, p = p_A + p_B = (22.74 + 43.37) \text{ mmHg} = 66.11 \text{ mmHg}$$

Mole fraction of B in vapour phase,

$$y_B = \frac{p_B}{p} = \frac{43.37 \text{ mmHg}}{66.11 \text{ mmHg}} = 0.656.$$

- 5.** Mass of water in the syrup =  $(214.2 - 34.2)$  g = 180.0 g

$$\text{Molality of the solution} = \frac{n_2}{m_1} = \frac{(34.2 \text{ g}/342 \text{ g mol}^{-1})}{(180.0 \times 10^{-3} \text{ kg})} = 0.556 \text{ mol kg}^{-1}$$

$$\text{Mole fraction of sugar} = \frac{34.2/342}{(34.2/342) + (180/18)} = 0.0099.$$

- 6.** From Raoult's law, we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{750 \text{ mmHg}}{760 \text{ mmHg}} = 0.987$$

$$\text{Mole fraction of solute}, x_2 = 1 - x_1 = 1 - 0.987 = 0.013$$

$$\text{Now, Molality of solute} = \frac{n_2}{m_1} = \frac{n_2}{n_1 M_1} = \frac{0.013 \text{ mol}}{(0.987 \text{ mol})(18 \times 10^{-3} \text{ kg mol}^{-1})} \\ = 0.732 \text{ mol kg}^{-1}.$$

**7.** Mass of 1 L solution =  $\rho V = (1.84 \text{ g mL}^{-1}) (1000 \text{ mL}) = 1840 \text{ g}$

$$\text{Mass of H}_2\text{SO}_4 \text{ in 1 L solution} = \frac{93 \text{ g}}{100 \text{ mL}} \times 1000 \text{ mL} = 930 \text{ g}$$

$$\text{Amount of H}_2\text{SO}_4 \text{ in 1 L solution} = \frac{930 \text{ g}}{98 \text{ g mol}^{-1}} = 9.49 \text{ mol}$$

$$\text{Mass of H}_2\text{O in 1 L solution} = 1840 \text{ g} - 930 \text{ g} = 910 \text{ g}$$

$$\text{Molality of solution} = \frac{9.49 \text{ mol}}{(910/1000) \text{ kg}} = 10.43 \text{ mol kg}^{-1}.$$

**8.** From the Raoult's law, we get

$$x_1 = \frac{p_1}{p_1^*} = \frac{600 \text{ mmHg}}{640 \text{ mmHg}} = 0.9375$$

$$\text{Now } x_1 = \frac{n_1}{n_1 + n_2}$$

$$0.9375 = \frac{(39.0/78.0) \text{ mol}}{(39.0/78.0) \text{ mol} + (2.175 \text{ g}/M)}$$

$$\text{which gives } M = \frac{2.175 \text{ g}}{0.5(1 - 0.9375) \text{ mol}} = 69.6 \text{ g mol}^{-1}.$$

**9.** We have

$$\text{Amount of the compound} = \frac{0.643 \text{ g}}{M}$$

$$\text{Mass of the solvent} = \rho V = (0.879 \text{ g mL}^{-1}) (50 \text{ mL}) = 43.95 \text{ g}$$

$$\text{Molality of the solution} = \frac{(0.643 \text{ g}/M)}{(43.95/1000) \text{ kg}}$$

$$\text{Lowering of the freezing point, } -\Delta T_f = (5.51 - 5.03) \text{ }^\circ\text{C} = 0.48 \text{ }^\circ\text{C} \equiv 0.48 \text{ K}$$

Now using the expression

$$-\Delta T_f = K_f m$$

$$\text{we get } 0.48 \text{ K} = (5.12 \text{ K kg mol}^{-1}) \left( \frac{0.643 \times 1000}{43.95 M} \frac{\text{g}}{\text{kg}} \right)$$

$$\text{or } M = \frac{5.12 \times 0.643 \times 1000}{0.48 \times 43.95} \text{ g mol}^{-1} = 156.06 \text{ g mol}^{-1}.$$

**10.** The vapour pressure of water is to be decreased by 25%.

$$\text{Hence, } -\frac{\Delta p_1}{p_1^*} = 0.25$$

According to Raoult's law  $-\frac{\Delta p_1}{p_1^*} = x_2$

where  $x_2$  is the mole fraction of solute, i.e.  $x_2 = n_2 / (n_1 + n_2)$

Substituting  $x_2 = 0.25$ , we get

$$n_2 = \frac{1}{3} n_1 = \frac{1}{3} \left( \frac{100 \text{ g}}{18 \text{ g mol}^{-1}} \right) = \frac{50}{27} \text{ mol}$$

$$\text{Mass of urea dissolved} = \left( \frac{50}{27} \text{ mol} \right) (60 \text{ g mol}^{-1}) = \frac{1000}{9} \text{ g}$$

$$\text{Molality of solution} = \frac{(50/27) \text{ mol}}{0.1 \text{ kg}} = \frac{500}{27} \text{ mol kg}^{-1}.$$

$$11. \text{ Molar volume of liquid benzene} = \frac{M}{\rho} = \frac{78 \text{ g mol}^{-1}}{0.877 \text{ g mL}^{-1}} = 88.94 \text{ mL}$$

Molar volume of benzene vapour at its vapour pressure

$$= (2750) (88.94 \text{ mL}) = 244585 \text{ mL} = 244.585 \text{ L}$$

Vapour pressure pure benzene is  $p_b^* = nRT/V$

$$\text{Hence } p_b^* = \frac{(1 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{(244.585 \text{ L})} = 0.0982 \text{ atm}$$

$$\text{Molar volume of liquid toluene} = \frac{M}{\rho} = \frac{92 \text{ g mol}^{-1}}{0.867 \text{ g mL}^{-1}} = 106.11 \text{ mL}$$

Molar volume of toluene vapour at its vapour pressure = (7720) (106.11 mL)

$$= 819169 \text{ mL} = 819.169 \text{ L}$$

Vapour pressure of toluene is  $p_t^* = nRT/V$

$$\text{Hence } p_t^* = \frac{(1 \text{ mol})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(293 \text{ K})}{(819.169 \text{ L})} = 0.0293 \text{ atm}$$

Let  $x_b$  be the mole fraction of benzene in the liquid phase. We will have

$$\begin{aligned} p_{\text{total}} &= x_b p_b^* + (1 - x_b) p_t^* = p_t^* + (p_b^* - p_t^*) x_b \\ \text{or } x_b &= \frac{p_{\text{total}} - p_t^*}{p_b^* - p_t^*} = \frac{(46.0/760) \text{ atm} - 0.0293 \text{ atm}}{0.0982 \text{ atm} - 0.0293 \text{ atm}} = 0.453 \end{aligned}$$

$$\begin{aligned} \text{Mole fraction of benzene in vapour phase, } y_b &= \frac{p_b}{p_{\text{total}}} \\ &= \frac{x_b p_b^*}{p_{\text{total}}} = \frac{(0.453)(0.0982 \text{ atm})}{(46/760) \text{ atm}} = 0.735 \end{aligned}$$

12. Using Raoult's law

$$p_1 = x_1 p_1^*$$

$$\text{we get } (98.88 \text{ mmHg}) = x_1 (100 \text{ mmHg})$$

$$\text{or } x_1 = 0.9888$$

Let 1 mol of the total amount of solvent and solute. We will have

$$\begin{aligned}n_1 &= 0.9888 \text{ mol} \quad \text{and} \quad n_2 = 0.0112 \text{ mol} \\m_1 &= n_1 M = (0.9888 \text{ mol}) (78 \text{ g mol}^{-1}) = 77.126 \text{ g}\end{aligned}$$

The molality of the solution is

$$m = \frac{n_1}{m_1} = \frac{0.0112 \text{ mol}}{77.126 \times 10^{-3} \text{ kg}} = 0.1452 \text{ mol kg}^{-1}$$

Freezing point depression constant of benzene would be

$$K_f = \frac{-\Delta T_f}{m} = \frac{0.73 \text{ K}}{0.1452 \text{ mol kg}^{-1}} = 5.028 \text{ K kg mol}^{-1}$$

**13.** From the data on the depression in freezing point, we get

$$m = \frac{-\Delta T_f}{K_f} = \frac{0.30 \text{ K}}{1.86 \text{ K kg mol}^{-1}} = 0.1613 \text{ mol kg}^{-1}$$

Mole fraction of solvent in the solution would be

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{(1000/18)}{(1000/18) + 0.1613} = 0.9971$$

Vapour pressure of the solution would be

$$p = x_1 p_1^* = (0.9971) (23.51 \text{ mmHg}) = 23.44 \text{ mmHg.}$$

**14.** Mass of acetic acid =  $3 \times 10^{-3} \text{ kg} = 3 \text{ g}$

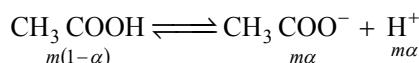
$$\text{Amount of acetic acid, } n_2 = \frac{3 \text{ g}}{60 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

$$\text{Volume of water, } V = 500 \text{ cm}^3$$

$$\text{Mass of water, } m_1 = V\rho = (500 \text{ cm}^3) (0.997 \text{ g cm}^{-3}) = 498.5 \text{ g} = 0.4985 \text{ kg}$$

$$\text{Molality of acetic acid, } m = \frac{n_2}{m_1} = \frac{0.05 \text{ mol}}{0.4985 \text{ kg}} = 0.1003 \text{ mol kg}^{-1}$$

Since 23% acetic acid is dissociated, its degree of dissociation will be 0.23. Hence, in solution we have



$$\text{Molality of species in solution} = m(1 - \alpha) + m\alpha + m\alpha = m(1 + \alpha)$$

$$\text{Hence, } -\Delta T_f = m(1 + \alpha)K_f = (0.1003 \text{ mol kg}^{-1})(1 + 0.23)(1.86 \text{ K kg mol}^{-1}) = 0.23 \text{ K}$$

**15.** We have

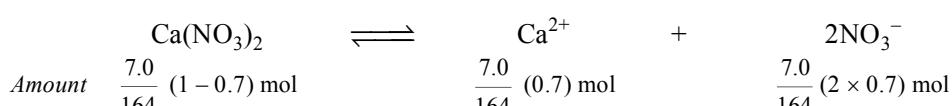
$$\text{Mass of Ca(NO}_3)_2 = 7.0 \text{ g}$$

$$\text{Molar mass of Ca(NO}_3)_2 = 164 \text{ g mol}^{-1}$$

$$\text{Amount of Ca(NO}_3)_2 = (7.0 / 164) \text{ mol}$$

$$\text{Amount of water} = (100 / 80) \text{ mol}$$

The dissociation of  $\text{Ca(NO}_3)_2$  along with the amounts of different species are as follows.



Total amount in the solution,  $n_{\text{total}}$

$$\begin{aligned} &= n(\text{H}_2\text{O}) + n(\text{Ca}(\text{NO}_3)_2) + n(\text{Ca}^{2+}) + n(\text{NO}_3^-) \\ &= \left\{ \frac{100}{18} + \frac{7.0}{164} (0.3 + 0.7 + 1.4) \right\} \text{ mol} = (5.556 + 0.102) \text{ mol} = 5.658 \text{ mol} \end{aligned}$$

Mole fraction of solvent,  $x_1 = \frac{5.556}{5.658}$

$$\begin{aligned} \text{Hence, } p_1 &= x_1 p_1^* = \left( \frac{5.556}{5.658} \right) (760 \text{ mmHg}) \\ &= 746.3 \text{ mmHg} \end{aligned}$$

**16.** Since  $K_b = MRT_b^*/\Delta_{\text{vap}}H$ , we have

$$K_b = \frac{MRT_b^*}{\Delta_{\text{vap}}H/T_b} = (\text{constant}) T_b^*$$

Note that  $\Delta_{\text{vap}}H/T_b^*$  is taken to be constant (Trouton's rule). Hence  $K_b \propto T_b^*$   
Thus, we have

$$K_b(X) = 0.73 \text{ Kg K mol}^{-1}; \quad K_b(Y) = 0.53 \text{ kg K mol}^{-1}; \quad K_b(Z) = 0.98 \text{ kg K mol}^{-1}$$

*Verification*

$$\frac{K_b(X)}{K_b(Y)} = \frac{0.73}{0.53} = 1.38 \quad \text{also} \quad \frac{T_b^*(X)}{T_b^*(Y)} = \frac{400}{300} = 1.33$$

$$\frac{K_b(X)}{K_b(Z)} = \frac{0.73}{0.98} = 0.74 \quad \text{also} \quad \frac{T_b^*(X)}{T_b^*(Z)} = \frac{400}{526} = 0.76$$

**17.** Let  $M$  be the molar mass of benzoic acid in the solution. The molality of the solution is

$$m = \frac{n}{m_l} = \frac{(12.2 \text{ g})/M}{1 \text{ kg}}$$

Since  $\Delta T_b = K_b m$ , we get

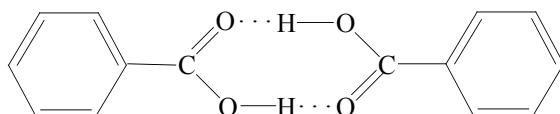
$$(a) \text{ Acetone solution} \quad 0.17 \text{ K} = (1.7 \text{ K kg mol}^{-1}) \left[ \frac{12.2 \text{ g}/M_1}{1 \text{ kg}} \right]$$

$$M_1 = \frac{1.7 \times 12.2}{0.17} \text{ g mol}^{-1} = 122 \text{ g mol}^{-1}$$

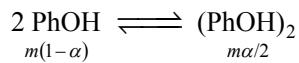
$$\text{Benzene solution} \quad 0.13 \text{ K} = (2.6 \text{ K kg mol}^{-1}) \left[ \frac{12.2 \text{ g}/M_2}{1 \text{ kg}} \right]$$

$$M_2 = \frac{2.6 \times 12.2}{0.13} \text{ g mol}^{-1} = 244 \text{ g mol}^{-1}$$

(b) The actual molar mass of benzoic acid ( $C_6H_5COOH$ ) is  $122 \text{ g mol}^{-1}$ . This means benzoic acid is present as monomer in acetone solution while it dimerises in benzene solution. The structure of dimerised benzoic acid is



18. We have



where  $m = \frac{n_2}{m_1} = \frac{75.2 \text{ g}/(94 \text{ g mol}^{-1})}{1 \text{ kg}} = 0.8 \text{ mol kg}^{-1}$

Molality of solution  $= m(1 - \alpha) + m \alpha / 2 = m(1 - \alpha / 2)$

Since  $\Delta T_f = K_f m$ , we get

$$7K = (14 \text{ K kg}^{-1} \text{ mol}) (0.8 \text{ mol kg}^{-1}) (1 - \alpha / 2)$$

This gives  $\alpha = 2 \left[ 1 - \frac{1}{2 \times 0.8} \right] = 0.75$



# CHEMICAL KINETICS

10

## Straight Objective Type

1. The rate constant of a reaction depends on
  - (a) temperature
  - (b) initial concentration of the reactants
  - (c) time of reaction
  - (d) extent of reaction(1981)
2. The rate constant of a first-order reaction depends on the
  - (a) concentration of the reactant
  - (b) concentration of the product
  - (c) time
  - (d) temperature(1983)
3. A catalyst is a substance which
  - (a) increases the equilibrium concentration of the product
  - (b) changes the equilibrium constant of the reaction
  - (c) shortens the time to reach equilibrium
  - (d) supplies energy to the reaction(1983)
4. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to
  - (a)  $(1/2)$  g
  - (b)  $(1/4)$  g
  - (c)  $(1/8)$  g
  - (d)  $(1/16)$  g(1986)
5. For an endothermic reaction where  $\Delta H$  represents the enthalpy of the reaction, the minimum value for the energy of activation will be
  - (a) less than  $\Delta H$
  - (b) zero
  - (c) more than  $\Delta H$
  - (d) equal to  $\Delta H$(1992)
6. The rate constant for the reaction,  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$  is  $3.0 \times 10^{-5} \text{ s}^{-1}$ . If the rate is  $2.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$ , then the concentration of  $\text{N}_2\text{O}_5$  (in  $\text{mol L}^{-1}$ ) is
  - (a) 1.4
  - (b) 1.2
  - (c) 0.04
  - (d) 0.8(2000)
7. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at  $25^\circ\text{C}$  are  $3.0 \times 10^{-4} \text{ s}^{-1}$ ,  $104.4 \text{ kJ mol}^{-1}$  and  $6.0 \times 10^{14} \text{ s}^{-1}$  respectively. The value of the rate constant as  $T \rightarrow \infty$  is,
  - (a)  $2.0 \times 10^{18} \text{ s}^{-1}$
  - (b)  $6.0 \times 10^{14} \text{ s}^{-1}$
  - (c) infinity
  - (d)  $3.6 \times 10^{30} \text{ s}^{-1}$(1996)
8. If ' $I'$  is the intensity of absorbed light and ' $c$ ' is the concentration of AB for the photochemical process  $\text{AB} + h\nu \rightarrow \text{AB}^*$ , the rate of formation of  $\text{AB}^*$  is directly proportional to
  - (a)  $c$
  - (b)  $I$
  - (c)  $I^2$
  - (d)  $c.I$(2001)
9. Consider the chemical reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ . The rate of this reaction can be expressed in terms of time derivative of concentration of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  or  $\text{NH}_3(\text{g})$ . Identify the correct relationship amongst the rate expressions
  - (a) Rate =  $- d[\text{N}_2]/dt = -(1/3) d[\text{H}_2]/dt = (1/2) d[\text{NH}_3]/dt$
  - (b) Rate =  $d[\text{N}_2]/dt = -3 d[\text{H}_2]/dt = 2 d[\text{NH}_3]/dt$

**10.2** IIT Chemistry: Topic-wise Solved Questions

- (c) Rate =  $d[N_2]/dt = (1/3) d[H_2]/dt = (1/2) d[NH_3]/dt$   
 (d) Rate =  $-d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$  (2002)

10. If the concentration of a reactant decreases from  $800 \text{ mol dm}^{-3}$  to  $50 \text{ mol dm}^{-3}$  in  $2 \times 10^5 \text{ s}$  in a first order reaction, the rate constant of the reaction would be

- (a)  $2 \times 10^{-5} \text{ s}$  (b)  $1.386 \times 10^{-5} \text{ s}$  (c)  $3.45 \times 10^{-5} \text{ s}$  (d)  $2 \times 10^5 \text{ s}$  (2003)

11. The reaction,  $A \rightarrow \text{products}$ , follows first order kinetics. In 45 min, the concentration of A changes from  $0.1 \text{ M}$  to  $0.0125 \text{ M}$ . The rate of reaction when  $[A] = 0.001 \text{ M}$  is

- (a)  $2.31 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$  (b)  $4.62 \times 10^{-5} \text{ mol L}^{-1} \text{ mol}^{-1}$   
 (c)  $2.31 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$  (d)  $4.62 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$  (2004)

12. Which of the following statements is incorrect about order of a reaction?

- (a) Order of a reaction can never be equal to zero or fractional value  
 (b) It is always determined experimentally  
 (c) It is equal to the molecularity of an elementary reaction  
 (d) It is sum of the powers of concentration terms in the differential rate law of a reaction. (2005)

13. Consider a reaction  $aG + bH \rightarrow \text{Products}$ . When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

- (a) 0 (b) 1 (c) 2 (d) 3 (2007)

14. Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio ( $k_1/k_0$ ) of the rate constants for first order ( $k_1$ ) and zero order ( $k_0$ ) of the reactions is

- (a)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (b)  $1.0 \text{ mol dm}^{-3}$  (c)  $1.5 \text{ mol dm}^{-3}$  (d)  $2.0 \text{ mol}^{-1} \text{ dm}^3$  (2008)

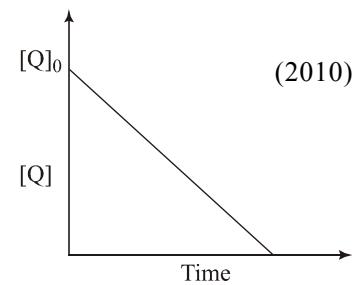
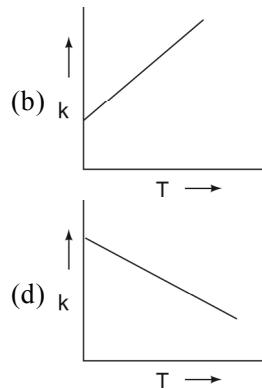
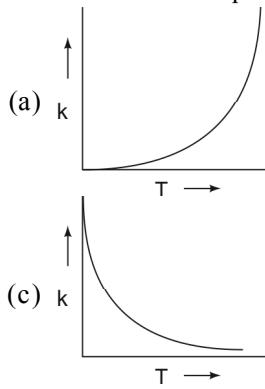
15. For a first order reaction  $A \rightarrow P$ , the temperature ( $T$ ) dependent rate constant ( $k$ ) was found to follow the equation

$$\log(k/\text{s}) = -\frac{2000 \text{ K}}{T} + 6.0$$

The pre-exponential factor  $A$  and the activation energy  $E_a$ , respectively, are

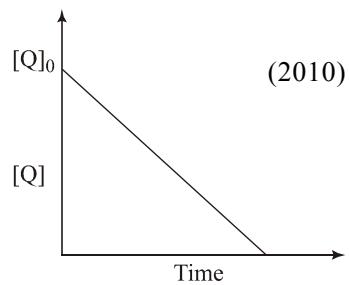
- (a)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $9.2 \text{ kJ mol}^{-1}$  (b)  $6.0 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$   
 (c)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$  (d)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $38.3 \text{ kJ mol}^{-1}$  (2009)

16. Plots showing the variation of the rate constant ( $k$ ) with temperature ( $T$ ) are given below. The plot that follows Arrhenius equation is



17. In the reaction  $P + Q \rightarrow R + S$ , the time taken for 75% reaction of P is twice the time taken for 50 % reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is

- (a) 2 (b) 3 (c) 0 (d) 1 (2013)



18. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid HA (1 M) is  $1/100^{\text{th}}$  of that of a strong acid HX (1 M) at 25 °C. The  $K_a^{\circ}$  of HA is  
 (a)  $1 \times 10^{-4}$       (b)  $1 \times 10^{-5}$       (c)  $1 \times 10^{-6}$       (d)  $1 \times 10^{-3}$       (2013)
19. For the reaction  $\text{M} \rightarrow \text{N}$ , the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is  
 (a) 4      (b) 3      (c) 2      (d) 1      (2014)

### Multiple Correct-Choice Type

1. A catalyst
  - (a) increases the average kinetic energy of reacting molecules
  - (b) decrease the activation energy
  - (c) alters the reaction mechanism
  - (d) increases the frequency of collisions of reacting species(1984)
2. The rate law for the reaction  $\text{RCl} + \text{NaOH(aq)} \rightarrow \text{ROH} + \text{NaCl}$  is given by, Rate =  $k_1 [\text{RCl}]$ . The rate of the reaction will be
  - (a) doubled on doubling the concentration of sodium hydroxide
  - (b) halved on reducing the concentration of alkyl halide to one half
  - (c) increased on increasing the temperature of the reaction
  - (d) unaffected by increasing the temperature of the reaction(1988)
3. For a first-order reaction
  - (a) the degree of dissociation is equal to  $(1 - e^{-kt})$ .
  - (b) a plot of reciprocal concentration of the reactant versus time gives a straight line.
  - (c) the time taken for the completion of 75% reaction is thrice that of  $t_{1/2}$  of the reaction.
  - (d) the pre-exponential factor in the Arrhenius equation has the dimension of time  $T^{-1}$ .(1998)
4. The following statement(s) is (are) correct:
  - (a) A plot of  $\log K_p$  versus  $1/T$  is linear
  - (b) A plot of  $\log [\text{X}]$  versus time is linear for a first order reaction,  $\text{X} \rightarrow \text{P}$
  - (c) A plot of  $\log p$  versus  $1/T$  is linear at constant volume
  - (d) A plot of  $p$  versus  $1/V$  is linear at constant temperature(1999)
5. For the first order reaction
 
$$2 \text{N}_2\text{O}_5(\text{g}) \longrightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
  - (a) The concentration of the reactant decreases exponentially with time
  - (b) The half-life of the reaction decreases with increasing temperature
  - (c) The half-life of the reaction depends on the initial concentration of the reactant
  - (d) The reaction proceeds to 99.6% completion in eight half-life duration.(2011)

### Fill-in-the-Blanks Type

1. The rate of chemical change is directly proportional to \_\_\_\_\_. (1985)
2. The hydrolysis of ethyl ethonate in \_\_\_\_\_ medium is a \_\_\_\_\_ order reaction. (1986)
3. For the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$  under certain conditions of temperature and partial pressure of the reactants, the rate of formation of  $\text{NH}_3$  is  $0.001 \text{ kg h}^{-1}$ . The rate of conversion of  $\text{H}_2$  under the same conditions is \_\_\_\_\_  $\text{kg h}^{-1}$ . (1994)
4. In the Arrhenius equation,  $k = A \exp(-E/RT)$ ,  $A$  may be termed as the rate constant at \_\_\_\_\_. (1997)

**Integer Answer Type**

1. The concentration of R in the reaction  $R \rightarrow P$  was measured as a function of time and the following data is obtained:

[R]/M	1.0	0.75	0.40	0.10
<i>t</i> /min	0.0	0.05	0.12	0.18

The order of the reaction is \_\_\_\_\_. (2010)

2. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are  $t_{1/8}$  and  $t_{1/10}$ , respectively. What is the value of  $(t_{1/8}/t_{1/10}) * 10$ ? ( $\log 2 = 0.3$ .) (2012)
3. In dilute aqueous  $H_2SO_4$ , the complex diaquodioxalatoferrate(II) is oxidized by  $MnO_4^-$ . For this reaction, the ratio of the rate of change of  $[H^+]$  to the rate of change of  $[MnO_4^-]$  is \_\_\_\_\_. (2015)

**True/False Type**

1. For a first order reaction, the rate of the reaction doubles as the concentration of the reactant(s) doubles. (1986)
2. Catalyst makes a reaction more exothermic. (1987)
3. The rate of an exothermic reaction increases with increasing temperature. (1990)

**Reasoning Type**

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subquestion.

- (a) If both assertion and statement are true and statement is an explanation of assertion.  
 (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.  
 (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.  
 (d) If both assertion and statement are wrong and statement is not explanation of assertion.

<i>Assertion</i>	<i>Statement</i>
For each ten degree rise of temperature the rate constant is nearly doubled.	Energy-wise distribution of molecules in a gas is an exponential function of temperature. (1989)

**Short Answer Type**

1. The differential rate law of the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  is given by

$$-\frac{d[O_2]}{dt} = k[NO]^2 [O_2]$$

The rate constant  $k$  is found to decrease with increase in temperature. Explain. (2003)

**Subjective Type**

1. Rate of reaction,  $A + B \rightarrow$  product is given as a function of different initial concentrations of A and B.

[A]/mol L <sup>-1</sup>	[B]/mol L <sup>-1</sup>	$r_0/\text{mol L}^{-1} \text{ min}^{-1}$
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

- Determine the order of the reaction with respect to A and with respect to B. What is the half-life of A in the reaction? (1982)
2. A first-order reaction is 20% complete in 10 minutes. Calculate (i) the rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion. (1983)
3. While studying the decomposition of gaseous  $\text{N}_2\text{O}_5$  it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation? (1985)
4. The first-order reaction has  $k = 1.5 \times 10^{-6} \text{ s}^{-1}$  at  $200^\circ\text{C}$ . If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed into the product? What is the half-life of this reaction? (1987)
5. A first-order reaction is 50 per cent completed in 30 min at  $27^\circ\text{C}$  and in 10 min at  $47^\circ\text{C}$ . Calculate the reaction rate constant at  $27^\circ\text{C}$  and the energy of activation of the reaction. (1988)
6. In the Arrhenius equation for a certain reaction, the value of  $A$  and  $E_a$  (activation energy) are  $4 \times 10^{13} \text{ s}^{-1}$  and  $98.6 \text{ kJ mol}^{-1}$ , respectively. If the reaction is of first-order, at what temperature will its half-life period be ten minutes? (1990)
7. The decomposition of  $\text{N}_2\text{O}_5$  according to the equation  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  is a first-order reaction. After 30 min from the start of decomposition in a closed vessel, the total pressure developed is found to be 284.5 mmHg and on complete decomposition, the total pressure is 584.5 mmHg. Calculate the rate constant of the reaction. (1991)
8. Two reactions (i) A  $\rightarrow$  products and (ii) B  $\rightarrow$  products follow first-order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 min. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K. (1992)
9. A first-order reaction, A  $\rightarrow$  B, requires activation energy of  $70 \text{ kJ mol}^{-1}$ . When a 20% solution of A was kept at  $25^\circ\text{C}$  for 20 minutes, 25% decomposition took place. What will be per cent decomposition in the same time in a 30% solution maintained at  $40^\circ\text{C}$ ? Assume that activation energy remains constant in this range of temperature. (1993)
10. The gas phase decomposition of dimethyl ether follows first-order kinetics



The reaction is carried out at constant volume container at  $500^\circ\text{C}$  and has a half-life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. (1993)

11. From the following data for the reaction between A and B, calculate (i) the order of the reaction with respect to A and with respect to B, (ii) the rate constant at 300 K, (iii) the energy of activation, and (iv) the pre-exponential factor.

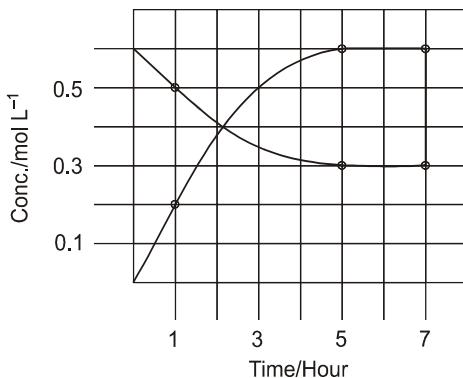
$[\text{A}]/\text{mol L}^{-1}$	$[\text{B}]/\text{mol L}^{-1}$	Initial rate/ $\text{mol L}^{-1} \text{ s}^{-1}$ at	
		300 K	320 K
$2.5 \times 10^{-4}$	$3.0 \times 10^{-5}$	$5.0 \times 10^{-4}$	$2.0 \times 10^{-3}$
$5.0 \times 10^{-4}$	$6.0 \times 10^{-5}$	$4.0 \times 10^{-3}$	—
$1.0 \times 10^{-3}$	$6.0 \times 10^{-2}$	$1.6 \times 10^{-2}$	—

(1994)

12. At  $380^\circ\text{C}$ , the half-life period for the first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is  $200 \text{ kJ mol}^{-1}$ . Calculate the time required for 75% decomposition of  $450^\circ\text{C}$ . (1995)
13. The ionization constant of  $\text{NH}_4^+$  in water is  $5.6 \times 10^{-10}$  at  $25^\circ\text{C}$ . The rate constant for the reaction of  $\text{NH}_4^+$  and  $\text{OH}^-$  to form  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  is  $3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . Calculate the rate constant for proton transfer from water to  $\text{NH}_3$ . (1996)

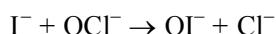
14. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is  $3.56 \times 10^9 \text{ s}^{-1}$ , calculate its rate constant at 318 K and also the energy of activation. (1997)
15. The rate constant for the first order decomposition of a certain reaction is described by the equation  

$$\log(k/\text{s}^{-1}) = 14.34 - (1.25 \times 10^4 \text{ K})/T$$
- (i) What is the energy of activation of this reaction?  
(ii) At what temperature will its half-life be 256 minutes? (1997)
16. The rate constant of a reaction is  $1.5 \times 10^7 \text{ s}^{-1}$  at 50 °C and  $4.5 \times 10^7 \text{ s}^{-1}$  at 100 °C. Evaluate the Arrhenius parameters  $A$  and  $E_a$ . (1998)
17. The rate constant for an isomerization reaction  $\text{A} \rightarrow \text{B}$  is  $4.5 \times 10^{-3} \text{ min}^{-1}$ . If the initial concentration of A is 1 M, calculate the rate of the reaction after 1 h. (1999)
18. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol<sup>-1</sup>. (2000)
19. The progress of the reaction  $\text{A} \rightleftharpoons n\text{B}$ , with time is presented in the Fig. 10.1. Determine  
(i) the value of  $n$ .  
(ii) the equilibrium constant,  $K$ , and  
(iii) the initial rate of conversion of A. (1994)



**Fig. 10.1**

20. The rate of a first-order reaction is  $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$  at 10 minutes and  $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$  at 20 minutes after initiation. Find the half life of the reaction. (2001)
21. The vapour pressure of two miscible liquids **A** and **B** are 300 and 500 mm of Hg respectively. In a flask 10 mol of **A** is mixed with 12 mol of **B**. However, as soon as **B** is added, **B** starts polymerising into a completely insoluble solid. This polymerisation follows first-order kinetics. After 100 minutes, 0.525 mol of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. **Assume** negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution. (2001)
22. For the reaction



in basic aqueous solution, the following data were obtained.

(a)  $[\text{OCl}^-]_0 = [\text{OH}^-]_0 = 0.1 \text{ M}$

$[\text{I}^-]_0/\text{M}$	0.01	0.03	0.05
Initial rate/ $\text{M s}^{-1}$	0.6	1.8	3.0

(b)  $[I^-]_0 = [OH^-]_0 = 0.1 \text{ M}$

$[OCl^-]_0/\text{M}$	0.01	0.03	0.05
Initial rate/ $\text{M s}^{-1}$	0.6	1.8	3.0

(c)  $[I^-]_0 = [OCl^-]_0 = 0.1 \text{ M}$

$[OH^-]/\text{M}$	0.01	0.03	0.05
Initial rate/ $\text{M s}^{-1}$	60	20	12

Determine (i) the orders of reaction with respect to  $I^-$ ,  $OCl^-$  and  $OH^-$ , and (ii) the rate constant of the reaction. (2004)

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (d)  | 3. (c)  | 4. (d)  | 5. (c)  | 6. (d)  | 7. (b)  |
| 8. (b)  | 9. (a)  | 10. (b) | 11. (b) | 12. (a) | 13. (d) | 14. (a) |
| 15. (d) | 16. (a) | 17. (d) | 18. (a) | 19. (b) |         |         |

### Multiple Correct-Choice Type

- |                  |             |             |                  |
|------------------|-------------|-------------|------------------|
| 1. (b), (c)      | 2. (b), (c) | 3. (a), (d) | 4. (a), (b), (d) |
| 5. (a), (b), (d) |             |             |                  |

### Fill-in-the-Blanks Type

- |                                      |  |
|--------------------------------------|--|
| 1. concentration of reacting species | 2. acidic, first or alkaline, second               |
| 3. $0.0015 \text{ kg h}^{-1}$        | 4. very high temperature or zero activation energy |

### Integer Answer Type

- |         |      |      |
|---------|------|------|
| 1. Zero | 2. 9 | 3. 8 |
|---------|------|------|

### True/False Type

- |         |          |         |
|---------|----------|---------|
| 1. True | 2. False | 3. True |
|---------|----------|---------|

### Reasoning Type

- |        |
|--------|
| 1. (a) |
|--------|

### Short Answer Type

1. The reaction proceeds with the following elementary steps.



**10.8** IIT Chemistry: Topic-wise Solved Questions

From the slow step, we can write

$$-\frac{d[\text{O}_2]}{dt} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

Since the first step is in rapid equilibrium, we can write  $K_{\text{eq}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$

With this, we get

$$-\frac{d[\text{O}_2]}{dt} = (k_2 K_{\text{eq}})[\text{NO}_2]^2[\text{O}_2]$$

Though  $k_2$  increases with increase in temperature, but  $K_{\text{eq}}$  decreases with increase in temperature. The latter out weighs the former with the result that the rate constant  $k$  decreases with increase in temperature.

### Subjective Type

1. First order with respect to A; 1.386 min
2. 0.0223 min<sup>-1</sup>; 62.18 min
3. rate constant; half life
4.  $4.62 \times 10^5$  s
5. 0.0231 min<sup>-1</sup>; 43.85 kJ mol<sup>-1</sup>
6. 311.35 K
7.  $5.21 \times 10^{-3}$  min<sup>-1</sup>
8. 0.0327 min<sup>-1</sup>
9. 67%
10. 0.7488 atm
11. (i) order is 2 and 1 with respect to A and B, respectively.  
 (ii)  $2.68 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$       (iii) 53.33 kJ mol<sup>-1</sup>      (iv)  $1.145 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$
12. 20.36 min<sup>-1</sup>
13.  $6.07 \times 10^5 \text{ s}^{-1}$
14. 76.57 kJ mol<sup>-1</sup>;  $9.43 \times 10^{-4}$  s<sup>-1</sup>
15. (i) 239 kJ mol<sup>-1</sup>; (ii) 669 K
16.  $5.45 \times 10^{10} \text{ s}^{-1}$ ; 22.013 kJ mol<sup>-1</sup>
- 17.
18. 100 kJ mol<sup>-1</sup>
19.  $n = 2$ ;  $K_{\text{eq}} = 1.2 \text{ M}$ ;  $0.1 \text{ mol L}^{-1} \text{ h}^{-1}$
20. 1445.3 s
21.  $1.68 \times 10^{-6} \text{ s}^{-1}$
22. 60 s<sup>-1</sup>

### HINTS AND SOLUTIONS

#### Straight Objective Type

1. The rate constant of a reaction depends on temperature.
2. Same answer as Q.1.
3. A catalyst shortens the time to reach equilibrium.
4. A radioactive follows first-order kinetics. 560 days are equivalent to four half-lives. Hence, the mass of radioactive element left is  $(1/2^4)$  g, i.e.  $(1/16)$  g.
5. The energy of activation will be more than  $\Delta H$ .
6.  $[\text{N}_2\text{O}_5] = r/k = (2.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1})/(3.0 \times 10^{-5} \text{ s}^{-1}) = 0.8 \text{ mol L}^{-1}$
7. The Arrhenius equation is

$$k = A \exp(-E_a/RT)$$

As  $T \rightarrow \infty$ ,  $\exp(-E_a/RT) \rightarrow 1$ . Hence,

$$k = A$$

where  $A$ , the Arrhenius parameter, is  $6.0 \times 10^{14} \text{ s}^{-1}$ .

9. Individual rate of appearance of a product or disappearance of a reactant becomes identical when divided by the corresponding stoichiometric coefficient.

10. We have

$$\ln \left( \frac{[A]_0}{[A]_t} \right) = kt$$

Hence  $2.303 \log \left( \frac{800}{50} \right) = k(2 \times 10^5 \text{ s})$

or  $k = \frac{1}{2 \times 10^5 \text{ s}} 2.303 \log (16) = \frac{2.303}{2 \times 10^5 \text{ s}} \log (2^4)$   
 $= \frac{2.303 \times 4 \times 0.3010}{2 \times 10^5 \text{ s}} = 1.386 \times 10^{-5} \text{ s}$

11. The concentration changes from 0.1 M to 0.0125 M is equivalent to three half lives. Hence,

$$3 t_{1/2} = 45 \text{ min} \quad \text{or} \quad t_{1/2} = 15 \text{ min}$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{15 \text{ min}} = 0.0462 \text{ min}^{-1}$$

$$\text{Rate of reaction} = \lambda [A] = (4.62 \times 10^{-2} \text{ min}^{-1}) (0.001 \text{ mol L}^{-1}) = 4.62 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$$

12. Order of a reaction may have zero or fractional value.

13. Let the order of the reaction with respect to G and H be  $m$  and  $n$ , respectively. The given informations are as follows.

$$r = k [G]^m [H]^n$$

$$8r = k \{2 [G]\}^m \{2 [H]\}^n = 2^{m+n} (k [G]^m [H]^n)$$

$$= 2^{m+n} r$$

Hence,  $m + n = 3$

[Note: It is also given that

$$2r = k \{2 [G]\}^m [H]^n = 2^m (k [G]^m [H]^n)$$

$$= 2^m r$$

This gives  $m = 1$ . Hence,  $n = 3 - m = 2$ . Thus, the reaction is first order with respect to G and second order with respect to H and the overall order of the reaction is three.]

14. The rate expressions are:

$$\text{First order} \quad \ln \{[A]_t/[A]_0\} = -k_1 t \quad \text{and} \quad \text{Zero order} \quad [A]_t - [A]_0 = k_0 t$$

$$\text{Hence, for first order reaction} \quad t_{1/2} = -\frac{1}{k_1} \ln \frac{1}{2} = \frac{0.693}{k_1} = 40 \text{ s}$$

$$\text{For zero order reaction} \quad t_{1/2} = \frac{[A]_0}{2k_0} = 20 \text{ s}$$

$$\text{Thus} \quad \frac{k_1}{k_0} = \frac{0.693/(40 \text{ s})}{(1.386 \text{ mol/dm}^3)/(2 \times 20 \text{ s})} = 0.5 \text{ mol}^{-1} \text{ dm}^3$$

15. The Arrhenius equation,  $k = A \exp(-E_a/RT)$ , may be written as

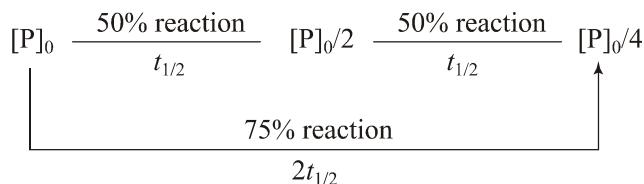
$$\log \left( \frac{k}{s} \right) = \log \left( \frac{A}{s} \right) - \frac{E_a}{2.303 RT}$$

On comparing this expression with the given expression, we find that

$$\log \left( \frac{A}{s} \right) = 6.0 \quad \Rightarrow \quad A = 106 \text{ s}$$

$$\frac{E_a}{2.303 R} = 2000 \text{ K} \Rightarrow E_a = (2.303) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (2000 \text{ K}) \\ = 3.829 \times 10^4 \text{ J mol}^{-1}$$

16. The Arrhenius equation is  $k = A \exp(-E_a/RT)$  which predicts that the rate constant increases exponentially with increase in temperature.
17. With respect to P, the reaction is first order as the successive decrease in concentration of P to a half value is independent of its initial concentration, i.e.



With respect to Q, the reaction is zero order as its concentration follows the rate equation

$$[Q] - [Q]_0 = -kt \text{ i.e. } [Q] = [Q]_0 - kt.$$

Thus, the overall order of the reaction is one.

Therefore, the **choice (d)** is correct.

18. Acid hydrolysis of an ester is first order with respect to the concentration of H<sup>+</sup>(aq). Since the initial rate of hydrolysis with weak acid HA(1M) is 1/100<sup>th</sup> of that of a strong acid HX (1 M, assumed to be completely dissociated), it follows that [H<sup>+</sup>] in the weak acid solution will be (1/100) M.

$$\text{Since } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]_0 - [\text{H}^+]}, \text{ we have } K_a = \frac{\{(1/100)\text{M}\}^2}{1\text{ M}} = 10^{-4} \text{ M}$$

Therefore, the **choice (a)** is correct.

19. For the given reaction, we write

$$r = k [\text{M}]^n$$

where n is the order of the reaction. Since on doubling the concentration of M, the rate of reaction becomes 8 times, it is obvious that n = 3.

### Multiple Correct-Choice Type

- A catalyst decreases the activation energy. It also alters the reaction mechanism.
- The rate of reaction will be halved on reducing the concentration of alkyl halide to half. The rate constant will also increase on increasing temperature.
- For a first-order reaction,  $\frac{[\text{A}]_0 - x}{[\text{A}]_0} = e^{-kt}$ . This gives  $\frac{x}{[\text{A}]_0} = 1 - e^{-kt}$ . In the equation  $k = Ae^{-kt}$ , A has the same dimension as that of k, i.e. T<sup>-1</sup>.
- The relevant expressions are as follows.

Choice (A)  $\log K_p = -\frac{\Delta H}{R} \frac{1}{T} + I$

Choice (B)  $\log [\text{X}] = \log [\text{X}]_0 + kt$

Choice (C)  $p/T = \text{constant}$  (V constant)

Choice (D)  $pV = \text{constant}$  (T constant)

5. The concentration of N<sub>2</sub>O<sub>5</sub> varies as

$$[\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5]_0 e^{-kt} \quad (\text{choice a})$$

The half-life is given as

$$t_{1/2} = 0.693/k$$

On increasing temperature, the rate constant  $k$  increases, thereby half-life decreases. (choice b)  
After eight half-life

$$\frac{[N_2O_5]}{[N_2O_5]_0} = \frac{1}{2^8}$$

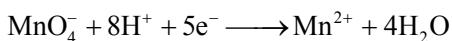
Per cent completion is

$$\begin{aligned}\frac{[N_2O_5]_0 - [N_2O_5]}{[N_2O_5]_0} \times 100 &= \left(1 - \frac{1}{2^8}\right) (100) \\ &= \left(1 - \frac{1}{256}\right) (100) = \frac{255 \times 100}{256} \\ &= 99.61\end{aligned}\quad (\text{choice d})$$

Hence, the **choices (a), (b) and (d)** are correct.

### Integer Answer Type

1. The reaction follows zero-order kinetics for which the concentration of R with time is given by the expression  $[R]_0 - [R]_t = kt$ , i.e. the change in concentration of R ( $= [R]_0 - [R]_t$ ) is directly proportional to  $t$  or the quantity  $\Delta[R]/\Delta t$  is constant (which represents rate constant). In this case,  $\Delta[R]/\Delta t$  is 5 mol dm<sup>-3</sup> min<sup>-1</sup>. The answer is **zero**.
2. For first-order decomposition of A, the rate law is  $\ln ([A]/[A]_0) = -kt$   
Hence  $\ln (1/8) = -k t_{1/8}$  and  $\ln (1/10) = -k t_{1/10}$   
Thus  $\frac{\ln (1/8)}{\ln (1/10)} = \frac{t_{1/8}}{t_{1/10}}$  or  $\frac{\log 8}{\log 10} = \frac{t_{1/8}}{t_{1/10}}$   
Hence  $(t_{1/8}/t_{1/10}) = \log 8 = \log 2^3 = 3 \log 2 = 3 \times 0.3 = 0.9$       or       $10(t_{1/8}/t_{1/10}) = 10 \times 0.9 = 9$   
Therefore, the answer is **9**.
3. The changes in  $[H^+]$  and  $[MnO_4^-]$  are due to the reaction.



Hence,

$$\frac{\text{Rate of change of } [H^+]}{\text{Rate of change of } [MnO_4^-]} = 8$$

### True/False Type

2. Catalyst does not change the enthalpy of reaction.
3. The rate of a reaction increases with increase in temperature. It is due to the increase in the rate constant of the reaction owing to the fact that at higher temperature more number of molecules attain the activation energy.

### Subjective Type

1. Inspection of the given data indicates that on doubling the concentration of A keeping that of B constant increases the initial rate of reaction to two fold. This implies that the reaction is first-order with respect to A. On the other hand, doubling the concentration of B keeping that of A constant has no affect on the initial rate of reaction. This implies that the reaction is zero-order with respect to B. Hence, the expression of rate of reaction is

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$$\text{rate} = k [A]^1 [B]^0 = k [A]$$

that is, the reaction is first-order with respect to A only.

To determine the half-life of A, we determine the rate constant using the above expression. Hence,

$$k = \frac{(\text{rate})_0}{[A]_0} = \frac{0.005 \text{ mol L}^{-1} \text{ min}^{-1}}{0.01 \text{ mol L}^{-1}} = 0.5 \text{ min}^{-1}$$

$$\text{Hence, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5 \text{ min}^{-1}} = 1.386 \text{ min.}$$

2. (i) For the first-order reaction, we have

$$k = -\frac{2.303}{t} \log \frac{[A]}{[A]_0} = -\frac{2.303}{(10 \text{ min})} \log \frac{80}{100} = 0.0223 \text{ min}^{-1}$$

(ii) We have

$$t = -\frac{2.303}{k} \log \frac{[A]}{[A]_0} = -\frac{2.303}{(0.0223 \text{ min}^{-1})} \log \frac{25}{100} = 62.18 \text{ min.}$$

3. For a first-order reaction, the integrated rate expression is

$$\log \frac{[A]_t}{[A]_0} = -\frac{k}{2.303} t \quad \text{i.e.} \quad \log [A]_t = \log [A]_0 - \frac{k}{2.303} t$$

Thus, a plot of  $\log [A]_t$  versus  $t$  is linear with slope equal to  $-k/2.303$  and intercept equal to  $\log [A]_0$ .

Hence, from the given plot of  $\log p_{N_2O_5}$  versus time, we can calculate the rate constant from the slope of the plot. The half-life of the reaction can also be calculated from such a plot.

4. For the first-order reaction, we have

$$\log \frac{[A]_t}{[A]_0} = -\frac{k}{2.303} t$$

Substituting the given data, we get

$$\log \frac{[A]}{[A]_0} = -\frac{1.5 \times 10^{-6} \text{ s}^{-1}}{2.303} (10 \times 60 \times 60 \text{ s}) = -0.02345$$

$$\text{This gives } \frac{[A]}{[A]_0} = 0.9474$$

Percentage conversion of reactant into product =  $(1 - 0.9474) \times 100 = 5.26$

$$\text{The half-life of the reaction is } t_{0.5} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6} \text{ s}^{-1}} = 4.62 \times 10^5 \text{ s.}$$

5. Rate constant at  $27^\circ\text{C}$  =  $\frac{0.693}{t_{1/2}} = \frac{0.693}{30 \text{ min}} = 0.0231 \text{ min}^{-1}$

$$\text{Rate constant at } 47^\circ\text{C} = \frac{0.693}{10 \text{ min}} = 0.0693 \text{ min}^{-1}$$

Now since  $k = A \exp(-E_a/RT)$ , we get

$$\log \frac{k_1}{k_2} = -\frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\begin{aligned} \text{Hence, } E_a &= -\frac{(2.303)R T_1 T_2}{(T_2 - T_1)} \log \frac{k_1}{k_2} = -\frac{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})(320 \text{ K})}{(320 \text{ K} - 300 \text{ K})} \log \frac{0.0231}{0.0693} \\ &= 43850 \text{ J mol}^{-1} = 43.85 \text{ kJ mol}^{-1} \end{aligned}$$

6. We have  $t_{1/2} = 10 \text{ min}$

$$\text{Hence } k = \frac{0.693}{10 \text{ min}} = 0.0693 \text{ min}^{-1} \approx 0.001155 \text{ s}^{-1}$$

Now using the Arrhenius equation

$$k = A e^{-E_a/RT}$$

we get

$$\ln k = A - \frac{E_a}{RT} \quad \text{or} \quad \log k = \log A - \frac{E_a}{2.303RT}$$

Substituting the given data, we get

$$\log 0.001155 = \log 4 \times 10^{13} - \frac{98.6 \times 10^3 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})T}$$

$$\text{or } -2.9374 = 13.6021 - \frac{5149.6}{(T/K)}$$

$$\text{Hence, } T = \frac{5149.6}{(13.6021 + 2.9374)} \text{ K} = 311.35 \text{ K.}$$

7. From the equation



we find that 2 mol of  $\text{N}_2\text{O}_5(\text{g})$  on decomposition gives a total of 5 mol of gaseous species (4 mol  $\text{NO}_2$  and 1 mol  $\text{O}_2$ ). Hence, pressure of  $\text{N}_2\text{O}_5$  to start with is given as

$$p_0 = (584.5 \text{ mmHg}) \left( \frac{2}{5} \right) = 233.8 \text{ mmHg}$$

Now, the partial pressure of  $\text{N}_2\text{O}_5$  after 30 min would be given as

$$p_t + (233.8 \text{ mmHg} - p_t) \left( \frac{5}{2} \right) = 284.5 \text{ mmHg}$$

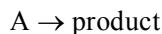
which gives  $p_t = 200 \text{ mmHg}$

$$\text{Now using the expression } \log \frac{p_t}{p_0} = - \frac{k}{2.303} t$$

$$\text{we get } \log \left( \frac{200}{233.8} \right) = - \left( \frac{k}{2.303} \right) (30 \text{ min})$$

$$\text{or } k = - \frac{(2.303)}{(30 \text{ min})} \log \frac{(200)}{(233.8)} = 5.21 \times 10^{-3} \text{ min}^{-1}.$$

8. Let us represent  $T_1 = 300 \text{ K}$  and  $T_2 = 310 \text{ K}$ . Let the corresponding rate constants be represented as  $k_1$  and  $k_2$ , respectively. Now for the reaction



it is given that

$$k_2 = 2 k_1$$

$$k_2 = \frac{0.693}{30 \text{ min}} = 0.0231 \text{ min}^{-1}$$

Now using Arrhenius equation, we get

$$k_1 = A \exp(-\Delta E_A/RT_1) \quad \text{and} \quad k_2 = A \exp(-\Delta E_A/R T_2)$$

Therefore,

$$\frac{k_2}{k_1} = \exp\left\{\frac{\Delta E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right\}$$

Substituting  $k_2/k_1 = 2$  and taking logarithm, we get

$$\ln 2 = \frac{\Delta E_A}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \quad \text{i.e.} \quad \Delta E_A = \frac{R (\ln 2) T_2 T_1}{(T_2 - T_1)}$$

Now for the reaction  $B \rightarrow \text{product}$  we have

$$k'_2 = 2 k_2 = 2 \times 0.0231 \text{ min}^{-1} = 0.0462 \text{ min}^{-1}$$

$$\Delta E_B = \frac{1}{2} \Delta E_A = \frac{1}{2} \frac{R (\ln 2) T_2 T_1}{(T_2 - T_1)}$$

The use of Arrhenius equation in this case gives

$$\begin{aligned} \frac{k'_1}{k'_2} &= \exp\left\{\frac{\Delta E_B}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right\} = \exp\left\{\frac{1}{R}\left(\frac{1}{2} \frac{R (\ln 2) T_1 T_2}{(T_2 - T_1)}\right)\left(\frac{T_1 - T_2}{T_1 T_2}\right)\right\} \\ &= \exp\left(-\frac{\ln 2}{2}\right) = \exp(\ln 2^{-1/2}) = 2^{-1/2} \end{aligned}$$

$$\text{Hence, } k'_1 = \frac{1}{\sqrt{2}} \quad k'_2 = \frac{0.0462 \text{ min}^{-1}}{\sqrt{2}} = 0.0327 \text{ min}^{-1}.$$

9. For a first-order reaction, the fraction of reactants reacted is independent of initial concentration. Hence, we ignore the terms 20% solution and 30% solution. Now it is given that 25% of A is decomposed in 20 min at 25 °C. Hence, at this temperature, the rate constant is given as

$$k = \left(\frac{1}{t}\right) \left(2.303 \log \frac{[A]_0}{[A]}\right) = \left(\frac{1}{20 \text{ min}}\right) \left(2.303 \log \frac{100}{75}\right) = 1.439 \times 10^{-2} \text{ min}^{-1}$$

Now using Arrhenius equation, we calculate the rate constant at 40 °C.

$$\text{We have } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{or } \log k_2 - \log (1.439 \times 10^{-2})$$

$$= - \frac{(70 \times 10^3 \text{ J mol}^{-1})}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left( \frac{1}{313.15 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\text{or } \log k_2 + 1.842 = \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 313.15 \times 298.15} = 0.587$$

$$\text{or } \log k_2 = 0.587 - 1.842 = -1.255$$

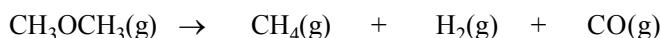
$$\text{or } k_2 = 5.56 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Finally } \log \frac{[A]}{[A]_0} = - \left( \frac{k_2}{2.303} \right) t = - \left( \frac{5.56 \times 10^{-2} \text{ min}^{-1}}{2.303} \right) (20 \text{ min}) = -0.4828$$

$$\text{or } \frac{[A]}{[A]_0} = 0.33$$

Per cent of A remaining = 33% and Per cent of A decomposed = 67%.

10. We have



$t = 0$	$p_0$	0	0	0
$t$	$p_0 - p$	$p$	$p$	$p$

Total pressure of the system at time  $t = p_0 + 2p$   
The rate expression for first order kinetics is

$$\log \frac{[A]}{[A]_0} = - \left( \frac{k}{2.303} \right) t$$

In the present case, we get

$$\log \frac{p_0 - p}{p_0} = - \frac{(0.693/t_{0.5})}{2.303} t = \frac{(-0.693/14.5 \text{ min})}{2.303} (12 \text{ min}) = -0.249$$

or  $\frac{p_0 - p}{p_0} = 0.564$

$$p = p_0 - 0.564 p_0 = p_0 (1 - 0.564) = (0.40 \text{ atm}) (0.436) = 0.1744 \text{ atm}$$

Hence, total pressure of the system is

$$p_0 + 2p = (0.40 + 2 \times 0.1744) \text{ atm} = 0.7488 \text{ atm.}$$

11. (i) Let  $a$  and  $b$  be the orders of the reaction with respect to A and B, respectively. We will have

$$r_0 = k [A]_0^a [B]_0^b$$

Making use of the second and third data in the given table, we get

$$\begin{aligned} 4.0 \times 10^{-3} \text{ M s}^{-1} &= k [5.0 \times 10^{-4} \text{ M}]^a [6.0 \times 10^{-5} \text{ M}]^b \\ 1.6 \times 10^{-2} \text{ M s}^{-1} &= k [1.0 \times 10^{-3} \text{ M}]^a [6.0 \times 10^{-5} \text{ M}]^b \end{aligned}$$

Dividing the two expressions, we get

$$\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = \left[ \frac{1.0 \times 10^{-3}}{5.0 \times 10^{-4}} \right]^a \quad \text{i.e.} \quad 4 = 2^a$$

Hence,  $a = 2$

From the first and second data, we write

$$\begin{aligned} 5.0 \times 10^{-4} \text{ M s}^{-1} &= k (2.5 \times 10^{-4} \text{ M})^2 (3.0 \times 10^{-5} \text{ M})^b \\ 4.0 \times 10^{-3} \text{ M s}^{-1} &= k (5.0 \times 10^{-4} \text{ M})^2 (6.0 \times 10^{-5} \text{ M})^b \end{aligned}$$

Dividing these two expressions, we get

$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \left( \frac{5.0 \times 10^{-4}}{2.5 \times 10^{-4}} \right)^2 \left( \frac{6.0 \times 10^{-5}}{3.0 \times 10^{-5}} \right)^b \quad \text{i.e.} \quad 8 = 2^2 2^b$$

Hence,  $b = 1$ .

Thus, the order of reaction with respect to A and B are 2 and 1, respectively.

- (ii) The rate constant is  $k = \frac{r_0}{[A]_0^2 [B]_0}$

From the first data at 300 K, we get

$$k = \frac{5.0 \times 10^{-4} \text{ M s}^{-1}}{(2.5 \times 10^{-4} \text{ M})^2 (3.0 \times 10^{-5} \text{ M})} = 2.67 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$$

- (iii) To calculate the energy of activation, we make use of Arrhenius equation  $k = A \exp(-E_a/R T)$   
For two temperatures, we get

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Since the rate constants are directly proportional to the corresponding rates, we write

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$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where  $r_2$  and  $r_1$  refer to the two rates at two temperatures for the same initial concentrations of A and B. Making use of the first data, we get

$$\log \left( \frac{2.0 \times 10^{-3}}{5.0 \times 10^{-4}} \right) = \frac{E_a}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left( \frac{1}{300 \text{ K}} - \frac{1}{320 \text{ K}} \right)$$

$$\begin{aligned} \text{Hence, } E_a &= \frac{(2.303)(8.314)(300)(320)(\log 4.0)}{(320 - 300)} \text{ J mol}^{-1} = 5.533 \times 10^4 \text{ J mol}^{-1} \\ &= 55.33 \text{ kJ mol}^{-1} \end{aligned}$$

(iv) Taking logarithm of Arrhenius equation, we get

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{or} \quad \log A = \log k + \frac{E_a}{2.303 RT}$$

Substituting the first data, we get

$$\begin{aligned} \log \frac{A}{\text{M}^{-2} \text{ s}^{-1}} &= \log (2.67 \times 10^8) + \frac{5.533 \times 10^4 \text{ J mol}^{-1}}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} \\ &= 8.4265 + 9.6324 = 18.0589 \end{aligned}$$

$$\text{or } A = 1.145 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}.$$

12. The rate constant at 380 °C is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{360 \text{ min}} = 1.925 \times 10^{-3} \text{ min}^{-1}$$

Substituting the data

$$T_1 = (380 + 273) \text{ K} = 653 \text{ K} \quad k_1 = 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$T_2 = (450 + 273) \text{ K} = 723 \text{ K} \quad k_2 = ?$$

$$E_a = 200 \times 10^3 \text{ J mol}^{-1}$$

in the expression

$$\log \left( \frac{k_2}{k_1} \right) = \frac{E_a}{2.303} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a (T_2 - T_1)}{2.303 R (T_1 T_2)}$$

$$\text{we get } \log \left( \frac{k_2}{1.925 \times 10^{-3} \text{ min}^{-1}} \right) = \frac{(200 \times 10^3 \text{ J mol}^{-1})(723 \text{ K} - 653 \text{ K})}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(653 \text{ K})(723 \text{ K})}$$

$$\begin{aligned} \text{or } \log (k_2 / \text{min}^{-1}) &= \log (1.925 \times 10^{-3}) + 1.5487 = -2.7156 + 1.5487 \\ &= -1.1669 = \bar{2}.8331 \end{aligned}$$

$$k_2 = 6.81 \times 10^{-2} \text{ min}^{-1}$$

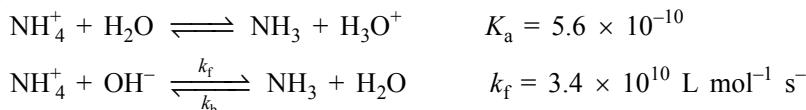
Now for the first order kinetics, we have

$$\log \frac{[A]}{[A]_0} = - \frac{k}{2.303} t$$

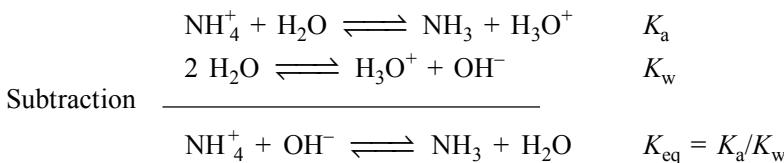
Substituting the data, we get

$$t = -\frac{2.303}{k} \log \frac{[A]}{[A]_0} = -\frac{2.303}{(6.81 \times 10^{-2} \text{ min}^{-1})} \log \left( \frac{25}{100} \right) = 20.36 \text{ min.}$$

13. We are given that



The second equation can be generated as follows.



Also  $K_{eq} = k_f/k_b$ . Hence

$$\frac{k_f}{k_b} = \frac{K_a}{K_w}$$

$$\text{or } k_b = k_f \left( \frac{K_w}{K_a} \right) = (3.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}) \left( \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}}{5.6 \times 10^{-10} \text{ mol L}^{-1}} \right) = 6.07 \times 10^5 \text{ s}^{-1}$$

14. For a first-order reaction

$$\log \frac{[A]}{[A]_0} = -\frac{k}{2.303} t$$

From the given data at two temperatures, we get

$$\text{For } T_2 = 308 \text{ K} \quad \log \frac{75}{100} = -\frac{k_2}{2.303} t$$

$$\text{For } T_1 = 298 \text{ K} \quad \log \frac{90}{100} = -\frac{k_1}{2.303} t$$

Dividing the two expressions, we get

$$\frac{\log(0.90)}{\log(0.75)} = \frac{k_1}{k_2} \quad \text{i.e.} \quad \frac{k_1}{k_2} = \frac{-0.0458}{-0.1249} = 0.3667$$

Now using the expression

$$\log \frac{k_1}{k_2} = -\frac{E_a}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\text{we get } \log(0.3667) = -\frac{E_a}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left[ \frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}} \right]$$

$$\text{or } E_a = \frac{(2.303)(8.314)(298)(308) \log(0.3667)}{(308 - 298)} \text{ J mol}^{-1}$$

$$= 76568 \text{ J mol}^{-1} \equiv 76.57 \text{ kJ mol}^{-1}$$

The Arrhenius equation becomes  $k = (3.56 \times 10^9 \text{ s}^{-1}) \exp(-76.57 \text{ kJ mol}^{-1}/RT)$

Hence, at 318 K we get

$$\begin{aligned} k &= (3.56 \times 10^9 \text{ s}^{-1}) \exp \left[ \frac{-76.57 \times 10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(318 \text{ K})} \right] = (3.56 \times 10^9 \text{ s}^{-1}) \exp(-28.96) \\ &= (3.56 \times 10^9 \text{ s}^{-1}) (2.65 \times 10^{-13}) = 9.43 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

15. The Arrhenius equation is

$$k = A \exp(-E_a/RT) \quad \text{or} \quad \log k = \log A - \frac{E_a}{2.303 R} \frac{1}{T}$$

Comparing this expression with the given one, we get

$$\frac{E_a}{2.303 R} = 1.25 \times 10^4 \text{ K}$$

$$\begin{aligned} \text{Hence, } E_a &= (1.25 \times 10^4 \text{ K}) (2.303) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= 2.39 \times 10^5 \text{ J mol}^{-1} = 239 \text{ kJ mol}^{-1} \end{aligned}$$

(ii) The reaction is first order as the unit of rate constant is  $\text{s}^{-1}$ . For a first-order reaction

$$t_{1/2} = 0.693/k \quad \text{Hence, } k = 0.693 / (256 \times 60 \text{ s}) = 4.51 \times 10^{-5} \text{ s}$$

Substituting this in the given expression, we get

$$\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^{-5} \text{ K}}{T}$$

Solving for  $T$ , we get  $T = 669 \text{ K}$ .

16. The Arrhenius equation is  $k = A \exp(-E_a/RT)$

For the two temperatures, we get

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting the given data, we get

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = -\frac{E_a}{(2.303)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left[ \frac{1}{373 \text{ K}} - \frac{1}{323 \text{ K}} \right]$$

$$\text{or } E_a = \frac{(2.303)(8.314)(373)(323)}{50} \log (3.0) = 22012.7 \text{ J mol}^{-1}$$

The value of  $A$  would be

$$\begin{aligned} A &= k \exp(E_a/RT) = (1.5 \times 10^7 \text{ s}^{-1}) \exp \left[ \frac{22012.7 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(323 \text{ K})} \right] \\ &= (1.5 \times 10^7 \text{ s}^{-1}) (3630.44) = 5.45 \times 10^{10} \text{ s}^{-1} \end{aligned}$$

17. From the unit of rate constant, it follows that the given isomerisation reaction is a first order reaction. The concentration of A after 1 h as determined from the expression

$$\log \frac{[A]}{[A]_0} = -\frac{k}{2.303} t$$

$$\text{is } \log([A]/\text{mol L}^{-1}) = -\frac{4.5 \times 10^{-3} \text{ min}^{-1}}{2.303} (60 \text{ min}) = -0.1172 \quad (\text{as } [A]_0 = 1 \text{ M})$$

$$[A] = 0.7634 \text{ M.}$$

$$\text{rate} = \left( \frac{4.5 \times 10^{-3} \text{ min}^{-1}}{2.303} \right) (0.7634 \text{ mol L}^{-1}) = 1.49 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

18. Using Arrhenius equation, we can write

$$k = A e^{-E_1/RT_1}$$

$$\text{Also } k = A e^{-E_2/RT_2}$$

From these, it follows that

$$e^{-E_1/RT_1} = e^{-E_2/RT_2}$$

or  $\frac{E_1}{RT_1} = \frac{E_2}{RT_2} \Rightarrow \frac{E_1}{T_1} = \frac{E_2}{T_2}$

Since  $E_2 = E_1 - 20 \text{ kJ mol}^{-1}$ , we get

$$\frac{E_1}{T_1} = \frac{E_1 - 20 \text{ kJ mol}^{-1}}{T_2} \quad \text{or} \quad E_1 \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{20 \text{ kJ mol}^{-1}}{T_2}$$

$$\text{or} \quad E_1 = \frac{(20 \text{ kJ mol}^{-1})(T_1)}{(T_1 - T_2)} = \frac{(20 \text{ kJ mol}^{-1})(500 \text{ K})}{(500 - 400) \text{ K}} = 100 \text{ kJ mol}^{-1}$$

19. (i) From the given graph, we find that over the time interval 1 to 5 h,

$$\Delta[A] = (0.3 - 0.5) \text{ M} = -0.2 \text{ M}$$

$$\Delta[B] = (0.6 - 0.2) \text{ M} = 0.4 \text{ M}$$

that is, the obtained amount of B is twice as large as the consumption of A. Hence,  $n$  in the equation  $A \rightleftharpoons nB$  is 2.

(ii) From the given graph, we find that

$$[A]_{\text{eq}} = 0.3 \text{ M} \quad \text{and} \quad [B]_{\text{eq}} = 0.6 \text{ M}$$

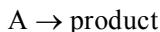
$$\text{Hence, } K_{\text{eq}} = \frac{[B]^2}{[A]} = \frac{(0.6 \text{ M})^2}{0.3 \text{ M}} = 1.2 \text{ M}$$

(iii) In the time interval 0 to 1 h, the plot of [A] and [B] are almost linear. Hence, the initial rate of conversion of A may be evaluated over this time interval.

$$-\Delta[A] = (0.6 - 0.5) \text{ M} = 0.1 \text{ M}$$

$$\text{Initial rate, } -\frac{\Delta[A]}{\Delta t} = \frac{0.1 \text{ M}}{1 \text{ h}} = 0.1 \text{ mol L}^{-1} \text{ h}^{-1}$$

20. For a first-order reaction



we can write

$$\text{rate} = -\frac{d[A]}{dt} = k[A]$$

$$\text{Hence, } -\int_{[A]_1}^{[A]} \frac{d[A]}{[A]} = k \int_{t_1}^{t_2} dt \quad \text{i.e.} \quad \ln \frac{[A]_1}{[A]_2} = k(t_2 - t_1)$$

$$\text{Also} \quad \frac{(\text{rate})_1}{(\text{rate})_2} = \frac{[A]_1}{[A]_2}. \quad \text{Hence} \quad \ln \frac{(\text{rate})_1}{(\text{rate})_2} = k(t_2 - t_1)$$

$$\text{This gives} \quad k = \frac{\ln \{(\text{rate})_1 / (\text{rate})_2\}}{(t_2 - t_1)} = \frac{\ln (0.04 / 0.3)}{(20 - 10) \text{ min}} = 2.88 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Finally} \quad t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.88 \times 10^{-2} \text{ min}^{-1}} = 24.09 \text{ min} \equiv 1445.3 \text{ s.}$$

21. We have

$$p_A^* = 300 \text{ mmHg} \quad \text{and} \quad p_B^* = 500 \text{ mmHg}$$

$$(n_A)_0 = 10 \text{ mol} \quad \text{and} \quad (n_B)_0 = 12 \text{ mol}$$

Let the amount of A after 100 min is reduced to  $n_A$ . At this stage,

**10.20** IIT Chemistry: Topic-wise Solved Questions

$$\begin{aligned}n_{\text{total}} &= n_A + n_B + n_{\text{solute}} = n_A + 12 \text{ mol} + 0.525 \text{ mol} \\&= n_A + 12.525 \text{ mol}\end{aligned}$$

The amount fractions of A and B in the solution will be

$$x_A = \frac{n_A}{n_A + 12.525 \text{ mol}} \quad \text{and} \quad x_B = \frac{12 \text{ mol}}{n_A + 12.525 \text{ mol}}$$

Since  $p_{\text{total}} = x_A p_A^* + x_B p_B^*$ , we get

$$400 \text{ mmHg} = \left( \frac{n_A}{n_A + 12.525 \text{ mol}} \right) (300 \text{ mmHg}) + \left( \frac{12 \text{ mol}}{n_A + 12.525 \text{ mol}} \right) (500 \text{ mmHg})$$

Solving for  $n_A$ , we get  $n_A = 9.90 \text{ mol}$

For the first-order kinetics, we have

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\text{or} \quad k = -\frac{\ln [A]_t / [A]_0}{t} = \frac{\ln (9.90/10)}{100 \text{ min}} = 1.00 \times 10^{-4} \text{ min}^{-1} = 1.68 \times 10^{-6} \text{ s}^{-1}$$

22. From the data a, we find that the rate of reaction increases in proportion to the changed concentration of  $I^-$  indicating that the reaction is first order with respect to  $I^-$ .

From the data b, we find that the rate of reaction increases in proportion to the changed concentration of  $OCl^-$  indicating that the reaction is first order with respect to  $OCl^-$ .

From the data c, we find that the rate of reaction decreases in proportion to the changed concentration of  $OH^-$  indicating that the order of reaction with respect to  $OH^-$  is  $-1$ .

Hence, the rate expression is

$$r = k \frac{[I^-][OCl]^{-1}}{[OH^-]}$$

- (b) Using the data  $[OCl]_0 = [OH^-]_0 = 0.1 \text{ M}$  and  $[I^-]_0 = 0.01 \text{ M}$ , we get

$$k = (\text{rate}) \left( \frac{[OH^-]}{[I^-][OCl]} \right) = (0.6 \text{ mol dm}^{-3} \text{ s}^{-1}) \left[ \frac{0.1 \text{ mol dm}^{-3}}{(0.01 \text{ mol dm}^{-3})(0.1 \text{ mol dm}^{-3})} \right] = 60 \text{ s}^{-1}$$

# **SURFACE CHEMISTRY**

**11**

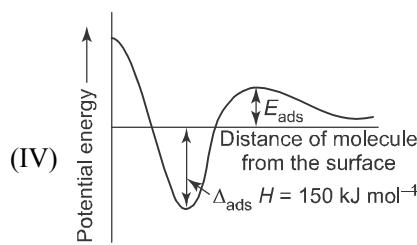
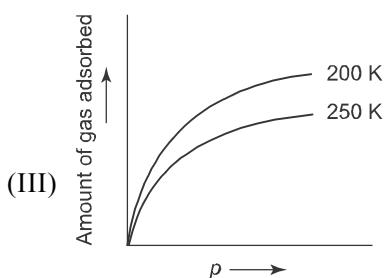
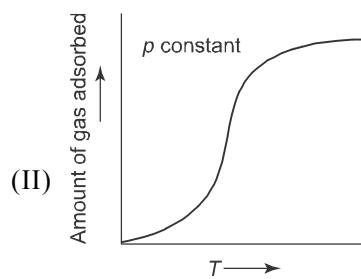
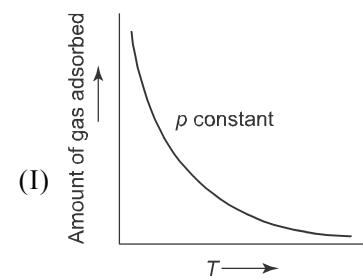
## **Straight Objective Type**

1. Adsorption of gases on solids is accompanied with
  - (a) increase in enthalpy
  - (b) increase in entropy
  - (c) decrease in entropy
  - (d) increase in free energy(2004)
2. Which of the following statements is correct for lyophilic sols?
  - (a) The coagulation of the sols is irreversible in nature
  - (b) They are formed by inorganic substances
  - (c) They are self stabilised
  - (d) They are readily coagulated by addition of electrolytes.(2005)
3. Among the following, the surfactant that will form micelles in aqueous solution at the lowest molar concentration at ambient conditions is
  - (a)  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^-$
  - (b)  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$
  - (c)  $\text{CH}_3(\text{CH}_2)_6\text{COO}^-\text{Na}^+$
  - (d)  $\text{CH}_3(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_3\text{Br}^-$(2008)
4. Among the electrolytes  $\text{Na}_2\text{SO}_4$ ,  $\text{CaCl}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{NH}_4\text{Cl}$ , the most effective coagulating agent for  $\text{Sb}_2\text{S}_3$  sol is
  - (a)  $\text{Na}_2\text{SO}_4$
  - (b)  $\text{CaCl}_2$
  - (c)  $\text{Al}_2(\text{SO}_4)_3$
  - (d)  $\text{NH}_4\text{Cl}$(2009)
5. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at  $25^\circ\text{C}$ . For this process, the correct statement is
  - (a) The adsorption requires activation at  $25^\circ\text{C}$
  - (b) The adsorption is accompanied by a decrease in enthalpy
  - (c) The adsorption increases with increase of temperature
  - (d) The adsorption is irreversible.(2013)

## **Multiple Correct-Choice Type**

1. The correct statement(s) pertaining to the adsorption of a gas on a solid surface is (are)
  - (a) Adsorption is always exothermic
  - (b) Physisorption may transform to chemisorption at high temperature
  - (c) Physisorption increases with increasing temperature but chemisorption decreases with increasing temperature
  - (d) Chemisorption is more exothermic than physisorption, however, it is very slow due to higher energy of activation.(2011)

2. Choose the correct reason(s) for the stability of lyophobic colloidal particles.
- Preferential adsorption of ions on their surface from the solution.
  - Preferential adsorption of solvent on their surface from the solution.
  - Attraction between different particles having opposite charges on their surface.
  - Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.
- (2012)
3. The given graph/data I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure. Which of the following choice(s) about I, II, III and IV is(are) correct.



- (a) I is physisorption and II is chemisorption  
 (c) IV is chemisorption and II is chemisorption
- (b) I is physisorption and III is chemisorption  
 (d) IV is chemisorption and III is chemisorption
4. When  $O_2$  is adsorbed on a metallic surface, electron transfer occurs from the metal to  $O_2$ . The TRUE statement(s) regarding this adsorption is(are)
- $O_2$  is physisorbed
  - Occupancy of  $\pi^*2p$  of  $O_2$  is increased
  - Heat is released
  - Bond length of  $O_2$  is increased
- (2015)

### Fill-in-the-Blanks Type

1. The absorption of hydrogen by palladium is commonly known as \_\_\_\_\_. (1983)

### Reasoning Type

1. STATEMENT-1: Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).  
**because**  
 STATEMENT-2: The conductivity of a solution having surfactant molecules decreases sharply at the CMC.
- Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
  - Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
  - Statement-1 is True, Statement-2 is False
  - Statement-1 is False, Statement-2 is True
- (2007)

## Subjective Type

1. One gram of charcoal adsorbs 125 mL of 0.4 M  $\text{CH}_3\text{COOH}$  to form a monolayer and thereby the molarity of  $\text{CH}_3\text{COOH}$  reduces to 0.392 M. Calculate the surface area of the charcoal occupied by each molecule of acetic acid if the surface area of charcoal is  $3.01 \times 10^2 \text{ m}^2/\text{g}$ . (2003)

## ANSWERS

### Straight Objective Type

1. (c)            2. (c)            3. (a)            4. (c)            5. (b)

### Multiple Correct-Choice Type

1. (a), (b), (d)    2. (a), (d)    3. (a), (c)    4. (b), (c), (d)

### Fill-in-the-Blanks Type

1. occlusion

### Reasoning Type

1. (b)

## Subjective Type

1.  $5 \times 10^{-19} \text{ m}^2$

## HINTS AND SOLUTIONS

### Straight Objective Type

- Adsorption is accompanied with decrease in entropy as the adsorbed molecules become more ordered.
- The lyophilic (solvent lovers) sols are quite stable and are not easily coagulated. The coagulation is reversible in nature.
- Larger the hydrocarbon chain, lesser concentration is required to form micelles.
- The colloidal particles are coagulated with the addition of electrolytes due to the neutralization of charges. According to Hardy-Schulze rule, larger the charge on the ion, larger its coagulation ability.  $\text{Sb}_2\text{S}_3$  being a negative sol, it will be coagulated most effectively by  $\text{Al}_2(\text{SO}_4)_3$  as  $\text{Al}^{3+}$  ion carries the larger positive charge.
- The adsorption of methylene blue on activated charcoal is a physical adsorption which requires no activation. This process is reversible and the adsorption decreases with increase of temperature. It is accompanied with decrease of enthalpy due to the attraction between adsorbent and adsorbate.  
Therefore, the choice (b) is correct.

## Multiple Correct-Choice Type

- Adsorption is always exothermic as it involves interaction between adsorbent and adsorbate. Physisorption may pass over to chemisorption on increasing temperature because the latter predominates at higher temperature. Because of larger activation energy, chemisorption is a slow process. Hence, the **choices (a), (b) and (d)** are correct.
- The stability of lyophobic colloidal particles is due to the preferential adsorption of common ion from the solution. Each colloidal particle has the same charge and are thus kept away from each other due to electronic repulsion (choice a). There exists potential difference between the fixed and diffused layer of opposite charge (choice d). Therefore, the **choice (a) and (d)** are correct.

- We have the following facts.

- Adsorption decreases with increase in temperature at constant pressure in case of physisorption
- Adsorption increases initially with increase in temperature at constant pressure in case of chemisorption as more molecules satisfy the energy of activation.
- The enthalpy change during chemisorptions is high due to the bond formation between adsorbent and adsorbate.

With these guidelines, we will have

Graph I represents physisorption

Graph II represents chemisorption

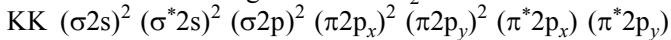
Graph III represents physisorption

Graph IV represents chemisorptions

Therefore, The **choices (a) and (c)** are correct.

- $O_2$  is **not** physisorbed as electron is transferred from the metal to  $O_2$ . During adsorption, heat is released due to the interaction between the adsorbent and adsorbate (Choice b)

The electronic configuration of  $O_2$  is



The electron transfer from the metal to  $O_2$  enters  $\pi^* 2p$  orbital (Choice c)

The bond length of  $O_2$  is increased due to decrease in bond order from 2 to 1.5 (Choice d)

## Reasoning Type

- Both the statements are correct. The statement 1 is not correct explanation of statement 2, but the reverse is correct.

## Subjective Type

- Amount of  $CH_3COOH$  in 125 mL of 0.008 M ( $= 0.40 \text{ M} - 0.392 \text{ M}$ ) is

$$n = MV = (0.008 \text{ mol L}^{-1}) (0.125 \text{ L}) = 0.001 \text{ mol}$$

Number of molecules of  $CH_3COOH$  in 0.001 mol of acetic acid is

$$N = nN_A = (0.001 \text{ mol}) (6.023 \times 10^{23} \text{ mol}^{-1}) = 6.02 \times 10^{20}$$

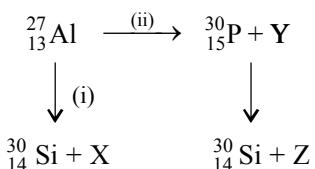
$$\text{Surface area covered by one molecule of acetic acid} = \frac{3.01 \times 10^2 \text{ m}^2}{6.02 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$

# NUCLEAR CHEMISTRY

12

## Straight Objective Type

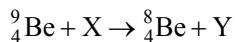
1. If uranium (mass number 238 and atomic number 92) emits an  $\alpha$ -particle, the product respectively has mass number and atomic number  
(a) 236 and 92      (b) 234 and 90      (c) 238 and 90      (d) 236 and 90      (1981)
2. The radiations from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are  
(a) definitely alpha rays      (b) definitely beta rays  
(c) both alpha and beta rays      (d) either alpha or beta rays      (1984)
3. The increasing order for the values of  $e/m$  (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle ( $\alpha$ ) is  
(a) e, p, n,  $\alpha$       (b) n, p, e,  $\alpha$       (c) n, p,  $\alpha$ , e      (d) n,  $\alpha$ , p, e      (1984)
4. The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will reduce to  
(a)  $(1/2)g$       (b)  $(1/4)g$       (c)  $(1/8)g$       (d)  $(1/16)g$       (1986)
5. Nuclear reaction(s) accompanied with emission of neutron(s) is/are  
(a)  $^{27}_{13}\text{Al} + ^4_2\text{He} \rightarrow ^{30}_{15}\text{P}$       (b)  $^{12}_{6}\text{C} + ^1_1\text{H} \rightarrow ^{13}_{7}\text{N}$   
(c)  $^{30}_{15}\text{P} \rightarrow ^{30}_{14}\text{Si} + ^0_1\text{e}$       (d)  $^{241}_{96}\text{Am} + ^4_2\text{He} \rightarrow ^{245}_{97}\text{Bk} + ^0_1\text{e}$       (1988)
6.  $^{27}_{13}\text{Al}$  is a stable isotope,  $^{29}_{13}\text{Al}$  is expected to disintegrate by  
(a)  $\alpha$ -emission      (b)  $\beta$ -emission      (c) positron emission      (d) proton emission      (1996)
7. The number of neutrons accompanying the formation of  $^{139}_{54}\text{Xe}$  and  $^{94}_{38}\text{Sr}$  from the absorption of a slow neutron by  $^{235}_{92}\text{U}$ , followed by nuclear fission is  
(a) 0      (b) 2      (c) 1      (d) 3      (1999)
8. The more stable isotope of sodium is  $^{23}\text{Na}$ . The atom  $^{24}\text{Na}$  can undergo radioactive decay via  
(a)  $\beta^-$  emission      (b)  $\alpha$  emission      (c)  $\beta^+$  emission      (d) K-electron capture      (2003)
9. A positron is emitted from  $^{23}_{11}\text{Na}$ . The ratio of the atomic mass and atomic number of the resulting nuclide is  
(a) 22/10      (b) 22/11      (c) 23/10      (d) 23/12      (2007)
10. Bombardment of aluminium by  $\alpha$ -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Particles X, Y and Z, respectively, are



- |                               |                               |         |
|-------------------------------|-------------------------------|---------|
| (a) proton, neutron, positron | (b) neutron, positron, proton |         |
| (c) proton, positron, neutron | (d) positron, proton, neutron | (20011) |

### Multiple Correct-Choice Type

1. Decrease in atomic number is observed during  
 (a) alpha emission (b) beta emission (c) positron emission (d) electron capture
2. In the nuclear transmutation



- (X, Y) is (are)  
 (a) ( $\gamma$ , n) (b) (p, D) (c) (n, D) (d) ( $\gamma$ , p) (2013)

### Fill in the Blanks Type

#### Integer Answer Type

1. The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction  ${}^{238}_{92}\text{U} \rightarrow {}^* {}^{214}_{82}\text{Pb}$  is \_\_\_\_\_. (2009)
2. The number of neutrons emitted when  ${}^{235}_{92}\text{U}$  undergoes controlled nuclear fission to  ${}^{142}_{54}\text{Xe}$  and  ${}^{90}_{38}\text{Sr}$  is \_\_\_\_\_. (2010)
3. The periodic table consists of 18 groups. An isotope of copper, on bombardment with protons, undergoes a nuclear reaction yielding element X as shown below. To which group, element X belongs in the periodic table?  

$${}^{63}_{29}\text{Cu} + {}^1_1\text{H} \rightarrow {}^6_0\text{n} + ? + {}^2_1\text{H} + \text{X}$$
 (2012)
4. A closed vessel with rigid walls contains 1 mol of  ${}^{238}_{92}\text{U}$  and 1 mol of air at 298 K. Considering complete decay of  ${}^{238}_{92}\text{U}$  to  ${}^{206}_{82}\text{Pb}$ , the ratio of the final pressure to the initial pressure of the system at 298 K is \_\_\_\_\_. (2015)

### True/False Type

1. In  $\beta$ -emission from a nucleus the atomic number of the daughter element decreases by one. (1990)
2. In a given electric field,  $\beta$ -particles are deflected more than  $\alpha$ -particles in spite of  $\alpha$ -particles having larger charge. (1993)

### Reasoning Type

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subquestion.

- (a) If both assertion and statement are true and statement is an explanation of assertion.
  - (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
  - (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
  - (d) If both assertion and statement are wrong and statement is not explanation of assertion.
1. Nuclide  ${}^{30}_{13}\text{Al}$  is less stable than  ${}^{40}_{20}\text{Ca}$  Nuclides having odd number of protons and neutrons are generally unstable. (1998)

2. STATEMENT-1: The plot of atomic number ( $y$ -axis) versus number of neutrons ( $x$ -axis) for stable nuclei shows a curvature towards  $x$ -axis from the line of  $45^\circ$  slope as the atomic number is increased.

and

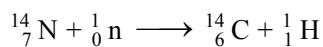
STATEMENT-2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

- (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
- (b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
- (c) STATEMENT-1 is True, STATEMENT-2 is False
- (d) STATEMENT-1 is False, STATEMENT-2 is True.

(2008)

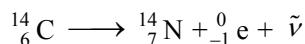
### Linked Comprehension Type

In the upper atmosphere, neutrons present in cosmic rays causes the following nuclear reaction.



The isotope  ${}_{\bar{6}}^{14}\text{C}$ , gets circulated in the atmosphere as well as in living species. In a place where nuclear explosion takes place, the concentration of  ${}^{14}\text{C}$  increases both in the atmosphere as well as in living species.

The isotope  ${}_{\bar{6}}^{14}\text{C}$  disintegrates according to the reaction



with a half life of 5760 years. When a species dies, the concentration of  ${}^{14}\text{C}$  in it decreases due to the above disintegration reaction. The time at which species had died can be estimated from the knowledge of its  ${}^{14}\text{C}$  content compared to that existing in atmosphere. Beyond 30000 years, the activity of disintegration is too low to be used for the estimation of time period.

1. In radiocarbon dating for finding the age of fossils, the correct statement is
  - (a) During the life time  ${}^{14}\text{C}$  assimilated by the human being is in equilibrium with the  ${}^{14}\text{C}$  that decomposes by  $\beta$  emission resulting in the constant ratio of  ${}^{14}\text{C}/{}^{12}\text{C}$  at a particular instant.
  - (b)  ${}^{14}\text{C}$  dating method is inappropriate for finding the life of a given sample because  ${}^{14}\text{C}$  undergoes  $\beta$  emission and the ratio  ${}^{14}\text{C}/{}^{12}\text{C}$  is not constant in human beings.
  - (c) For a dead human being, the decay of  ${}^{14}\text{C}$  depends on place to place.
  - (d) None of the above
2. Two organisms died on the same day. One died at a place where nuclear explosion had taken place while the other died at a place where no such explosion has occurred. The ratio of  ${}^{14}\text{C}$  during life to that present in the fossil at an instant is  $r_1$  for the former and  $r_2$  for the latter. The age of the former was calculated at  $t_1$  and for the latter as  $t_2$ . The correct choice for the timings  $t_1$  and  $t_2$  is
  - (a)  $t_1 > t_2$
  - (b)  $t_1 < t_2$
  - (c)  $t_1 = t_2$
  - (d) none of these
3. If both the fossils are brought to a common place where no explosion has occurred then
  - (a)  $t_1 > t_2$
  - (b)  $t_1 < t_2$
  - (c)  $t_1 = t_2$
  - (d) none of these

(2006)

### Short Answer Type

1. Write a balanced equation for the reaction of  ${}^{14}\text{N}$  with  $\alpha$ -particle. (1997)
2.  ${}_{90}^{232}\text{Th} \longrightarrow 6\alpha + 4\beta + {}_Z^AX$ . Identify  ${}_Z^AX$ . (2007)

### Subjective Type

- Naturally occurring boron consists of two isotopes whose atomic masses are 10.01 and 11.01 amu. The atomic mass of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. (1982)
- Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant for the decay? What fraction would remain after 11540 years? (1984)
- $^{234}_{90}\text{Th}$  disintegrates to give  $^{206}_{82}\text{Pb}$  as the final product. How many alpha and beta particles are emitted during this process? (1986)
- An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of  $^{99}_{42}\text{Mo}$ , which is a beta emitter, is 66.6 hours. Find the minimum amount of  $^{99}_{42}\text{Mo}$  required to carry out the experiment in 6.909 hours. (1989)
- One of the hazards of nuclear explosion is the generation of  $^{90}\text{Sr}$  and its subsequent incorporation in bones. This nuclide has a half-life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much  $^{90}\text{Sr}$  will remain in his bones after 20 years? (1995)
- $^{227}\text{Ac}$  has a half-life of 22.0 years with respect to radioactive decay. The decays follows two parallel paths, one leading to  $^{227}\text{Th}$  and the other to  $^{223}\text{Fr}$ . The percentage yields of these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants ( $\lambda$ ) for each of the separate paths? (1996)
- With what velocity should an  $\alpha$ -particle travel towards the nucleus of a copper atom so as to arrive at a distance  $10^{-13}$  m from the nucleus of the Cu atom? (1997)
- $^{238}_{92}\text{U}$  is radioactive and it emits  $\alpha$  and  $\beta$  particles to form  $^{206}_{82}\text{Pb}$ . Calculate the number of  $\alpha$  and  $\beta$  particles emitted in the conversion. An ore of  $^{238}_{92}\text{U}$  is found to contain  $^{238}_{92}\text{U}$  and  $^{206}_{82}\text{Pb}$  in the mass ratio of 1:0.1. The half life period of  $^{238}_{92}\text{U}$  is  $4.5 \times 10^9$  years. Calculate the age of the ore. (2000)
- The nucleidic ratio,  $^3\text{H}$  to  $^1\text{H}$  in a sample of water is  $8.0 \times 10^{-18} : 1$ . Tritium undergoes decay with a half life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected? (1992)
- $^{64}\text{Cu}$  (half-life = 12.8 h) decays by  $\beta^-$  emission (38%),  $\beta^+$  emission (19%) and electron capture (43%). Write the decay products and calculate partial half-life for each of the decay processes. (2002)

### ANSWERS

#### Straight Objective Type

1. (b)      2. (d)      3. (d)      4. (d)      5. (a)      6. (b)      7. (d)  
 8. (a)      9. (c)      10. (a)

#### Multiple Correct-Choice Type

1. (a), (c), (d)      2. (a), (b)

#### Fill-in-the-Blanks Type

#### Integer Answer Type

1. 8      2. 3      3. 8      4. 9

#### True/False Type

1. False      2. True

**Reasoning Type**

1. (b)

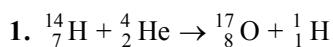
2. (a)

**Linked Comprehension Type**

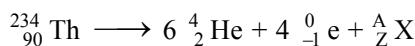
1. (a)

2. (a)

3. (c)

**Short Answer Type**

2. Given nuclear reaction is



Balancing the atomic number and mass number, we get

$$6 \times 2 + 4(-1) + Z = 90 \Rightarrow Z = 82$$

$$6 \times 4 + 4 \times 0 + A = 232 \Rightarrow A = 208$$

The element having  $Z = 82$  is lead. Hence, the species  ${}_Z^A\text{X}$  is  ${}_{82}^{208}\text{Pb}$ .

**Subjective Type**

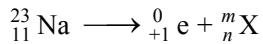
- |  |  |
|--|--|
| 1. 20% of B of 10.01 amu; 80% of B of 11.01 amu  | 2. $1.201 \times 10^{-4} \text{ y}^{-1}$ ; 25%         |
| 3. 7 $\alpha$ -particles; 6 $\beta$ -particles   | 4. $3.43 \times 10^{-18} \text{ mol}$                  |
| 5. 0.6107 $\mu\text{g}$  | 6. $0.00063 \text{ y}^{-1}$ ; $0.03087 \text{ y}^{-1}$ |
| 7. $8.97 \times 10^6 \text{ m s}^{-1}$   | 8. $7.09 \times 10^8 \text{ y}$                        |
| 9. $5.624 \times 10^7$   |  |
| 10. $\beta^-$ emission; ${}_{29}^{64}\text{Cu} \rightarrow {}_{30}^{64}\text{Zn} + {}_{-1}^0\text{e}$ ; 33.67 h<br>$\beta^+$ emission; ${}_{29}^{64}\text{Cu} \rightarrow {}_{28}^{64}\text{Ni} + {}_{+1}^0\text{e}$ ;<br>67.35 h<br>Electron capture: ${}_{29}^{64}\text{Cu} + {}_{-1}^0\text{e} \rightarrow {}_{28}^{64}\text{Ni}$ ; 29.77 h |  |

**HINTS AND SOLUTIONS****Straight Objective Type**

- Mass number =  $238 - 4 = 234$  and atomic number =  $92 - 2 = 90$ .
- Either alpha or beta rays are deflected in a magnetic field in one direction.
- Neutron has  $e/m$  value zero. The next higher value is of  $\alpha$ -particle. This is followed by proton and finally by electron.
- 560 days are equivalent to four half-lives. The element left will be  $(1/2)^4$  (1 g), i.e.  $(1/16)$  g.
- In the reaction  ${}_{13}^{27}\text{Al} + {}_2^4\text{He} \rightarrow {}_{15}^{30}\text{P}$ , atomic number is balanced and mass number decreases by one. This reaction will be associated with the emission of a neutron.
- ${}_{13}^{29}\text{Al}$  contains more neutrons than the stable isotope  ${}_{13}^{27}\text{Al}$ . It will get rid of neutrons by the reaction neutron  $\rightarrow$  proton  $\rightarrow$  electron.

## 12.6 IIT Chemistry: Topic-wise Solved Questions

7. The reaction is  $^{235}_{92}\text{U} + {}^1_0\text{n} \rightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + 3 {}^1_0\text{n}$
8. Only  $\beta^-$  emission decreases n/p ratio towards stability.
9. The given nuclear reaction may be depicted as follows.

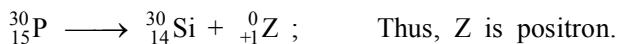
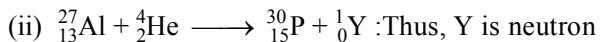
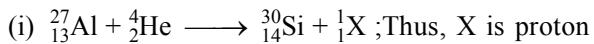


Balancing the atomic number and mass number gives

$$m + 0 = 23 \Rightarrow m = 23 \quad \text{and} \quad n + 1 = 11 \Rightarrow n = 10$$

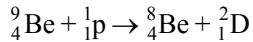
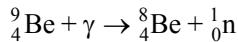
Hence,  $m/n = 23/10$ .

10. Balancing charges and mass numbers give

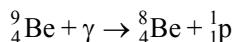
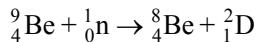


## Multiple Correct-Choice Type

2. The given transmutation involves (i) no change in atomic number and (ii) a decrease of one in mass number. The choices (a) and (b) satisfy this requirement as shown in the following.



The choices (c) and (d) involve an increase in atomic number



Therefore, the **choices (a) and (b)** are correct.

## Fill-in-the-Blanks Type

### Integer Answer Type

1. Alpha emission: 
$${}^A_Z\text{X} \rightarrow {}^{A-4}_{Z-2}\text{Y} + {}^4_2\text{He}$$
  - Positron emission: 
$${}^A_Z\text{X} \rightarrow {}^A_{Z-1}\text{Y} + {}^0_{+1}\text{e} + \nu$$
  - Electron capture: 
$${}^1_1\text{p} + {}^0_{-1}\text{e} \rightarrow {}^1_0\text{n} + \nu$$
- If  $x$  and  $y$  are the number of  $\alpha$  and  $\beta$  particles emitted, respectively, then we will have  
From mass numbers, we have  $-4(x) = 214 - 238 \Rightarrow x = 6$   
From atomic numbers, we have  $-2(x) + 1(y) = 82 - 92 \Rightarrow y = 2$   
The total number of  $\alpha$ - and  $\beta$ -particles emitted is 8.  
Therefore, the correct answer is 8.
2. The reaction is  ${}^{235}_{92}\text{U} \longrightarrow {}^{142}_{54}\text{Xe} + {}^{90}_{38}\text{Sr} + n ({}^1_0\text{n})$   
Balance of mass number gives  $142 + 90 + n(1) = 235 \Rightarrow n = 3$

3. The reaction is  $^{63}_{29}\text{Cu} + ^1\text{H} \rightarrow 6^0_0\text{n} + ^4_2\text{He} + 2^1_1\text{H} + {}_Z^X\text{X}$   
 Balancing the atomic numbers on both sides, we get  $29 + 1 = 6(0) + 1(2) + 2(1) + 1(Z)$   
 which gives  $Z = 26$

Copper belongs to Group 11 of the periodic table as shown in the following.

Atomic number	29
Elements in First period	-2
Elements in Second period	-8
Elements in Third period	-8
Number in Fourth period	11th Group

The element with atomic number 26 will belong to the following group.  $26 - 2 - 8 - 8 = 8$ th Group  
 Therefore, the Group number of X is **8**.

4. Since mass number in a radioactive decay changes due to emission of  $\alpha$ -particles (i.e.  $\text{He}^{2+}$ ), the amount of  $\alpha$ -particles emitted when  $^{238}\text{U}$  changes to  $^{206}\text{Pb}$ , is

$$n_\alpha = \frac{238 - 206}{4} = 8$$

The total amount of gases at the final stage will be 9 ( $= 8 \text{ mol He} + 1 \text{ mol air}$ ). Thus,

$$\frac{P_{\text{final}}}{P_{\text{initial}}} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{9 \text{ mol}}{1 \text{ mol}} = 9$$

### True/False Type

- In  $\beta$ -emission, the reaction taking place in the nucleus is  $n \rightarrow p + e$   
 Thus, there is an increase in the atomic number by one.
- The deflection in a given electric field depends on the value of  $e/m$ . For  $\beta$ -particles,  $e/m$  is larger than  $\alpha$ -particles because electrons are much lighter than  $\text{He}^+$  species.

### Reasoning Type

- STATEMENT-1 is correct since the number of protons is less than number of neutrons for stable nuclei.  
 STATEMENT-2 is also correct since the heavier nuclides become less stable and show radioactivity due to the fact the proton-proton electrostatic repulsions are larger than proton-neutron attractions.

### Linked Comprehension Type

2. We have:

$$r_1 = \frac{[{}^{14}\text{C}]_{\text{living, explosion}}}{[{}^{14}\text{C}]_{\text{dead}}} \text{ and } r_2 = \frac{[{}^{14}\text{C}]_{\text{living, no explosion}}}{[{}^{14}\text{C}]_{\text{dead}}}$$

Since  $[{}^{14}\text{C}]_{\text{living, explosion}} > [{}^{14}\text{C}]_{\text{living, no explosion}}$ , we will have  $r_1 > r_2$ . Moreover, since

$\ln r = (1/\lambda) t$ , it follows that  $t_1 > t_2$ .

3. Here  $r_1 = r_2$ . Hence,  $t_1 = t_2$

## Subjective Type

1. Let  $x$  be the percentage of isotope of atomic mass 10.01 amu. We will have

$$\frac{x(10.01 \text{ amu}) + (100 - x)(11.01 \text{ amu})}{100} = 10.81 \text{ amu}$$

Solving for  $x$ , we get  $x = 20$

Hence, Abundance of isotope of atomic mass 10.01 amu = 20%

Abundance of isotope of atomic mass 11.01 amu = 80%.

2. We have

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770 \text{ y}} = 1.201 \times 10^{-4} \text{ y}^{-1}$$

Since 11540 years is equivalent two half-lives, we would have 25% radioactive carbon left after 11540 years.

3. Since the change in mass number is only due to the emission of  $\alpha$ -particle, we have

$$\text{Number of } \alpha\text{-particles emitted} = \frac{234 - 206}{4} = 7$$

Now, the associated decrease in atomic number would be 14 ( $= 2 \times 7$ ) and thus the atomic number of the daughter atom would be 76 ( $= 90 - 14$ ). But the actual atomic number of lead is 82, i.e. the atomic number is six more than expected. This is because of the emission of  $\beta$ -particles. Since there is an increase of one in atomic number due to the emission of one  $\beta$ -particle, we have

$$\text{Number of } \beta\text{-particles emitted} = \frac{82 - 76}{1} = 6$$

Hence, Number of  $\alpha$ -particles emitted = 7

Number of  $\beta$ -particles emitted = 6

4. Minimum  $\beta$ -activity required =  $346 \text{ min}^{-1}$

Number of  $\beta$ -particle required to carry out the experiment for 6.909 h

$$= (346 \text{ min}^{-1}) (6.909 \times 60 \text{ min}) = 143431$$

$$\text{Amount of } \beta\text{-particles required} = \frac{143431}{6.023 \times 10^{23} \text{ mol}^{-1}} = 2.3814 \times 10^{-19} \text{ mol}$$

Now, the rate constant of radioactive decay is

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{66.6 \text{ h}} = 0.01404 \text{ h}^{-1}$$

Now using the integrated rate expression

$$\log \frac{n_0 - n_{\text{consumed}}}{n_0} = -\frac{\lambda t}{2.303}$$

$$\text{we get } \log \frac{n_0 - 2.3184 \times 10^{-19} \text{ mol}}{n_0} = -\frac{(0.01404 \text{ h}^{-1})(6.909 \text{ h})}{2.303} = -0.03121$$

$$\text{or } \frac{n_0 - 2.3184 \times 10^{-19} \text{ mol}}{n_0} = 0.9306$$

$$\Rightarrow n_0 = \frac{2.3184 \times 10^{-19} \text{ mol}}{1 - 0.9306} = 3.43 \times 10^{-18} \text{ mol.}$$

5. For the half-life  $t_{1/2} = 28.1 \text{ y}$ , the decay constant is

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1 \text{ y}}$$

Since the radioactivity decay follows the first order kinetics, we have

$$\log \frac{[A]}{[A]_0} = -\frac{\lambda}{2.303} t$$

$$\text{Thus } \log \frac{[A]}{1.0 \mu\text{g}} = -\frac{0.693}{28.1 \text{ y}} \times \frac{20 \text{ y}}{2.303} \quad \text{or} \quad \log [A]/\mu\text{g} = -0.2142$$

$$\text{or} \quad [A] = 0.6107 \mu\text{g.}$$

6. The rate constant of the decay is

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{22.0 \text{ y}}$$

If  $k_1$  and  $k_2$  are the rate constants of the reactions leading to  $^{227}\text{Th}$  and  $^{223}\text{Fr}$ , respectively, we have

$$\lambda_1 + \lambda_2 = \frac{0.693}{22.0 \text{ y}} \quad \text{and} \quad \frac{\lambda_1}{\lambda_2} = \frac{2}{98}$$

Solving for  $k_1$  and  $k_2$ , we get

$$\lambda_1 = 0.00063 \text{ y}^{-1} \quad \text{and} \quad \lambda_2 = 0.03087 \text{ y}^{-1}$$

7. Potential energy of an  $\alpha$ -particle at a distance  $10^{-13} \text{ m}$  from the nucleus of copper atom is

$$V = -\frac{Z_1 Z_2 e^2}{(4\pi\epsilon_0) r} = -\frac{(29)(4)(1.6 \times 10^{-19} \text{ C})^2}{(4)(3.14)(8.85 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})(10^{-13} \text{ m})} = -2.67 \times 10^{-13} \text{ J}$$

Velocity at which  $\alpha$ -particle should move is

$$v = \sqrt{\frac{2|V|}{m}} = \left[ \frac{2(2.67 \times 10^{-13} \text{ J})}{(4.0 \times 10^{-3} \text{ kg mol}^{-1})/(6.023 \times 10^{23} \text{ mol}^{-1})} \right]^{1/2} = 8.97 \times 10^6 \text{ m s}^{-1}$$

8. The release of an  $\alpha$ -particle causes

Decrease in atomic number = 2 and decrease in mass number = 4

The release of a  $\beta$ -particle causes

Increase in atomic number = 1 and no change in mass number

Since the mass number changes only due to the emission of  $\alpha$ -particles, we will have

$$\text{Number of } \alpha\text{-particles emitted} = \frac{238 - 206}{4} = \frac{32}{4} = 8$$

The associated decrease in atomic number would be  $8 \times 2 = 16$ . But the actual decrease is only 10. The increase in atomic number from 76 ( $= 92 - 16$ ) to 82 is due to emission of  $\beta$ -particles. Hence

Number of  $\beta$ -particles emitted =  $82 - 76 = 6$

Assuming atomic mass equal to mass number, we will have

**12.10** IIT Chemistry: Topic-wise Solved Questions

	U	Pb
Mass ratio	1	:
Amount ratio	$\frac{1}{238}$	:

$$\frac{0.1}{206} \quad \text{i.e. } 4.202 \times 10^{-3} : 4.854 \times 10^{-4}$$

$$\begin{aligned}\text{Original amount of U, } [U]_0 &= [U] + [Pb] = (4.202 \times 10^{-3} + 4.854 \times 10^{-4}) \text{ mol} \\ &= 4.687 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\text{Present amount of U, } [U] = 4.202 \times 10^{-3} \text{ mol}$$

The rate constant of radioactive decay is given by

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{ y}} = 1.54 \times 10^{-10} \text{ y}^{-1}$$

Now, using the expression

$$\ln \frac{[U]}{[U]_0} = -\lambda t \text{ we get}$$

$$\begin{aligned}t &= -\frac{1}{\lambda} \left( 2.303 \log \frac{[U]}{[U]_0} \right) = -\frac{1}{(1.54 \times 10^{-10} \text{ y}^{-1})} \left[ 2.303 \log \left( \frac{4.202 \times 10^{-3}}{4.687 \times 10^{-3}} \right) \right] \\ &= 7.09 \times 10^8 \text{ y}\end{aligned}$$

9. We have

$$\frac{\text{Number of tritium (T) atoms}}{\text{Number of hydrogen(H) atoms}} = \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or } \frac{\text{Number of T}_2\text{O molecules}}{\text{Number of H}_2\text{O molecules}} = \frac{8.0 \times 10^{-18}/2}{1/2} = \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or } \frac{\text{Amount of T}_2\text{O molecules}}{\text{Amount of H}_2\text{O molecules}} = \frac{8.0 \times 10^{-18} / 6.023 \times 10^{23}}{1/6.023 \times 10^{23}}$$

$$= \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or } \frac{\text{Mass of T}_2\text{O molecules}}{\text{Mass of H}_2\text{O molecules}} = \frac{22 \times 8 \times 10^{-18}}{18}$$

Mass of T<sub>2</sub>O molecules in 10.0 g of sample of water

$$\begin{aligned}&= \frac{22 \times 8 \times 10^{-18}}{18 + 22 \times 8 \times 10^{-18}} \times 10.0 \text{ g} = \frac{22 \times 8 \times 10^{-18}}{18} \times 10.0 \text{ g} \\ &= 9.777 \times 10^{-17} \text{ g}\end{aligned}$$

$$\text{Amount of T}_2\text{O molecules} = \frac{9.777 \times 10^{-17} \text{ g}}{22 \text{ g mol}^{-1}} = 4.444 \times 10^{-16} \text{ mol}$$

Now using the integrated rate expression

$$\log \frac{[\text{T}_2\text{O}]}{[\text{T}_2\text{O}]_0} = -\frac{k}{2.303} t$$

for the first order reaction, we get

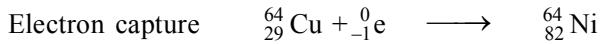
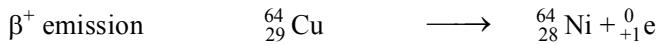
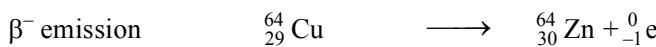
$$\begin{aligned}\log n(T_2O) &= \log n_0(T_2O) - \frac{1}{2.303} \left( \frac{0.693}{t_{0.5}} \right) t \\ &= \log (4.444 \times 10^{-16}) - \frac{1}{2.303} \left( \frac{0.693}{12.3 \text{ y}} \right) (40 \text{ y}) \\ &= -15.3522 - 0.9786 = -16.3308\end{aligned}$$

or  $n(T_2O) = 4.6687 \times 10^{-17} \text{ mol}$

$$\begin{aligned}\text{Number of } T_2O \text{ molecules} &= (4.6687 \times 10^{-17}) (6.023 \times 10^{23}) \\ &= 2.812 \times 10^7\end{aligned}$$

$$\text{Number of T atoms} = 2 \times 2.812 \times 10^7 = 5.624 \times 10^7$$

**10.** The nuclear reactions are as follows.



If  $r_1$ ,  $r_2$  and  $r_3$  are the respective rates of decay of Cu and  $r$  is the overall rate of decay of Cu, we will have

$$r = r_1 + r_2 + r_3$$

$$\Rightarrow \lambda [\text{Cu}] = \lambda_1 [\text{Cu}] + \lambda_2 [\text{Cu}] + \lambda_3 [\text{Cu}]$$

$$\text{i.e. } \lambda = \lambda_1 + \lambda_2 + \lambda_3 \quad (1)$$

The overall decay constant  $\lambda$  is given by

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8 \text{ h}} = 5.414 \times 10^{-2} \text{ h}^{-1} \quad (2)$$

$$\text{It is given that } \frac{\lambda_1}{\lambda_3} = \frac{38}{43} = 0.884 \quad \text{and} \quad \frac{\lambda_2}{\lambda_3} = \frac{19}{43} = 0.442$$

Substituting these in Eq. (1), we get

$$\lambda = 0.884 \lambda_3 + 0.442 \lambda_3 + \lambda_3 = 2.326 \lambda_3$$

$$\text{Hence, } \lambda_3 = \frac{\lambda}{2.326} = \frac{5.414 \times 10^{-2} \text{ h}^{-1}}{2.326} = 2.328 \times 10^{-2} \text{ h}^{-1}$$

$$(t_{1/2})_3 = \frac{0.693}{\lambda_3} = \frac{0.693}{2.328 \times 10^{-2} \text{ h}^{-1}} = 29.77 \text{ h}$$

$$\lambda_1 = 0.884 \lambda_3 = (0.884) (2.328 \times 10^{-2} \text{ h}^{-1}) = 2.058 \times 10^{-2} \text{ h}^{-1}$$

$$(t_{1/2})_1 = \frac{0.693}{\lambda_1} = \frac{0.693}{2.058 \times 10^{-2} \text{ h}^{-1}} = 33.67 \text{ h}$$

$$\lambda_2 = 0.442 \lambda_3 = (0.442) (2.328 \times 10^{-2} \text{ h}^{-1}) = 1.029 \times 10^{-2} \text{ h}^{-1}$$

$$(t_{1/2})_2 = \frac{0.693}{\lambda_2} = \frac{0.693}{1.029 \times 10^{-2} \text{ h}^{-1}} = 67.35 \text{ h}$$



# NONMETALS

13

## Straight Objective Type

1. When the same amount of zinc is treated separately with excess of sulphuric acid and excess of sodium hydroxide, the ratio of volumes of hydrogen evolved is  
(a) 1 : 1      (b) 1 : 2      (c) 2 : 1      (d) 9 : 4      (1979)
2. Lead pencil contains  
(a) Pb      (b) FeS      (c) Graphite      (d) PbS      (1980)
3. The element with the highest first ionization potential is  
(a) boron      (b) carbon      (c) nitrogen      (d) oxygen      (1982)
4. Moderate electrical conductivity is shown by  
(a) silica      (b) graphite      (c) diamond      (d) carborundum      (1982)
5. Chlorine acts as a bleaching agent only in presence of  
(a) dry air      (b) moisture      (c) sunlight      (d) pure oxygen      (1983)
6. A gas that cannot be collected over water is  
(a) N<sub>2</sub>      (b) O<sub>2</sub>      (c) SO<sub>2</sub>      (d) PH<sub>3</sub>      (1985)
7. The compound which gives off oxygen on moderate heating is  
(a) cupric oxide      (b) mercuric oxide      (c) zinc oxide      (d) aluminium oxide      (1986)
8. Bromine can be liberated from potassium bromide solution by action of  
(a) iodine solution      (b) chlorine solution      (c) sodium chloride      (d) potassium iodide      (1987)
9. Concentrated HNO<sub>3</sub> reacts with iodine to give  
(a) HI      (b) HOI      (c) HOIO<sub>2</sub>      (d) HOIO<sub>3</sub>      (1989)
10. The material used in solar cells contains  
(a) Cs      (b) Si      (c) Sn      (d) Ti      (1993)
11. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'  
(a) X = CO<sub>2</sub>, Y = Cl<sub>2</sub>      (b) X = Cl<sub>2</sub>, Y = CO<sub>2</sub>  
(c) X = Cl<sub>2</sub>, Y = H<sub>2</sub>      (d) X = H<sub>2</sub>, Y = Cl<sub>2</sub>      (2002)
12. Which of the following isomers of phosphorus are thermodynamically least and most stable?  
(a) White (least), Red (most)      (b) Yellow (least), Red (most)  
(c) Red (least), White (most)      (d) White (least), Black (most)      (2005)
13. Extra pure N<sub>2</sub> can be obtained by heating  
(a) NH<sub>3</sub> with CuO      (b) NH<sub>4</sub>NO<sub>3</sub>      (c) (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>      (d) Ba(N<sub>3</sub>)<sub>2</sub>      (2011)

## **Multiple Correct-Choice Type**



### **Fill-in-the-Blanks Type**

1. Fill in the blanks.

  - Bromine is manufactured by the action of \_\_\_\_\_ on the bromite present in sea water.
  - Bromine reacts with moist sulphur dioxide to give \_\_\_\_\_.
  - Iodine reacts with potassium chlorate in the presence of nitric acid to produce \_\_\_\_\_ and chlorine.
  - Of the halide ions, \_\_\_\_\_ is the most powerful reducing agent. (1978)

2. Iodine reacts with hot NaOH solution. The products are NaI and \_\_\_\_\_. (1980)

3. There are \_\_\_\_\_  $\pi$  bonds in a nitrogen molecule. (1982)

4. The increase in the solubility of iodine in an aqueous solution of potassium iodide is due to the formation of \_\_\_\_\_. (1982)

5. \_\_\_\_\_ phosphorus is reactive because of its highly strained tetrahedral structure. (1987)

6. Sulphur acts as \_\_\_\_\_ agent in vulcanization of rubber. (1989)

7. The hydrolysis of alkyl substituted chlorosilane gives \_\_\_\_\_. (1991)

8. The unit cell of diamond is \_\_\_\_\_. (1991)

9. One recently discovered allotrope of carbon (e.g. C<sub>60</sub>) is commonly known as \_\_\_\_\_. (1994)

10. Solubility of iodine in water is greatly increased by the addition of iodide ions because of the formation of \_\_\_\_\_. (1994)

11. The angle P-P-P in P<sub>4</sub> molecule is \_\_\_\_\_ degree. (1997)

12. On heating, Rb(1Cl<sub>2</sub>) will decompose giving \_\_\_\_\_ and \_\_\_\_\_. (1997)

## **True/False Type**

- Red phosphorus is less volatile than white phosphorus because the former has a tetrahedral structure. (1982)
  - In an aqueous solution chlorine is a stronger oxidizing agent than fluorine. (1984)
  - Graphite is a better lubricant on the moon than on the earth. (1987)

4. The decreasing order of electron affinity of F, Cl, Br is F > Cl > Br. (1993)  
 5. Diamond is harder than graphite. (1993)  
 6. The tendency for catenation is much higher for C than for Si. (1993)

### **Reasoning Type**

1. STATEMENT-1: Boron always forms covalent bond.  
**because**  
 STATEMENT-2: The small size of  $B^{3+}$  favours formation of covalent bond.  
 (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1  
 (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (c) Statement-1 is True, Statement-2 is False  
 (d) Statement-1 is False, Statement-2 is True (2007)

### **Short Answer Type**

1. Graphite is used as a solid lubricant. (1985)  
 2. Write balanced equations for the preparation of crystalline silicon from  $SiCl_4$ . (1990)  
 3. Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water. (1994)  
 4. Give an example of oxidation of one halide by another halogen. Explain the feasibility of the reaction. (2000)  
 5. (a) Give reasons(s) why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorus is a tetraatomic molecule. (2000)

## **ANSWERS**

### **Straight Objective Type**

- |        |        |         |         |         |         |         |
|--------|--------|---------|---------|---------|---------|---------|
| 1. (a) | 2. (c) | 3. (c)  | 4. (b)  | 5. (b)  | 6. (c)  | 7. (b)  |
| 8. (b) | 9. (c) | 10. (b) | 11. (c) | 12. (d) | 13. (d) | 14. (c) |

### **Multiple Correct-Choice Type**

- |                  |                  |                  |
|------------------|------------------|------------------|
| 1. (a), (c), (d) | 2. (b), (c), (d) | 3. (a), (c), (d) |
|------------------|------------------|------------------|

### **Fill-in-the-Blanks Type**

- |                     |                       |
|---------------------|-----------------------|
| 1. (i) Chlorine     | 2. $NaIO_3$           |
| (ii) Sulphuric acid |                       |
| (iii) iodate        |                       |
| (iv) iodide         |                       |
| 3. two              | 4. $KI_3$ or $I_3^-$  |
| 5. White            | 6. polymerizing       |
| 7. silicones        | 8. face-centered cube |

9. fullerene                    10.  $I_3^-$   
 11.  $60^\circ$                     12. RbCl, ICl  
 13.  $Ba(N_3)_2 \longrightarrow Ba + 3 N_2$

**True/False Type**

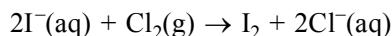
1. False                    2. False                    3. False                    4. False                    5. True                    6. True

**Reasoning Type**

1. (a)

**Short Answer Type**

- Graphite has layered-type structure. One layer can easily slide over the other giving graphite a greasy touch.
- Preparation of crystalline Si from  $SiCl_4$ :  
The vapours of  $SiCl_4$  are passed over molten Al:  
$$3SiCl_4 + 4Al \rightarrow 4AlCl_3 + 3Si$$
- Aluminium is stable in air and water as a thin protective layer of oxide is formed on its surface which prevents the further reaction.
- The example is



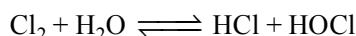
- The standard reduction potential of  $Cl_2$  to  $Cl^-$  is larger than that of  $I_2$  to  $I^-$ .
- Because of the smaller size of nitrogen atom, it can form multiple bonds involving its valence orbitals 2s and 2p's. The size of phosphorus atom is comparatively larger and it cannot form multiple bonds involving its valence orbitals 3s, 3p's and 3d's.  
From the data on bond enthalpies, it can be concluded that the species  $N \equiv N$  is more stable than three  $N - N$  bonds whereas  $P \equiv P$  is less stable than three  $P - P$  bonds.

$$\begin{array}{ll} \varepsilon(N \equiv N) = 946 \text{ kJ mol}^{-1} & \varepsilon(>N - N<) = 160 \text{ kJ mol}^{-1} \\ \varepsilon(P \equiv P) = 490 \text{ kJ mol}^{-1} & \varepsilon(>P - P<) = 200 \text{ kJ mol}^{-1} \end{array}$$

The elementary phosphorus is tetratomic molecule having tetrahedral geometry. Each phosphorus atom is linked to three phosphorus atoms.

**HINTS AND SOLUTIONS****Straight Objective Type**

11.  $Cl_2$  in water undergoes disproportionation reaction.



A white precipitate with  $AgNO_3$  is due to  $Cl^-$  ions. The dissolution of magnesium ribbon liberates  $H_2$  gas.  
 $Mg + 2H^+ \rightarrow Mg^{2+} + H_2$

12. White phosphorus ( $P_4$ ) is arranged tetrahedrally with interatomic distances of 221 pm and interbond angles of  $60^\circ$ . White phosphorus acquires yellow colour on standing due to the formation of a film of red variety on the surface.

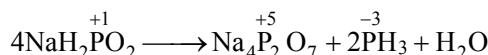
Red phosphorus is believed to be polymeric and consists of chains of  $P_4$  tetrahedrally linked together. Black phosphorus is obtained by heating white phosphorus to 473 K under high pressure.

White phosphorus is thermodynamically least stable than the other solid phases under normal conditions. Black phosphorus is the most stable allotrope.

13. The reaction is  $Ba(N_3)_2 \longrightarrow Ba + 3 N_2$

14. The reaction is  $P_4^0 + 3NaOH + 3H_2O \longrightarrow P^{-3}_3 + 3NaH_2PO_2^{+1}$

The salt  $NaH_2PO_2$  undergoes the following changes on heating.



The reaction is disproportionation reaction and the oxidation states of phosphorus are  $-3$  (in phosphine) and  $+5$  in the second product.

### Multiple Correct-Choice Type

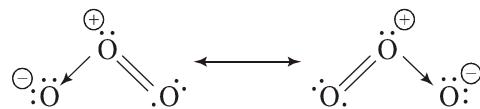
1. The four atoms in a  $P_4$  molecule are situated at the corners of a tetrahedron. There are six  $P - P$  single bonds with  $PPP$  bond angle equal to  $60^\circ$ . Each phosphorus has a lone pair of electrons.

2. The given facts about graphite and diamond are as follows.

Graphite is less hard than diamond. Graphite has higher electrical and thermal conductivities than diamond. This is due to highly delocalized nature of  $\pi$  electrons. Graphite has higher C—C bond order (due to  $\sigma$  and  $\pi$  bonds) than that of diamond (which has only  $\sigma$  bonds)

3. The reaction  $O_3 \rightleftharpoons (3/2) O_2$  is an exothermic reaction.

Because of resonating structures



Both the O—O bond lengths are equal.

Ozone has a bent structure and is diamagnetic in nature.

### True/False Type

1. Red phosphorus has polymeric structure and not a tetrahedral, due to which red phosphorus is less volatile than white phosphorus.

2. Because the hydration energy of  $F^-$  is more than that of  $Cl^-$ .

3. The lubricating properties of graphite depend not only on the slippage between the planes, but also on a film of moisture or gas molecules adsorbed on the surface of the graphite layers. The adsorbed substance decreases the friction as the layers in graphite slide past each other. Dry graphite in vacuum is not slippery.

4. The correct order is  $F < Cl > Br$ . The larger electronic repulsion in F due to smaller size makes its electron affinity less than that of Cl.

5. In diamond, all the four valencies of carbon are involved in stronger  $\sigma$  bonding whereas in graphite, three are involved in  $\sigma$  bonding whereas the fourth one is involved in weak  $\pi$  bonding.

### Reasoning Type

1. Both the statements are correct. Also, the statement 2 is correct explanation of the statement 1. It follows from Fajan's rule that smaller cation with high charge density have a tendency to form covalent bond due to the larger polarization effect.



# **COMPOUNDS OF METALS**

14

## **Straight Objective Type**



### Multiple Correct-Choice Type

1. Which of the following statement(s) is/are correct when a mixture of NaCl and  $K_2Cr_2O_7$  is gently warmed with concentrated  $H_2SO_4$ ?
  - A deep red vapour is evolved
  - The vapour when passed into NaOH solution gives a yellow solution of  $Na_2CrO_4$
  - Chlorine gas is evolved
  - Chromyl chloride is formed(1998)
  
2. Sodium nitrate decomposes above  $\sim 800$  °C to give
  - $N_2$
  - $O_2$
  - $NO_2$
  - $Na_2O$(1998)
  
3. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because:
  - the hydration energy of sodium sulphate is more than its lattice energy
  - the lattice energy of barium sulphate is more than its hydration energy
  - the lattice energy has no role to play in solubility
  - the hydration energy of sodium sulphate is less than its lattice energy.(1989)
  
4. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water, the sodium ions are exchanged with
  - $H^+$  ions
  - $Ca^{2+}$  ions
  - $SO_4^{2-}$  ions
  - $Mg^{2+}$  ions
  - $OH^-$  ions(1990)
  
5. Which of the following oxides is/are amphoteric?
  - $Na_2O$
  - $CaO$
  - $Al_2O_3$
  - $SnO_2$(1993)
  
6. The compound(s) formed upon combustion of sodium metal in excess air is (are)
  - $Na_2O_2$
  - $Na_2O$
  - $NaO_2$
  - $NaOH$(2009)
  
7. The reagent(s) used for softening the temporary hardness of water is(are)
  - $Ca_3(PO_4)_2$
  - $Ca(OH)_2$
  - $Na_2CO_3$
  - $NaOCl$(2010)
  
8. The pair(s) of reagents that yield paramagnetic species is/are
 

<ol style="list-style-type: none"> <li>Na and excess of <math>NH_3</math></li> <li><math>Cu</math> and dilute <math>HNO_3</math></li> </ol>	<ol style="list-style-type: none"> <li>K and excess of <math>O_2</math></li> <li><math>O_2</math> and 2-ethylanthraquinol</li> </ol>
---	--

(2014)

### Fill-in-the-Blanks Type

1. Anhydrous  $MgCl_2$  is obtained by heating the hydrated salt with \_\_\_\_\_. (1980)
2.  $Mn^{2+}$  can be oxidized to  $MnO_4^-$  by \_\_\_\_\_. ( $SnO_2$ ,  $PbO_2$ ,  $BaO_2$ ) (1981)
3. If metal ions of group III are precipitated by  $NH_4Cl$  and  $NH_4OH$  without prior oxidation by concentrated  $HNO_3$ , \_\_\_\_\_ is not completely precipitated. (1984)
4. Silver chloride is sparingly soluble in water because its lattice energy is greater than \_\_\_\_\_ energy. (1987)
5. The salts \_\_\_\_\_ and \_\_\_\_\_ are isostructural ( $FeSO_4 \cdot 7H_2O$ ;  $CuSO_4 \cdot 5H_2O$ ;  $MnSO_4 \cdot 4H_2O$ ;  $ZnSO_4 \cdot 7H_2O$ ) (1988)
6. Hydrogen gas is liberated by the action of aluminium with concentrated solution of \_\_\_\_\_. (1987)
7. Compounds that formally contain  $Pb^{4+}$  are easily reduced to  $Pb^{2+}$ . The stability of the lower oxidation state is due to \_\_\_\_\_. (1997)

### Integer Answer Type

1. The coordination number of A1 in the crystalline state of  $AlCl_3$  is \_\_\_\_\_. (2009)

### True/False Type

1.  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  on heating gives anhydrous  $\text{MgCl}_2$ . (1982)
2. Aluminium chloride ( $\text{AlCl}_3$ ) is a Lewis acid because it can donate electrons. (1982)
3. When  $\text{PbO}_2$  reacts with a dilute acid, it gives hydrogen peroxide. (1982)
4. Silver fluoride is fairly soluble in water. (1982)
5.  $\text{SnCl}_2$  is a nonlinear molecules. (1985)
6. Solubility of sodium hydroxide increases with increase in temperature. (1985)
7. All the Al—Cl bonds in  $\text{Al}_2\text{Cl}_6$  are equivalent. (1989)
8.  $\text{Cu}^+$  disproportionates to  $\text{Cu}^{2+}$  and elemental copper in solution. (1991)
9. Sodium when burnt in excess of oxygen gives sodium oxide. (1987)

### Reasoning Type

The question below (1 and 2) consist of an ‘Assertion’ in column 1 and the ‘Reason’ in column 2. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.
- (b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.
- (c) If assertion is CORRECT, but reason is INCORRECT.
- (d) If assertion is INCORRECT, but reason is CORRECT.

Assertion (Column 1)	Reason (Column 2)
1. The alkali metals can form ionic hydrides which contain the hydride ion $\text{H}^-$ .	The alkali metal have low electronegativity; their hydrides conduct electricity when fused and liberate hydrogen at anode. (1994)
2. $\text{Al}(\text{OH})_3$ is amphoteric in nature	$\text{Al}-\text{O}$ and $\text{O}-\text{H}$ bonds can be broken with equal ease in $\text{Al}(\text{OH})_3$ . (1998)
3. STATEMENT-1: $\text{Pb}^{4+}$ compounds are stronger oxidizing agents than $\text{Sn}^{4+}$ compounds. and STATEMENT-2: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1 (b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1 (c) STATEMENT-1 is True, STATEMENT-2 is False (d) STATEMENT-1 is False, STATEMENT-2 is True	(2008)

### Matching Type

- |                               |                       |
|-------------------------------|-----------------------|
| 1. (a) Welding                | (p) Baeyer's process  |
| (b) Production of ammonia     | (q) Thermite process  |
| (c) Ore purification          | (r) Cyanamide process |
| (d) Production of nitric acid | (s) Ostwald's process |
- (1981)

### Short Answer Type

- Thionyl chloride can be synthesized by chlorinating  $\text{SO}_2$  using  $\text{PCl}_5$ . Thionyl chloride is used to prepare anhydrous ferric chloride starting from its hexahydrated salt. Alternatively, the anhydrous ferric chloride can also be prepared from its hexahydrated salt by treating with 2, 2-dimethoxypropane. Discuss all this using balanced chemical equations. (1998)
- A white solid is either  $\text{Na}_2\text{O}$  or  $\text{Na}_2\text{O}_2$ . A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the white solid. (1999)
  - Identify the substance and explain with balanced equation.
  - Explain what would happen to the red litmus if the white solid were the other compound. (1999)
- Give reasons for the following in one or two sentences only.
  - $\text{BeCl}_2$  can be easily hydrolysed.
  - $\text{CrO}_3$  is an acid anhydride. (1999)
- Write the balanced chemical equation for developing photographic films. (2000)
- Which one is more soluble in diethyl ether, anhydrous  $\text{AlCl}_3$  or hydrous  $\text{AlCl}_3$ ? Explain in terms of bonding. (2003)
- $\text{AlF}_3$  does not dissolve in anhydrous HF but dissolves in KF. (a) Explain the reason. (b) When  $\text{BF}_3$  is added to the above solution containing KF, aluminium trifluoride is precipitated. Give balanced chemical equation. (2004)
- Give equations for the preparation of (i) potassium permanganate from manganese hydroxide and (ii) alumina from aluminium. (1983)

### ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (d)  | 2. (d)  | 3. (b)  | 4. (b)  | 5. (b)  | 6. (d)  | 7. None |
| 8. (c)  | 9. (b)  | 10. (d) | 11. (d) | 12. (c) | 13. (a) | 14. (b) |
| 15. (c) | 16. (b) | 17. (b) | 18. (d) | 19. (a) | 20. (d) | 21. (b) |
| 22. (a) | 23. (a) | 24. (b) |         |         |         |         |

### Multiple Correct-Choice Type

- |                  |                  |             |                  |
|------------------|------------------|-------------|------------------|
| 1. (a), (b), (d) | 2. (a), (b), (d) | 3. (a), (b) | 4. (b), (d)      |
| 5. (c), (d)      | 6. (a), (b)      | 7. (b), (c) | 8. (a), (b), (c) |

### Fill-in-the-Blanks Type

- |                     |  |                     |
|---------------------|--|---------------------|
| 1. anhydrous HCl    | 2. $\text{PbO}_2$  | 3. $\text{Fe}^{2+}$ |
| 4. hydration        | 5. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ |                     |
| 6. sodium hydroxide | 7. inert-pair effect.  |                     |

### Integer Answer Type

1. 6

**True/False Type**

1. False      2. False      3. False      4. True      5. True      6. False      7. False  
 8. True      9. False

**Reasoning Type**

1. (a)      2. (c)      3. (c)

**Matching Type**

1. (a)-(q); (b)-(r); (c)-(p); (d)-(s)

**Short Answer Type**

1.  $\text{SO}_2 + \text{PCl}_5 \rightarrow \text{SOCl}_2 + \text{POCl}_3$   
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{SOCl}_2 \rightarrow \text{FeCl}_3 + 6\text{SO}_2 + 12\text{HCl}$   
 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 6\text{CH}_3-\overset{\text{OCH}_3}{\underset{\text{OCH}_3}{\text{C}}}-\text{CH}_3 \rightarrow \text{FeCl}_3 + 12\text{CH}_3\text{OH} + 6\text{CH}_3\text{COCH}_3$
2. (i) The substance is  $\text{Na}_2\text{O}_2$ . When dissolved in water, the solution becomes alkaline with the liberation of  $\text{H}_2\text{O}_2$ .  

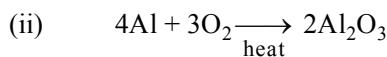
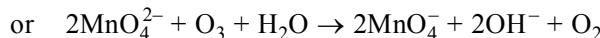
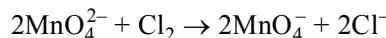
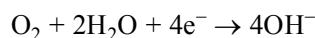
$$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$$
  
 Due to the alkaline solution, the red litmus paper will be turned into blue, which subsequently will change into white due to the oxidation caused by  $\text{H}_2\text{O}_2$ .  
(ii) The substance  $\text{Na}_2\text{O}$  merely produces alkaline solution and thus the red litmus paper will turn into blue:  

$$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$$
3. (i)  $\text{BeCl}_2$  being an electron-deficient compound is easily hydrolysed.  
(ii)  $\text{CrO}_3$  is an acidic anhydride as it combines with  $\text{H}_2\text{O}$  molecule to give dichromic acid  

$$2\text{CrO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{Cr}_2\text{O}_7$$
4. A developer is a weak acid, e.g. an alkaline solution of quinol. In the developing bath the part affected most by light are reduced to the maximum extent while parts not affected by light remains unattacked by the developer. The reaction occurring is  

$$2\text{AgBr} + \text{C}_6\text{H}_4(\text{OH})_2 \rightarrow 2\text{Ag} + 2\text{HBr} + \text{C}_6\text{H}_4\text{O}_2$$
  
 Hydroquinone      Silver      Quinone  
 particles
- The image becomes visible but its shade is in negative relationship with the shade of the object.
5. Anhydrous  $\text{AlCl}_3$  will be more soluble in diethyl ether due to the sharing of lone pair of electrons on oxygen of ether by the vacant 3p orbitals of Al.
6. (a) Hydrogen fluoride is a covalent compound with extensive hydrogen bonding. It does not form complex with  $\text{AlF}_3$  and thus the latter is insoluble in anhydrous HF. However,  $\text{AlF}_3$  is soluble in KF due to the formation of complex  $\text{K}_3[\text{AlF}_6]$ .  
(b) The chemical equation occurring is  $\text{K}_3[\text{AlF}_6] + 3\text{BF}_3 \rightarrow \text{AlF}_3 \downarrow + 3\text{K}[\text{BF}_4]$

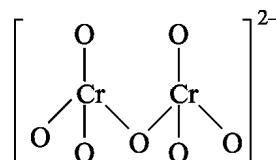
7. (i) Potassium permanganate is manufactured by the fusion of  $\text{MnO}_2$  with KOH followed by oxidation of formed potassium manganate, either electrolytically or by passing  $\text{Cl}_2$ (or  $\text{O}_3$ ) into solution.



## HINTS AND SOLUTIONS

### Straight Objective Type

17. The structure of  $\text{Cr}_2\text{O}_7^{2-}$  is



There are

six normal Cr—O bonds  
and two bridged Cr—O bonds.

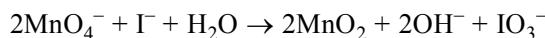
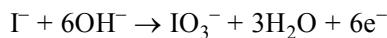
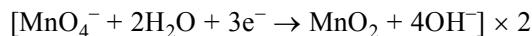
The six normal Cr—O bonds are expected to be equivalent and different from those of the bridged Cr—O bonds.

20. The reaction is

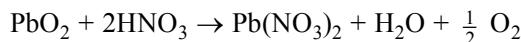


22. The metallic oxides are basic oxides. Larger the basic strength of metallic oxide (or hydroxide), lesser its acid strength. Calcium oxide is more basic than copper oxide and hence the acid strength of  $\text{CaO}$  is lesser than that of  $\text{CuO}$ . The species  $\text{CO}_2$  is an acidic oxide. Water being a neutral compound is lesser acidic than carbon dioxide.

23. The reaction occurring are

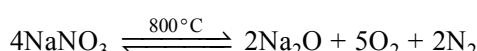
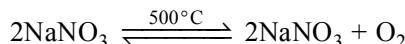


24. The reaction is



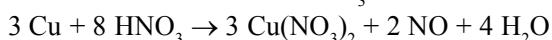
### Multiple Correct-Choice Type

2. The nitrates of Group I decompose on heating into nitrites and to oxides on strongly heating at higher temperatures.



6. The compounds formed are  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{O}$ .
7. Temporary hardness of water is due to the presence of bicarbonates of magnesium and calcium. These can be precipitated by adding  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$ .
8. Na in excess of  $\text{NH}_3$  produces deep blue solution and contains solvated electrons. Due to the latter, solution shows paramagnetic behaviour.  
K in excess of  $\text{O}_2$  produces potassium superoxide  $\text{KO}_2$ . The species  $\text{O}_2^-$  contains one unpaired electron and thus is paramagnetic

The reaction of Cu with dilute  $\text{HNO}_3$  is



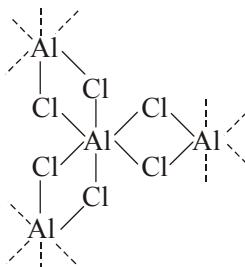
Nitric oxide has 11 valence electrons. The presence of an odd electron makes the molecule paramagnetic.

The oxidation of 2-ethylanthraquinol produces 2-ethylanthraquinone and  $\text{H}_2\text{O}_2$ . None of the two species are paramagnetic.

### Fill-in-the-Blanks Type

#### Integer Answer Type

The structure of  $\text{AlCl}_3$  in solid state is



Each Al is in an octahedral environment with each Cl serving in a bridging capacity. Its coordination number is 6.

### True/False Type

2.  $\text{AlCl}_3$  is a Lewis acid because it accepts rather than donating electrons.
3.  $\text{PbO}_2$  is a dioxide and not peroxide.
4. The solubility of halides of silver varies as  $\text{AgF} > \text{AgCl} > \text{AgBr} > \text{AgI}$ .
6. Sodium hydroxide dissolves in water with the evolution of heat. Hence, its solubility decreases with increase in temperature.
7. The structure of  $\text{Al}_2\text{Cl}_6$  is
8. The reaction  $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$  is possible as  $E_{\text{Cu}^+|\text{Cu}}^\circ > E_{\text{Cu}^{2+}|\text{Cu}}^\circ$
9. Sodium when burnt in excess of oxygen gives sodium peroxide.

### Reasoning Type

2. Due to inert-pair effect, the higher oxidation states for the group 14 elements are less stable for the heavier members of the group and have a tendency to reduce to lesser oxidation state (i.e. these are stronger oxidising agent). It is because of this  $\text{Pb}^{4+}$  compounds are stronger oxidising agents than  $\text{Sn}^{4+}$  compounds.

# **COMPOUNDS OF NONMETALS**

15

## Straight Objective Type

1. Ammonia gas is dried by using  
(a)  $P_2O_5$       (b)  $CaCl_2$       (c)  $CaO$       (d)  $H_2SO_4$   
(e) None of these      (1978)

2. Hydrogen is evolved by the action of cold dilute  $HNO_3$  on  
(a) Fe      (b) Cu      (c) Mn      (d) Al  
(e) None of these      (1978)

3. The reddish-brown coloured gas formed when nitric oxide is oxidised by air is  
(a)  $N_2O_5$       (b)  $N_2O_4$       (c)  $NO_2$       (d)  $N_2O_2$       (1979)

4. Ammonia can be dried by  
(a) conc.  $H_2SO_4$       (b)  $P_2O_5$       (c) anhydrous  $CaCl_2$       (d) anhydrous  $CuSO_4$       (1980)

5. Which of the following is coloured?  
(a) NO      (b)  $N_2O$       (c)  $SO_2$       (d) CO      (1980)

6. Sodium thiosulphate is used in photography because of its  
(a) reducing behaviour      (b) oxidizing behaviour  
(c) complex forming behaviour      (d) reaction with light      (1981)

7. Among the following, the molecule that is linear is  
(a)  $CO_2$       (b)  $NO_2$       (c)  $SO_2$       (d)  $ClO_2$       (1982)

8. Heavy water is  
(a)  $H_2^{18}O$       (b) Water obtained by repeated distillation  
(c)  $D_2O$       (d) Water at  $4\text{ }^{\circ}C$       (1983)

9. Nitrogen dioxide cannot be obtained by heating  
(a)  $KNO_3$       (b)  $Pb(NO_3)_2$       (c)  $Cu(NO_3)_2$       (d)  $AgNO_3$       (1985)

10. Which of the following oxides of nitrogen is a coloured gas?  
(a)  $N_2O$       (b) NO      (c)  $N_2O_4$       (d)  $NO_2$       (1987)

11. Amongst the trihalides of nitrogen, the least basic is  
(a)  $NF_3$       (b)  $NCl_3$       (c)  $NBr_3$       (d)  $NI_3$       (1987)

12. Which one of the following is the strongest base?  
(a)  $AsH_3$       (b)  $NH_3$       (c)  $PH_3$       (d)  $SbH_3$       (1989)

13. Which of the following is the strongest acid?  
(a)  $ClO_3(OH)$       (b)  $ClO_2(OH)$       (c)  $SO(OH)_2$       (d)  $SO_2(OH)_2$       (1989)

14. There is no S—S bond in  
 (a)  $\text{S}_2\text{O}_4^{2-}$       (b)  $\text{S}_2\text{O}_5^{2-}$       (c)  $\text{S}_2\text{O}_3^{2-}$       (d)  $\text{S}_2\text{O}_7^{2-}$  (1991)
15. The volume strength of 1.5 N  $\text{H}_2\text{O}_2$  solution is  
 (a) 4.8      (b) 8.4      (c) 3.0      (d) 8.0 (1991)
16. The type of hybrid orbitals used by the chlorine atom in  $\text{ClO}_2^-$  is  
 (a)  $\text{sp}^3$       (b)  $\text{sp}^2$       (c)  $\text{sp}$       (d) none of these (1992)
17. The maximum possible number of hydrogen bonds a water molecule can form is  
 (a) 2      (b) 4      (c) 3      (d) 1 (1992)
18. Hydrolysis of one mole of peroxodisulphuric acid produces  
 (a) two moles of sulphuric acid  
 (b) two moles of peroxyomonosulphuric acid  
 (c) one mole of sulphuric acid and one mole of peroxyomonosulphuric acid  
 (d) one mole of sulphuric acid, one mole of peroxyomonosulphuric acid and one mole of hydrogen peroxide (1996)
19. Among the following species, identify the isostructural pairs.  
 (a)  $[\text{NF}_3, \text{NO}_3^-]$  and  $[\text{BF}_3, \text{H}_3\text{O}^+]$       (b)  $[\text{NF}_3, \text{HN}_3]$  and  $[\text{NO}_3^-, \text{BF}_3]$   
 (c)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{NO}_3^-, \text{BF}_3]$       (d)  $[\text{NF}_3, \text{H}_3\text{O}^+]$  and  $[\text{HN}_3, \text{BF}_3]$  (1996)
20. The number and type of bonds between two carbon atoms in  $\text{CaC}_2$  are  
 (a) one sigma ( $\sigma$ ) and one pi ( $\pi$ ) bond  
 (b) one sigma ( $\sigma$ ) and two pi ( $\pi$ ) bonds  
 (c) one sigma ( $\sigma$ ) and one and a half pi ( $\pi$ ) bonds  
 (d) one sigma ( $\sigma$ ) bond (1996)
21. Which of the following statements is correct for  $\text{CsBr}_3$ ?  
 (a) It is a covalent compound      (b) It contains  $\text{Cs}^{3+}$  and  $\text{Br}^-$  ions  
 (c) It contains  $\text{Cs}^+$  and  $\text{Br}_3^-$  ions      (d) It contains  $\text{Cs}^+$ ,  $\text{Br}^-$  and lattice of  $\text{Br}_2$  molecule. (1996)
22. KF combines with HF to form  $\text{KHF}_2$ . The compound contains the species  
 (a)  $\text{K}^+, \text{F}^-$  and  $\text{H}^+$       (b)  $\text{K}^+, \text{F}^-$  and HF      (c)  $\text{K}^+$  and  $[\text{HF}_2]^-$       (d)  $[\text{KHF}]^+$  and  $\text{F}^-$  (1996)
23. Sodium thiosulphate is prepared by  
 (a) reducing  $\text{Na}_2\text{SO}_4$  solution with  $\text{H}_2\text{S}$   
 (b) boiling  $\text{Na}_2\text{SO}_3$  solution with S in alkaline medium  
 (c) neutralising  $\text{H}_2\text{S}_2\text{O}_3$  solution with  $\text{NaOH}$   
 (d) boiling  $\text{Na}_2\text{SO}_3$  solution with S in acidic medium (1996)
24. Which one of the following species is not a pseudohalide?  
 (a)  $\text{CNO}^-$       (b)  $\text{RCCO}^-$   
 (c)  $\text{OCN}^-$       (d)  $\text{NNN}^-$  (1997)
25. One mole of calcium phosphide on reaction with excess water gives  
 (a) one mole of phosphoric acid      (b) two moles of phosphoric acid  
 (c) two moles of phosphine      (d) one mole of phosphorus pentoxide (1999)
26. In compounds of type  $\text{ECl}_3$ , where E = B, P, As or Bi, the angles  $\text{Cl}^--\text{E}-\text{Cl}^-$  for different E are in order  
 (a)  $\text{B} > \text{P} = \text{As} = \text{Bi}$       (b)  $\text{B} > \text{P} > \text{As} > \text{Bi}$   
 (c)  $\text{B} < \text{P} = \text{As} = \text{Bi}$       (d)  $\text{B} < \text{P} < \text{As} < \text{Bi}$  (1999)
27. Ammonia, on reaction with hypochlorite anion, can form  
 (a) NO      (b)  $\text{NH}_4\text{Cl}$       (c)  $\text{N}_2\text{H}_4$       (d)  $\text{HNO}_2$  (1999)

28. The correct order of acid strength is

- |   |  |
|---|--|
| (a) $\text{Cl}_2\text{O}_7 > \text{SO}_2 > \text{P}_4\text{O}_{11}$ | (b) $\text{CO}_2 > \text{N}_2\text{O}_5 > \text{SO}_3$ |
| (c) $\text{Na}_2\text{O} > \text{MgO} > \text{Al}_2\text{O}_3$      | (d) $\text{K}_2\text{O} > \text{CaO} > \text{MgO}$     |

(2000)

29. The number of P—O—P bonds in cyclic metaphosphoric acid is

- (a) zero      (b) two      (c) three      (d) four

(2000)

30. Molecular shapes of  $\text{SF}_4$ ,  $\text{CF}_4$  and  $\text{XeF}_4$  are

- |  |  |
|--|--|
| (a) the same with 2, 0 and 1 lone pairs of electrons respectively  | (b) the same with 1, 1 and 1 lone pairs of electrons respectively  |
| (c) different with 0, 1 and 2 lone pairs of electrons respectively | (d) different with 1, 0 and 2 lone pairs of electrons respectively |

(2000)

31. Ammonia can be dried by

- (a) conc.  $\text{H}_2\text{SO}_4$     (b)  $\text{P}_4\text{O}_{10}$     (c)  $\text{CaO}$     (d) anhydrous  $\text{CaCl}_2$

(2000)

32. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is

- |   |   |
|---|---|
| (a) $\text{H}_2\text{O}$ because of hydrogen bonding. | (b) $\text{H}_2\text{Te}$ because of higher molecular weight. |
| (c) $\text{H}_2\text{S}$ because of hydrogen bonding. | (d) $\text{H}_2\text{Se}$ because of lower molecular weight.  |

(2000)

33. The number of S—S bonds in sulphur trioxide trimer ( $\text{S}_3\text{O}_9$ ) is

- (a) three    (b) two    (c) one    (d) zero

(2001)

34. The set with correct order of acidity is

- |   |   |
|---|---|
| (a) $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$ | (b) $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$ |
| (c) $\text{HClO} < \text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2$ | (d) $\text{HClO}_4 < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}$ |

(2001)

35. Polyphosphates are used as water softening agents because they

- |  |                                  |
|--|----------------------------------|
| (a) form soluble complexes with anionic species  | (b) precipitate anionic species  |
| (c) form soluble complexes with cationic species | (d) precipitate cationic species |

(2002)

36. Which of the following statements is correct?

- |   |  |
|---|--|
| (a) $\text{H}_3\text{PO}_3$ is dibasic and reducing     | (b) $\text{H}_3\text{PO}_3$ is tribasic and reducing     |
| (c) $\text{H}_3\text{PO}_3$ is tribasic and nonreducing | (d) $\text{H}_3\text{PO}_3$ is diabasic and nonreducing. |

(2003)

37. Boric acid is a

- |                                       |   |
|---------------------------------------|---|
| (a) weak monobasic Lewis acid         | (b) weak monobasic Arrhenius acid only                |
| (c) weak monobasic Bronsted acid only | (d) weak monobasic Arrhenius as well as Bronsted acid |

(2003)

38.  $(\text{CH}_3)_2\text{SiCl}_2$  on hydrolysis produces

- |  |   |
|--|---|
| (a) $(\text{CH}_3)_2\text{Si}(\text{OH})_2$            | (b) $(\text{CH}_3)_2\text{Si}=\text{O}$     |
| (c) $\{\text{O}-(\text{CH}_3)_2\text{Si}-\text{O}\}_n$ | (d) $(\text{CH}_3)_2\text{SiCl}(\text{OH})$ |

(2003)

39. Which of the following oxoacids of sulphur has —O—O—linkage?

- (a)  $\text{H}_2\text{S}_2\text{O}_3$     (b)  $\text{H}_2\text{S}_2\text{O}_5$     (c)  $\text{H}_2\text{S}_2\text{O}_6$     (d)  $\text{H}_2\text{S}_2\text{O}_8$

(2004)

40. Distillation of concentrated  $\text{HNO}_3$  with phosphorus pentoxide produces

- (a) NO    (b)  $\text{N}_2\text{O}$     (c)  $\text{NO}_2$     (d)  $\text{N}_2\text{O}_5$

(2004)

## **Multiple Correct-Choice Type**

3. High pure dilute solution of sodium in liquid ammonia

  - (a) shows blue colour
  - (b) exhibits electrical conductivity
  - (c) produces sodium amide
  - (d) produces hydrogen gas

4. The compounds used as refrigerant are

  - (a)  $\text{NH}_3$
  - (b)  $\text{CCl}_4$
  - (c)  $\text{CF}_4$
  - (d)  $\text{CF}_2\text{Cl}_2$
  - (e)  $\text{CH}_2\text{F}_2$  (1990)

5. A solution of colourless salt **H** on boiling with excess  $\text{NaOH}$  produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) **H** is (are)

  - (a)  $\text{NH}_4\text{NO}_3$
  - (b)  $\text{NH}_4\text{NO}_2$
  - (c)  $\text{NH}_4\text{Cl}$
  - (d)  $(\text{NH}_4)_2\text{SO}_4$

6. The nitrogen oxide(s) that contain N—N bond(s) is/are

  - (a)  $\text{N}_2\text{O}$
  - (b)  $\text{N}_2\text{O}_3$
  - (c)  $\text{N}_2\text{O}_4$
  - (d)  $\text{N}_2\text{O}_5$

7. In the reaction  $2\text{X} + \text{B}_2\text{H}_6 \longrightarrow [\text{BH}_2(\text{X})_2]^+ [\text{BH}_4]^-$  the amine(s) X is/are

  - (a)  $\text{NH}_3$
  - (b)  $\text{CH}_3\text{NH}_2$
  - (c)  $(\text{CH}_3)_2\text{NH}$
  - (d)  $(\text{CH}_3)_3\text{N}$

8. Which of the following halides react(s) with  $\text{AgNO}_3(\text{aq})$  to give a precipitate that dissolves in  $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$ ?

  - (a)  $\text{HCl}$
  - (b)  $\text{HF}$
  - (c)  $\text{HBr}$
  - (d)  $\text{HI}$

9. The correct statement(s) for orthoboric acid is/are

  - (a) It behaves as a weak acid in water due to self ionization.
  - (b) Acidity of its aqueous solution increases upon addition of ethylene glycol.
  - (c) It has a three-dimensional structure due to hydrogen bonding.
  - (d) It is a weak electrolyte in water.

10.  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  by using

  - (a)  $\text{H}_2\text{O}_2$  in presence of  $\text{NaOH}$
  - (b)  $\text{Na}_2\text{O}_2$  in water
  - (c)  $\text{H}_2\text{O}_2$  in presence of  $\text{H}_2\text{SO}_4$
  - (d)  $\text{Na}_2\text{O}_2$  in presence of  $\text{H}_2\text{SO}_4$

11. The correct statement(s) regarding, (i)  $\text{HClO}$ , (ii)  $\text{HClO}_2$ , (iii)  $\text{HClO}_3$  and (iv)  $\text{HClO}_4$ , is (are)

  - (a) The number of  $\text{Cl}=\text{O}$  bonds in (ii) and (iii) together is two
  - (b) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
  - (c) The hybridization of Cl in (iv) is  $\text{sp}^3$
  - (d) Amongst (i) to (iv), the strongest acid is (i)

### **Fill-in-the-Blanks Type**

- \_\_\_\_\_ is a weak acid (HF, HCl, HBr). (1981)
  - \_\_\_\_\_ hybrid orbitals of nitrogen atom are involved in the formation of ammonium ion. (1982)
  - The conjugate base of  $\text{HSO}_4^-$  in aqueous solution is \_\_\_\_\_. (1983)
  - \_\_\_\_\_ acid gives hypo \_\_\_\_\_ ion. (hydrobromic, hypobromous, perbromic, bromide, bromite, perbromate). (1988)
  - The basicity of phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is \_\_\_\_\_. (1990)
  - In  $\text{P}_4\text{O}_{10}$ , the number of oxygen atoms bonded to each phosphorus atom is \_\_\_\_\_. (1992)
  - The lead chamber process involves oxidation of  $\text{SO}_2$  by atmospheric oxygen under the influence of \_\_\_\_\_ as catalyst. (1992)
  - The hydrolysis of trialkylchlorosilane,  $\text{R}_3\text{SiCl}$ , yields \_\_\_\_\_. (1994)
  - The two types of bonds present in  $\text{B}_2\text{H}_6$  are covalent and \_\_\_\_\_. (1994)
  - A solution of sodium in liquid ammonia at  $-33^\circ\text{C}$  conducts electricity. On cooling, the conductivity of this solution \_\_\_\_\_. (1997)

**Integer Answer Type**

1. The value of  $n$  in the molecular formula  $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$  is \_\_\_\_\_. (2010)
2. The total number of diprotic acids among the following is \_\_\_\_\_.  
 H<sub>3</sub>PO<sub>4</sub>      H<sub>2</sub>SO<sub>4</sub>      H<sub>3</sub>PO<sub>3</sub>      H<sub>2</sub>CO<sub>3</sub>      H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>  
 H<sub>3</sub>BO<sub>3</sub>      H<sub>3</sub>PO<sub>2</sub>      H<sub>2</sub>CrO<sub>4</sub>      H<sub>2</sub>SO<sub>3</sub>      (2010)
3. Among the compounds O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub> and P<sub>4</sub>O<sub>10</sub>, the number of compounds that react with PCl<sub>5</sub> to give POCl<sub>3</sub> is \_\_\_\_\_. (2011)
4. Three moles of B<sub>2</sub>H<sub>6</sub> are completely reacted with methanol. The number of moles of boron containing products formed is \_\_\_\_\_. (2015)

**True/False Type**

1. Nitrous oxide is heavier than oxygen. (1978)
2. The formula of heavy water is H<sub>2</sub>O. (1978)
3. Ammonia can be used as a refrigerant. (1978)
4. The H—N—H bond angle in NH<sub>3</sub> is greater than H—As—H bond angle in AsH<sub>3</sub>. (1984)
5. Nitric oxide, though an odd electron molecule, is diamagnetic in liquid state. (1991)
6. HBr is a stronger acid than HI because of hydrogen bonding. (1993)

**Reasoning Type**

The questions below (1, 2 and 3) consist of an ‘Assertion’ in column 1 and the ‘Reason’ in column 2. Use the following key to choose the appropriate answer.

- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.
- (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
- (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
- (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

<b>Assertion (column 1)</b>	<b>Reason (column 2)</b>
1. Although PF <sub>5</sub> , PCl <sub>5</sub> and PBr <sub>5</sub> are known, the pentahalides of nitrogen have not been observed.	Phosphorus has lower electronegativity than nitrogen. (1994)
2. HNO <sub>3</sub> is a stronger acid than HNO <sub>2</sub> .	In HNO <sub>3</sub> there are two nitrogen-to-oxygen bonds whereas in HNO <sub>2</sub> there is only one. (1998)
3. Between SiCl <sub>4</sub> and CCl <sub>4</sub> , only SiCl <sub>4</sub> reacts with water.	SiCl <sub>4</sub> is ionic and CCl <sub>4</sub> is covalent. (2001)
4. STATEMENT-1: In water, orthoboric acid behaves as a weak monobasic acid. because STATEMENT-2: In water, orthoboric acid acts as a proton donor.	
	(a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1 (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1 (c) Statement-1 is True, Statement-2 is False (d) Statement-1 is False, Statement-2 is True (2007)

## Linked-Comprehension Type

### Passage-1

The noble gases have closed-shell electronic configuration and are monoatomic gases under normal conditions. The low boiling points of the lighter noble gases are due to weak dispersion forces between the atoms and the absence of other interatomic interactions.

The direct reaction of xenon with fluorine leads to a series of compounds with oxidation numbers +2, +4 and +6.  $\text{XeF}_4$  reacts violently with water to give  $\text{XeO}_3$ . The compounds of xenon exhibit rich stereochemistry and their geometries can be deduced considering the total number of electron pairs in the valence shell.

1. Argon is used in arc welding because of its

- (a) low reactivity with metal
- (b) ability to lower the melting point of metal
- (c) flammability
- (d) high calorific value

2. The structure of  $\text{XeO}_3$  is

- (a) linear
- (b) planar
- (c) pyramidal
- (d) T-shaped

3.  $\text{XeF}_4$  and  $\text{XeF}_6$  are expected to be

- (a) oxidising
  - (b) reducing
  - (c) unreactive
  - (d) strongly basic
- (2007)

### Passage-2

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms larger number of complexes with transition metal ions. Hybridisation easily explains the ease of sigma donation capability of  $\text{NH}_3$  and  $\text{PH}_3$ . Phosphine is a flammable gas and is prepared from white phosphorous.

1. Among the following, the correct statement is

- (a) Phosphates have no biological significance in humans
- (b) Between nitrates and phosphates, phosphates are less abundant in earth's crust
- (c) Between nitrates and phosphates, nitrates are less abundant in earth's crust
- (d) Oxidation of nitrates is possible in soil

2. Among the following, the correct statement is

- (a) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
- (b) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional
- (c) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{NH}_3$  is a better electron donor because the lone pair of electrons occupies  $\text{sp}^3$  orbital and is more directional.
- (d) Between  $\text{NH}_3$  and  $\text{PH}_3$ ,  $\text{PH}_3$  is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

3. White phosphorus on reaction with  $\text{NaOH}$  gives  $\text{PH}_3$  as one of the products. This is a

- (a) dimerization reaction
  - (b) disproportionation reaction
  - (c) condensation reaction
  - (d) precipitation reaction
- (2008)

## **Matrix Match Type**

1. Match each of reactions given in **Column I** with the corresponding product(s) given in **Column II**

<b>Column I</b>	<b>Column II</b>
(a) Cu + dil. HNO <sub>3</sub>	(p) NO
(b) Cu + conc. HNO <sub>3</sub>	(q) NO <sub>2</sub>
(c) Zn + dil. HNO <sub>3</sub>	(r) N <sub>2</sub> O
(d) Zn + conc. HNO <sub>3</sub>	(s) Cu(NO <sub>3</sub> ) <sub>2</sub>
	(t) Zn(NO <sub>3</sub> ) <sub>2</sub>

2. All the compounds listed in **Column I** react with water. Match the result of the respective reactions with the appropriate options listed in **Column II**.

<b>Column I</b>	<b>Column II</b>
(a) $(CH_3)_2SiCl_2$	(p) Hydrogen halide formation
(b) $XeF_4$	(q) Redox reaction
(c) $Cl_2$	(r) Reacts with glass
(d) $VCl_5$	(s) Polymerization (t) $O_2$ formation

## **Short Answer Type**

1. Give the structural formula for the following.

2. Orthophosphoric acid,  $H_3PO_4$ , is tribasic, but phosphorous acid,  $H_3PO_3$ , is dibasic. (1982, 1989)

3. Hydrogen peroxide is a better oxidising agent than water. (1986)

4. Phosphine has lower boiling point than ammonia. (1989)

5. Give chemical equation for

(i) the preparation of phosphine from CaO and white phosphorus.

(ii) the preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide. (1990)

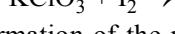
6. Hydrogen peroxide acts as an oxidising as well as a reducing agent. (1992)

7. Sulphur dioxide is a more powerful reducing agent in an alkaline medium than in acidic medium. (1992)

8. Draw the structure of  $P_2O_{10}$  and identify the number of single and double P—O bonds. (1996)

9. Complete the following chemical equations:

9. Complete the following chemical equations:



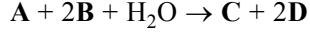
Justify the formation of the products in the above reactions. (1998) (1999)

10. Draw the structure of a cyclic silicate,  $(Si_3O_9)^{4-}$  with proper labelling. (1998)

11. Reaction of phosphoric acid with  $\text{Ca}_5(\text{PO}_4)_3$  F yields a fertilizer "triple superphosphate". Represent the same through balanced chemical equation. (1998)

12. Hydrogen peroxide acts both as an oxidising and as a reducing agent in alkaline solution towards certain first row transition metal ions. Illustrate both these properties of  $H_2O_2$  using chemical equations. (1998)

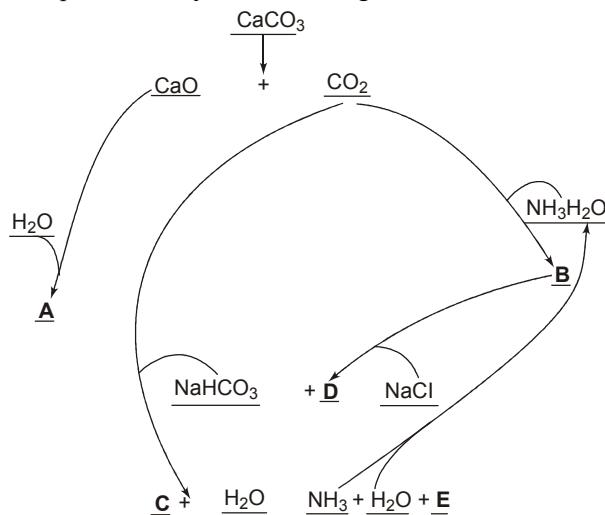
13. (a) In the following equation,



(**A** =  $\text{HNO}_2$ , **B** =  $\text{H}_2\text{SO}_3$ , **C** =  $\text{NH}_2\text{OH}$ ). Identify **D**. Draw the structures of **A**, **B**, **C** and **D**. (1999)

- (b) In the Contact process for industrial manufacture of sulphuric acid some amount of sulphuric acid is used as a starting material. Explain briefly. What is the catalyst used in the oxidation of  $\text{SO}_2$ ?

14. The Haber process can be represented by the following scheme:



Identify A, B, C, D and E.

(1999)

15. Write the chemical reactions associated with the 'borax bead test of cobalt(II) oxide.

(2000)

16. Draw the molecular structures of  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeO}_2\text{F}_2$ , indicating the location of lone pair(s) of electrons.

(2000)

17. Starting from  $\text{SiCl}_4$ , prepare the following in steps not exceeding the number given in parentheses (give reactions only):

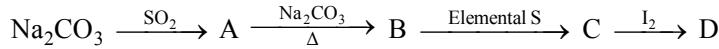
(2001)

- silicon (1)
- linear silicone containing methyl groups only (4)
- $\text{Na}_2\text{SiO}_3$ (3)

18. How is boron obtained from borax? Give chemical equations with reaction conditions. Write the structure of  $\text{B}_2\text{H}_6$  and its reaction with HCl.

(2002)

19. Identify the following.

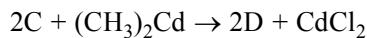
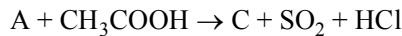
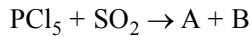


Also mention the oxidation of S in all the compounds.

(2003)

20. Identify the compounds A and B in the reactions.

(1994)



## ANSWERS

### Straight Objective Type

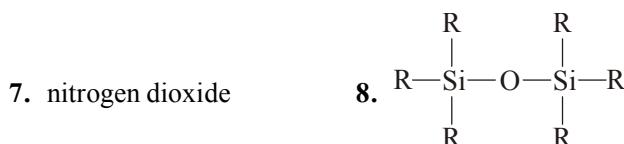
- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (c)  | 3. (c)  | 4. None | 5. None | 6. (c)  | 7. (a)  |
| 8. (c)  | 9. (a)  | 10. (d) | 11. (a) | 12. (b) | 13. (a) | 14. (d) |
| 15. (b) | 16. (a) | 17. (b) | 18. (c) | 19. (c) | 20. (b) | 21. (c) |
| 22. (c) | 23. (b) | 24. (b) | 25. (c) | 26. (b) | 27. (c) | 28. (a) |
| 29. (c) | 30. (d) | 31. (c) | 32. (a) | 33. (d) | 34. (a) | 35. (c) |
| 36. (a) | 37. (a) | 38. (c) | 39. (d) | 40. (d) | 41. (b) | 42. (d) |
| 43. (b) | 44. (b) | 45. (b) | 46. (d) | 47. (b) | 48. (a) | 49. (c) |
| 50. (a) | 51. (b) |         |         |         |         |         |

### Multiple Correct-Choice Type

- |             |                  |                  |                  |
|-------------|------------------|------------------|------------------|
| 1. (a), (d) | 2. (a), (c)      | 3. (a), (b)      | 4. (a), (d)      |
| 5. (a), (b) | 6. (a), (b), (c) | 7. (a), (b), (c) | 8. (a), (c), (d) |
| 9. (b), (d) | 10. (a), (b)     | 11. (b), (c)     |                  |

### Fill-in-the-Blanks Type

- |                         |                  |                       |
|-------------------------|------------------|-----------------------|
| 1. HF                   | 2. $\text{sp}^3$ | 3. $\text{SO}_4^{2-}$ |
| 4. hypobromous bromite, | 5. two           | 6. four               |



- |   |               |
|---|---------------|
| 9. three-centre electron pair bond or banana bond | 10. decreases |
|---|---------------|

### Integer Answer Type

- |      |      |      |      |
|------|------|------|------|
| 1. 3 | 2. 6 | 3. 4 | 4. 6 |
|------|------|------|------|

### True/False Type

- |         |          |         |         |          |          |
|---------|----------|---------|---------|----------|----------|
| 1. True | 2. False | 3. True | 4. True | 5. False | 6. False |
|---------|----------|---------|---------|----------|----------|

### Reasoning Type

- |        |        |        |        |
|--------|--------|--------|--------|
| 1. (b) | 2. (a) | 3. (c) | 4. (c) |
|--------|--------|--------|--------|

### Linked-Comprehension Type

#### Passage-1

- |        |        |        |
|--------|--------|--------|
| 1. (a) | 2. (c) | 3. (a) |
|--------|--------|--------|

#### Passage-2

- |        |        |        |
|--------|--------|--------|
| 1. (c) | 2. (c) | 3. (b) |
|--------|--------|--------|

### Matrix Match Type

1. The correct bubbled diagram is

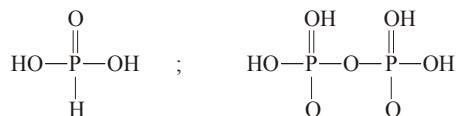
	p	q	r	s	t
a	●	○	○	●	○
b	○	●	○	●	○
c	○	○	●	○	●
d	○	●	○	○	●

2. The matching goes as follows.

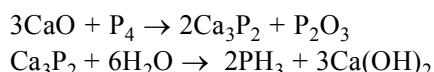
- |               |                        |               |         |
|---------------|------------------------|---------------|---------|
| (a) (p), (s); | (b) (p), (q), (r), (t) | (c) (p), (q); | (d) (p) |
|---------------|------------------------|---------------|---------|

## Short Answer Type

1. The structures are

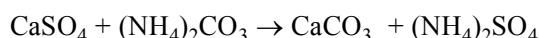


2. In  $\text{H}_3\text{PO}_4$ , there are three replaceable hydrogen atoms, while in  $\text{H}_3\text{PO}_3$ , there are only two replaceable hydrogen atoms.  
 3. The reduction potential of  $\text{H}_2\text{O}_2$  is more than that of water. It readily gives nascent oxygen for oxidation.  
 4. In ammonia, there is extensive hydrogen bonding whereas in phosphine it is not so because of more diffuse electron density.  
 5. (i) Preparation of phosphine from CaO and white phosphorus

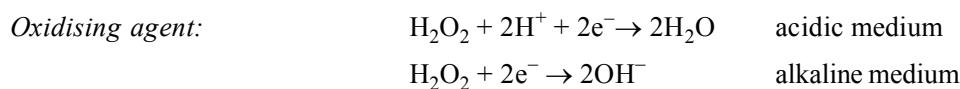


- (ii) Preparation of ammonium sulphate from gypsum, ammonia and carbon dioxide.

Ammonium sulphate is manufactured by passing synthetic ammonia gas into a suspension of finely powdered  $\text{CaSO}_4$  in water, through which a stream of  $\text{CO}_2$  is also passed. The equations involved are:



6. This is due to the following reactions

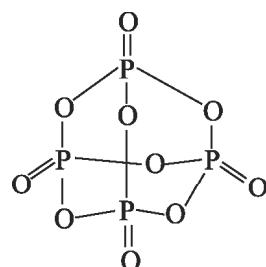


7. Sulphur dioxide as a reducing agent undergoes the reaction



Obviously, the reaction proceeds in the forward direction with increase in  $\text{OH}^-$  ions concentration.

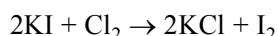
- 8.



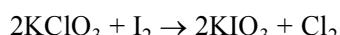
Number of single bonds = 12

Number of double bonds = 4

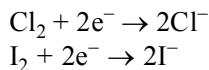
9.  $\text{Cl}_2$  is a more powerful oxidising agent than  $\text{I}_2$ . So,  $\text{Cl}_2$  displaces  $\text{I}^-$  as  $\text{I}_2$ .



$\text{ClO}_3^-$  is a more powerful oxidising agent than  $\text{IO}_3^-$ . So, Cl is displaced by I.

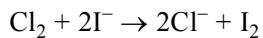


The above reactions may be verified from the half-cell potentials.

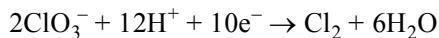


$$\begin{array}{ll} E^\circ = 1.36 \text{ V} \\ E^\circ = 0.54 \text{ V} \end{array}$$

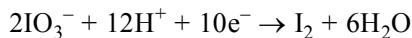
Subtract \_\_\_\_\_



$$E^\circ_{\text{cell}} = 0.82 \text{ V}$$

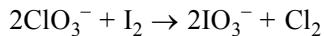


$$E^\circ = 1.47 \text{ V}$$



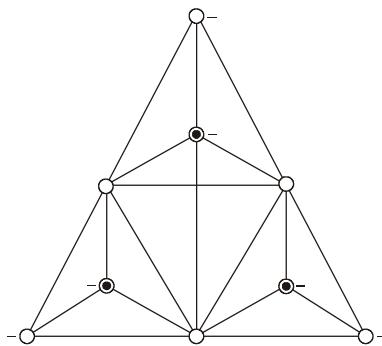
$$E^\circ = 1.195 \text{ V}$$

Subtract \_\_\_\_\_

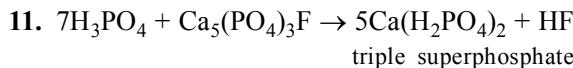


$$E^\circ_{\text{cell}} = 0.275 \text{ V}$$

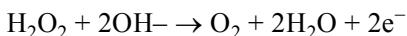
- 10.** In cyclic  $\text{Si}_3\text{O}_9^{6-}$ , three tetrahedra of  $\text{SiO}_4$  are joined together sharing two oxygen atoms per tetrahedron.



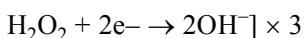
Structure of  $\text{Si}_3\text{O}_9^{6-}$ ; Dark circle represents Si and open circle represents oxygen.



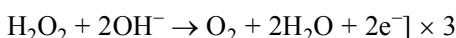
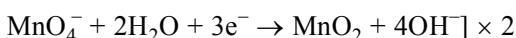
- 12.** As an oxidising agent, the reaction occurring is  $\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$   
and as a reducing agent, the reaction is



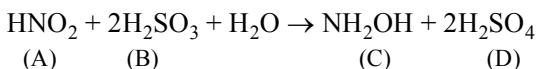
For example,  $\text{Cr(OH)}_3$  is oxidised to  $\text{CrO}_4^{2-}$  in an alkaline medium.



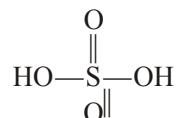
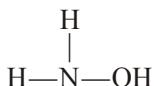
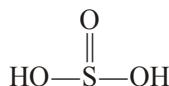
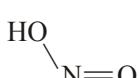
The reaction involving  $\text{H}_2\text{O}_2$  as a reducing agent is the reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$ .



- 13. (a)** The reaction is



The structures of A, B, C and D are as follows.

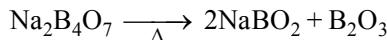


- (b) Sulphur trioxide produced in the Contact process is absorbed by sulphuric acid. It is not dissolved in water as it gives a dense fog of sulphuric acid particles.

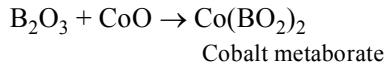
The catalyst used in the Contact process is vanadium pentoxide.

14. A is  $\text{Ca}(\text{OH})_2$ ; B is  $\text{NH}_4\text{HCO}_3$ ; C is  $\text{Na}_2\text{CO}_3$ ; D is  $\text{NH}_4\text{Cl}$ ; E is  $\text{CaCl}_2$

15. A little borax taken in a platinum loop is heated in non-luminous flame to give a colourless glassy bead.

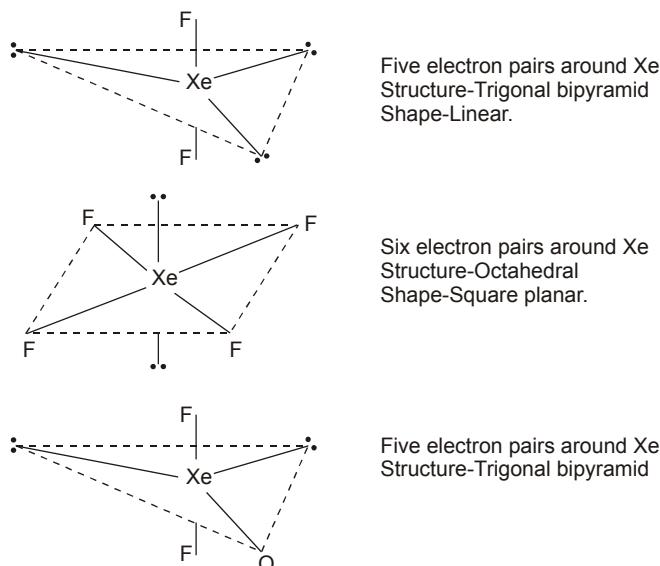


The glassy bead is dipped into cobalt(II) oxide and heated. The boric anhydride reacts with metallic oxides forming metaborates:

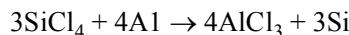


The colour of cobalt metaborate is blue both in oxidising and reducing flames.

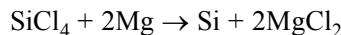
16. The required molecular structures are as follows.



17. Silicon from  $\text{SiCl}_4$  can be obtained by passing a current of  $\text{SiCl}_4$  over molten aluminium

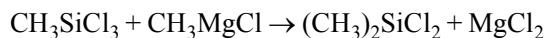
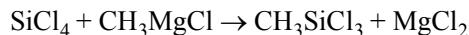


Alternatively, it may be obtained by reducing  $\text{SiCl}_4$  with Mg or Zn

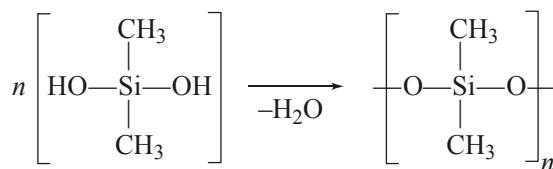
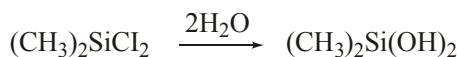


or  $\text{SiCl}_4 + 2\text{Zn} \rightarrow \text{Si} + 2\text{ZnCl}_2$

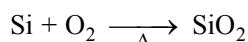
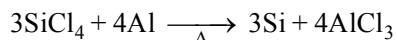
- (ii) First of all,  $\text{SiCl}_4$  is converted into dimethyldichlorosilane by using  $\text{CH}_3\text{MgCl}$



Subsequently, dimethyl dichlorosilane is hydrolysed to give straight-chain polymer.

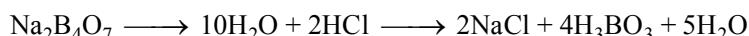


(iii) First of all,  $\text{SiCl}_4$  is reduced to Si. It is then oxidised to  $\text{SiO}_2$ , followed by treatment with NaOH.

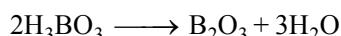


**18.** Boron may be obtained from borax as follows.

(i) Treatment of borax with HCl



(ii) Heat the boric acid to red heat

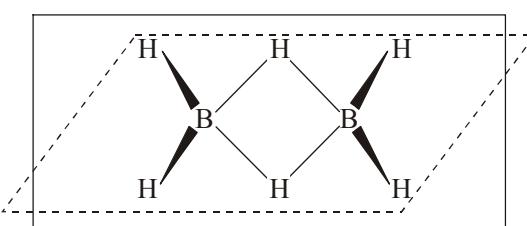


(iii) Reduce  $B_2O_3$  with Mg at high temperature



Magnesium boride and borate formed can be removed by treating with boiling hydrochloric acid.

The structure of  $\text{B}_2\text{H}_6$  is as follows.



Terminal B—H is 2c–2e bond with bond length of 119 pm.

Bridged B—H is 3c–2e bond with bond length of 133 pm.

Terminal H—B—H angle is  $121.5^\circ$ .

Bridged H—B—H angle is 97°

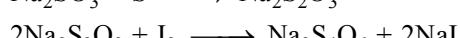
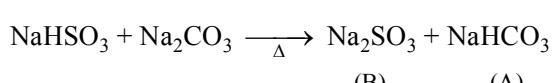
Bridged H atoms are perpendicular to the planar skeleton of rest of atoms

Boron-boron distance is 177 pm

The reaction of B<sub>2</sub>H<sub>6</sub> with HCl is



**19** The given reactions are as follows



(C) (D)

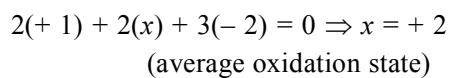
(C) (D)  
The oxidation of S in the compounds are

$$\begin{array}{cccc} +1 & +1 & x & -2 \\ \text{Na} & \text{H} & \text{S} & \text{O}_3 \\ +1 & x & -2 \end{array} \quad +1 + 1 + x + 3(-2) = 0 \Rightarrow x = +4$$

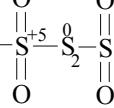
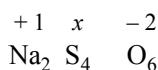


$$\begin{array}{ccc} +1 & x & -2 \\ \text{Na}_2 & \text{S}_2 & \text{O}_3 \end{array}$$

$$2(+1) + x + 3(-2) = 0 \Rightarrow x = +4$$

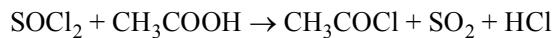
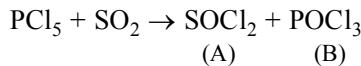


Based on its structure,  $\text{O}^- \text{S}^{+6}=\text{O}^{-2}$  the oxidation states are + 6 and - 2.



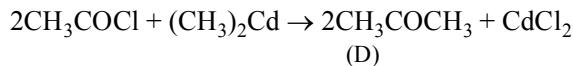
The reactions are

20. The reactions are



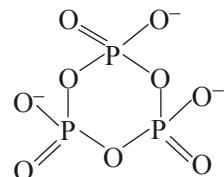
(A)

(C)



## HINTS AND SOLUTIONS

## **Straight Objective Type**

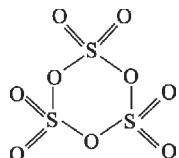


30. For the given molecules, we have

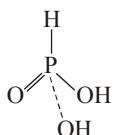
	$\text{SF}_4$	$\text{CF}_4$	$\text{XeF}_4$
Number of valence electrons	34	32	36
Lewis structure			
Number of lone pairs on the central atom	1	0	2
Number of pairs of electrons (bonded + lone) around the central atom	5	4	6
Probable structure	trigonal bipyramidal	tetrahedral	octahedral

31. Ammonia cannot be dried over concentrated sulphuric acid, calcium chloride or phosphorus pentoxide as the gas reacts with these substances. However, quicklime can be used.

33. The structure of sulphur trioxide trimes ( $\text{S}_3\text{O}_4$ ) is



34. The larger the number of oxygen atoms attached to the chlorine, the larger the acidity.

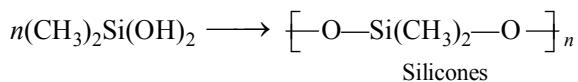
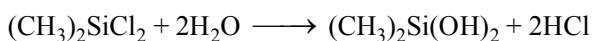


36. The structure of  $\text{H}_3\text{PO}_3$  is

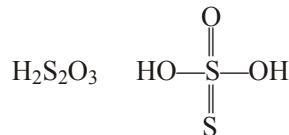
Since it contains two  $-\text{OH}$  groups, it is dibasic. Also it contains H atom directly attached to P, hence, it is reducing.

37. Boric acid acts as a weak monobasic acid by accepting a lone pair of electrons from  $-\text{OH}$  ion, thereby, acting as a Lewis acid.

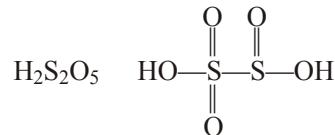
38. The involved reactions are



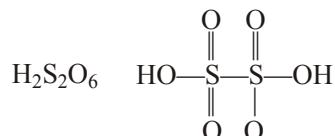
39. The structures of the given species are:



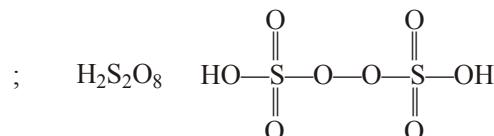
(Thiosulphuric acid)



(Pyrosulphurous acid)



(Dithionic acid)



(Peroxodisulphuric acid)

Thus, the compound  $\text{H}_2\text{S}_2\text{O}_8$  contains  $-\text{O}-\text{O}-$  linkage.

40. The reaction occurring is  $2\text{HNO}_3 \xrightarrow[-\text{H}_2\text{O}]{\text{P}_2\text{O}_5} \text{N}_2\text{O}_5$

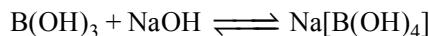
41.  $\text{N}_2\text{O}_3$  is obtained by condensing equimolar mixture of NO and  $\text{NO}_2$ .

42. Pyrosilicates involve sharing of one oxygen atom between two  $\text{SiO}_4^{4-}$  tetrahedra.

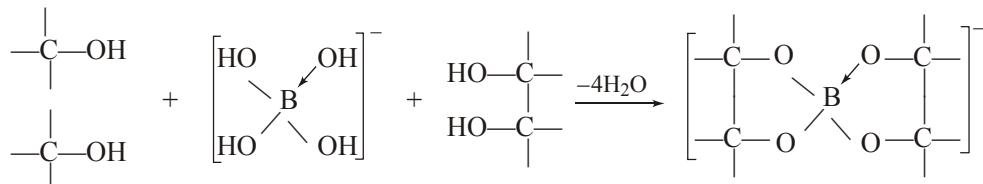
Chain and cyclic silicates involve sharing of two oxygen atoms of a  $\text{SiO}_4^{4-}$  tetrahedron with two other tetrahedra.

Sheet silicates involve sharing of three oxygen atoms by each tetrahedron.

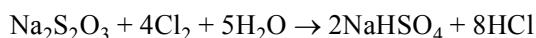
43. Boric acid is a weak monobasic acid. it does not donate proton but accepts  $\text{OH}^-$  ions.



It cannot be titrated with NaOH as a sharp end point is not obtained. However, in the presence of a *cis*-diol,  $\text{B}(\text{OH})_4^-$  forms very stable complex thereby forcing the above reaction to proceed to the right side.

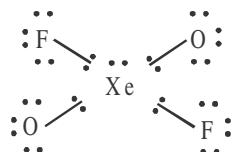


44. The reaction is

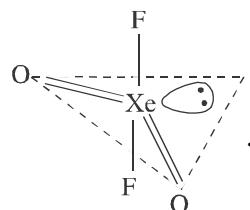


45.  $\text{P}_4\text{O}_6$  is obtained when  $\text{P}_4$  is burned in a deficit of oxygen.

46. The number of valence electrons in  $\text{XeO}_2\text{F}_2$  is  $8 + 2 \times 6 + 2 \times 7 = 34$ . These are distributed as shown in the following.



There are five pairs of electrons around Xe. To accommodate these, Xe undergoes  $\text{dsp}^3$  hybridization leading to the trigonal bipyramidal arrangement of five pairs of electrons. The structure of  $\text{XeO}_2\text{F}_2$  is

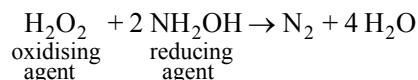
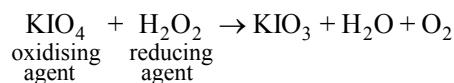


The shape of  $\text{XeO}_2\text{F}_2$  is sea-saw.

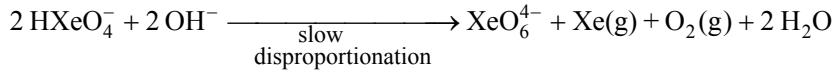
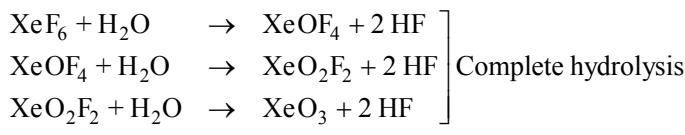
47. The concentrated nitric acid acquires yellow-brown colour due to the decomposition of nitric acid into  $\text{NO}_2$  and  $\text{O}_2$ .



48. Hydrogen peroxide is an oxidising as well as a reducing agent. In the presence of very strong oxidising agent such as  $\text{KIO}_4$ , it behaves as a reducing agent. The reactions of  $\text{H}_2\text{O}_2$  with  $\text{KIO}_4$  and  $\text{NH}_2\text{OH}$  are as follows.

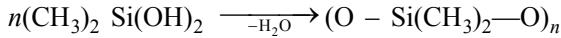
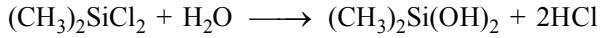


49. The reactions are:

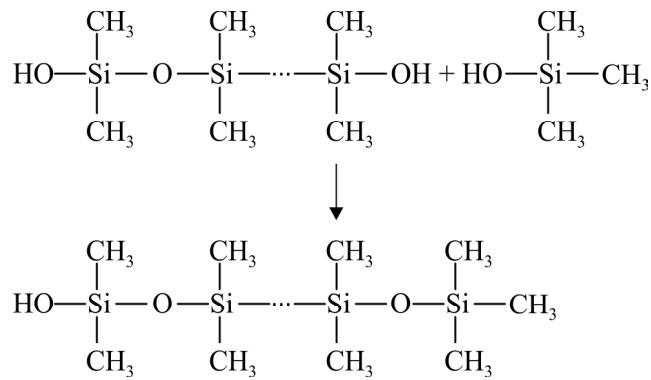


50. The reaction is  $\text{P}_4 + 8 \text{SOCl}_2 \rightarrow 4 \text{PCl}_3 + 4 \text{SO}_2 + 2 \text{S}_2\text{Cl}_2$

51. Linear polymer is produced from  $(\text{CH}_3)_2\text{SiCl}_2$



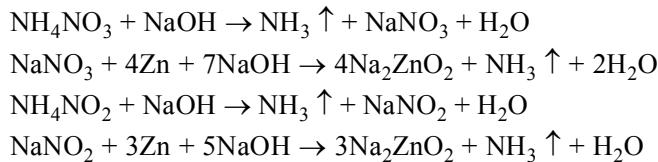
The chain termination is brought about by the use of  $(\text{CH}_3)_3\text{SiCl}$



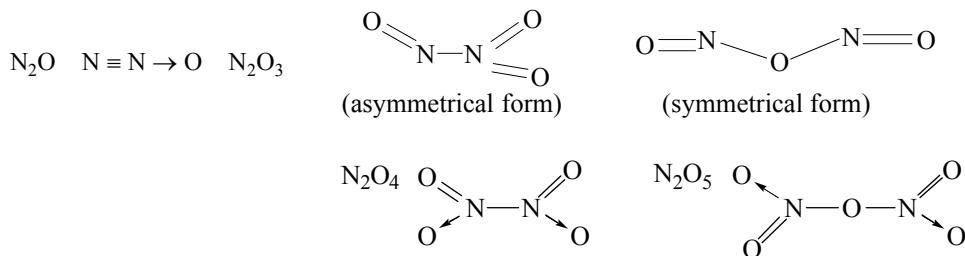
### Multiple Correct-Choice Type

5. All the four choices produce  $\text{NH}_3$  gas on boiling with excess of  $\text{NaOH}$ . However, only the choices  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$  will show re-evolution of the gas due to the reduction of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  by  $\text{Zn}$  in alkaline medium.

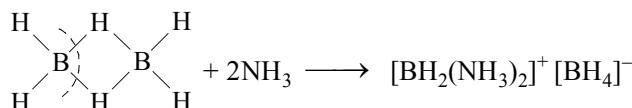
The involved reactions are:



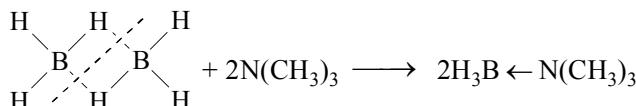
6. The structures of given species are as follows.



7. The given reaction involves unsymmetrical cleavage of boron as depicted in the following.

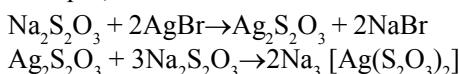


The above reaction is shown by strong, sterically uncrowded bases at low temperatures. With sterically crowded base, symmetrical cleavage occurs, which results into the formation of complex of the type shown in the following.



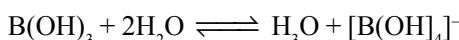
$\text{NH}_3$  and  $\text{CH}_3\text{NH}_2$  show greater tendency for unsymmetrical cleavage. With  $(\text{CH}_3)_2\text{NH}$ , this tendency is small while with  $(\text{CH}_3)_3\text{N}$ , there is no such tendency.

8. The precipitates of  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  are soluble in  $\text{Na}_2\text{S}_2\text{O}_3$ (aq) forming the complex  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$ . For example,

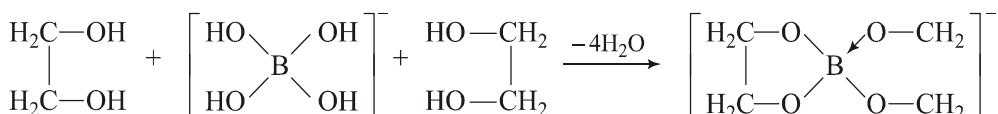


$\text{AgF}$  is soluble in water.

9. Boric acid, also known as orthoboric acid, is  $\text{H}_3\text{BO}_3$ , i.e.  $\text{B}(\text{OH})_3$ . It is a weak acid not due to self ionization but due to acceptance of  $\text{OH}^-$  ions. Thus, it behaves as a Lewis acid.



In the presence of ethylene glycol, boric acid acts as a strong acid (i.e. its acid strength is increased). This is due to the formation of very stable complex with  $[\text{B}(\text{OH})_4]^-$ .

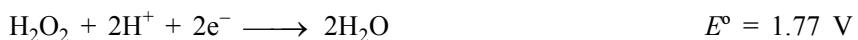


Because of this complex formation, the equilibrium shown above between  $\text{B}(\text{OH})_3$  and  $\text{H}_2\text{O}$  is displaced to the right causing complete ionization of  $\text{H}_3\text{BO}_3$ .

In boric acid, B is  $\text{sp}^2$  hybridised forming planar structure. In the solid, the boric acid units are hydrogen bonded together into two-dimensional sheets.

Boric acid acts as a weak electrolyte.

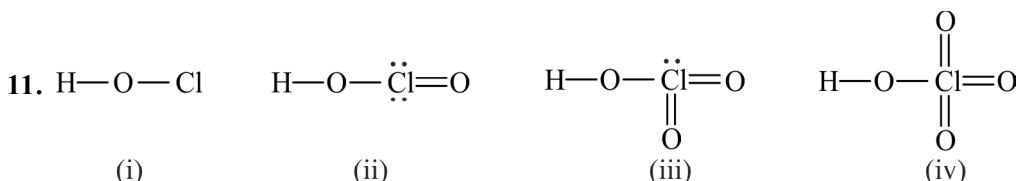
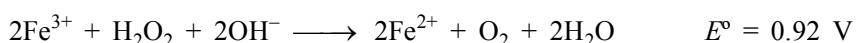
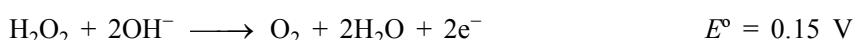
10. The reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is possible provided reduction potential of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  is larger than the reduction potential of  $\text{H}_2\text{O}_2$ . The standard reduction potentials are :



It follows that  $\text{H}_2\text{O}_2$  is more powerful reducing agent in alkaline medium as compared to acidic medium.  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  by alkaline  $\text{H}_2\text{O}_2$ .  $\text{Na}_2\text{O}_2$  in water is equivalent to  $2\text{NaOH} + \text{H}_2\text{O}_2$ .

Hence, the choice (a) and (b) are correct.

The net reaction is



$\text{sp}^3$  hybrid orbitals of Cl are involved in the bonding with oxygen atoms. Larger the number of oxygen atoms attached to Cl, stronger the acid. From the structures, it is obvious that the choice (b) and (c) are correct.

## **Fill-in-the Blanks Type**

## **Integer Answer Type**

- The number of oxygen atoms shared in  $\text{Si}_6\text{O}_{18}$  is  $6(\text{SiO}_4) - \text{Si}_6\text{O}_{18} = 6\text{O}$   
 The net negative charge on  $\text{Si}_6\text{O}_{18}$  will be  
 $6 \text{ (negative charge on SiO}_4\text{)} - 6 \text{ (negative charge on O)} = 6(-4) - 6(-2) = -12$   
 The net positive charge contributed by  $\text{Be}_n\text{Al}_2$  in  $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18} = +12$ . Hence, the value of  $n$  is  
 $n(+2) + 2(+3) = 12 \Rightarrow n = 3$
  - Diprotic acids are:  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{S}_2\text{O}_7$ .  
 Hence, the correct answer is **six**.
  - The compounds  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{P}_4\text{O}_{10}$  can result into the desired product.  

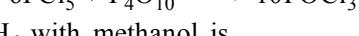
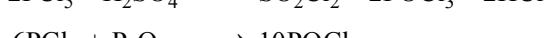
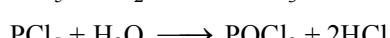
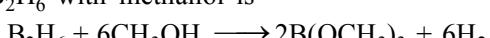
$$\text{PCl}_5 + \text{SO}_2 \longrightarrow \text{POCl}_3 + \text{SOCl}_2$$

$$\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow \text{POCl}_3 + 2\text{HCl}$$

$$2\text{PCl}_5 + \text{H}_2\text{SO}_4 \longrightarrow \text{SO}_2\text{Cl}_2 + 2\text{POCl}_3 + 2\text{HCl}$$

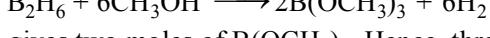
$$6\text{PCl}_5 + \text{P}_4\text{O}_{10} \longrightarrow 10\text{POCl}_3$$

- 4 The reaction of  $\text{B}_7\text{H}_9$  with methanol is



4. The reaction of  $\text{B}_2\text{H}_6$  with methanol is

$$\text{B}_2\text{H}_6 + 6\text{CH}_3\text{OH} \rightarrow \dots$$



One mole of  $\text{B}_2\text{H}_6$  gives two moles of  $\text{B}(\text{OCH}_3)_3$ . Hence, three moles of  $\text{B}_2\text{H}_6$  will give **6** mol of  $\text{B}(\text{OCH}_3)_3$ . The answer is **6**.

### True/False Type

5. There occurs only partial dimerization of nitric oxide in the liquid state.
6. Stronger the hydrogen bonding, weaker the acid.

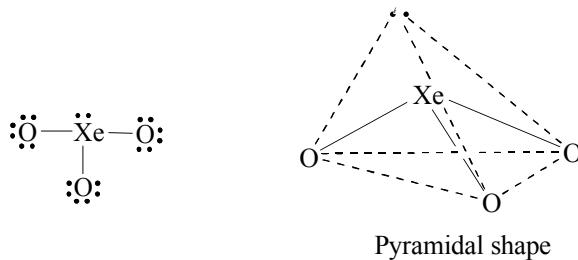
### Reasoning Type

2. Hydrolysis of  $\text{SiCl}_4$  is due to the presence of d orbitals.
3. The statement 1 is correct but the statement 2 is not correct as orthoboric acid acts as a Lewis acid. It does not liberate  $\text{H}^+$  ion but accepts a  $\text{OH}^-$  ion from water.

### Linked-Comprehension Type

#### Passage-1

1. Argon is used to provide an inert atmosphere in arc welding.
2. The total number of valence electrons in  $\text{XeO}_3$  is  $8 + 3 \times 6 = 26$ . There are four electrons around Xe. Hence, these electrons acquire tetrahedral orientations. The shape of the molecule is pyramidal.



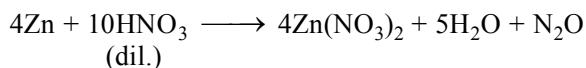
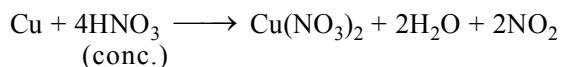
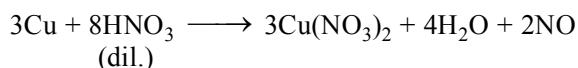
**Solution:**  $\text{XeF}_4$  and  $\text{XeF}_6$  are oxidising agents. These can oxidise  $\text{H}_2$  to  $\text{H}^+$ ,  $\text{Cl}^-$  to  $\text{Cl}_2$ ,  $\text{I}^-$  to  $\text{I}_2$  and Ce(III) to Ce(IV).

#### Passage-2

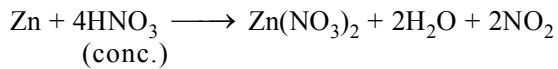
1. Between nitrates and phosphates, nitrates are less abundant in earth's crust because nitrates are more soluble in water.
2.  $\text{NH}_3$  is a better electron donor than  $\text{PH}_3$  because the lone pair of electrons occupies  $\text{sp}^3$  orbital formed from the more compact 2s and 2p orbitals as compared to 3s and 3p orbitals of phosphorous in  $\text{PH}_3$ .
3. The reaction is  $\text{P}_4 + 3\text{OH}^- + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{H}_2\text{PO}_2^-$   
The oxidation state of phosphorus in  $\text{P}_4$ ,  $\text{PH}_3$  and  $\text{H}_2\text{PO}_2^-$  are 0, -3 and +1, respectively. Thus, the reaction is disproportionation reaction.

### Matrix Match Type

1. The reactions given in Column I are as follows.



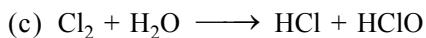
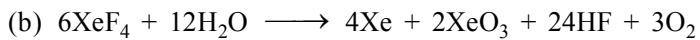
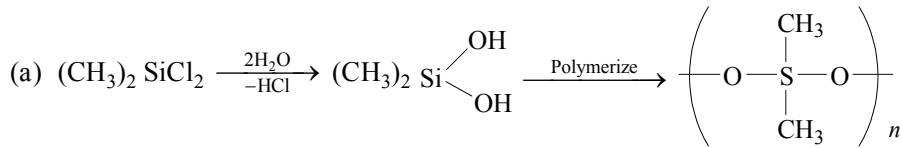
**15.22** IIT Chemistry: Topic-wise Solved Questions



The correct matching are

- (a)—(p) and (s)    (b)—(q) and (s)    (c)—(r) and (t)    (d)—(q) and (t)

2. The reaction are as follows.



# TRANSITION ELEMENTS

16

## **Straight Objective Type**

1. One of the constituents of German silver is  
 (a) Ag                    (b) Cu                    (c) Mg                    (d) Al                    (1980)

2. How many unpaired electrons are there in  $\text{Ni}^{2+}$ ?  
 (a) 0                    (b) 2                    (c) 4                    (d) 6                    (1981)

3. Iron is rendered passive by treatment with concentrated  
 (a)  $\text{H}_2\text{SO}_4$                     (b)  $\text{H}_3\text{PO}_4$                     (c) HCl                    (d)  $\text{HNO}_3$                     (1982)

4. Among the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by  
 (a)  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$                     (b)  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$                     (c)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$                     (d)  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$                     (1988)

5. Amongst  $\text{Ni}(\text{CO})_4$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{NiCl}_4^{2-}$   
 (a)  $\text{Ni}(\text{CO})_4$  and  $\text{NiCl}_4^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic  
 (b)  $\text{NiCl}_4^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{Ni}(\text{CO})_4$  is paramagnetic  
 (c)  $\text{Ni}(\text{CO})_4$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $\text{NiCl}_4^{2-}$  is paramagnetic  
 (d)  $\text{Ni}(\text{CO})_4$  is diamagnetic and,  $\text{NiCl}_4^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic                    (1991)

6. Amongst the following ions which one has the highest paramagnetism?  
 (a)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$                     (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$                     (c)  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$                     (d)  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$                     (1990)

7. Which compound is formed when excess KCN is added to aqueous solution of copper sulphate?  
 (a)  $\text{Cu}(\text{CN})_2$                     (b)  $\text{K}_2[\text{Cu}(\text{CN})_4]$                     (c)  $\text{K}[\text{Cu}(\text{CN})_2]$                     (d)  $\text{K}_3[\text{Cu}(\text{CN})_4]$                     (1996)

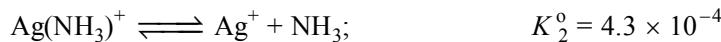
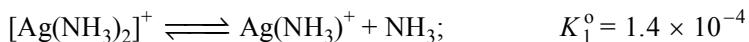
8. Which of the following compounds is expected to be coloured?  
 (a)  $\text{Ag}_2\text{SO}_4$                     (b)  $\text{CuF}_2$                     (c)  $\text{MgF}_2$                     (d)  $\text{CuCl}$                     (1997)

9. In nitroprusside ion the iron and NO exists as  $\text{Fe}^{\text{II}}$  and  $\text{NO}^+$  rather than  $\text{Fe}^{\text{III}}$  and NO. These forms can be differentiated by  
 (a) estimating the concentration of iron  
 (b) measuring the concentration of CN  
 (c) measuring the solid state magnetic moment  
 (d) thermally decomposing the compound                    (1998)

10. The geometry of  $\text{Ni}(\text{CO})_4$  and  $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$  are  
 (a) both square planar                    (b) tetrahedral and square planar, respectively  
 (c) both tetrahedral                    (d) square planar and tetrahedral, respectively.                    (1999)

- 11.** Ionic radii of  
 (a)  $\text{Ti}^{4+} < \text{Mn}^{7+}$       (b)  ${}^{35}\text{Cl}^- < {}^{37}\text{Cl}^-$       (c)  $\text{K}^+ > \text{Cl}^-$       (d)  $\text{P}^{3+} > \text{P}^{5+}$  (1999)
- 12.** Which of the following has the maximum number of unpaired electrons?  
 (a)  $\text{Mg}^{2+}$       (b)  $\text{Ti}^{3+}$       (c)  $\text{V}^{3+}$       (d)  $\text{Fe}^{2+}$  (1996)
- 13.** Among the following, the compound that is both paramagnetic and coloured is  
 (a)  $\text{K}_2\text{CrO}_7$       (b)  $(\text{NH}_4)_2(\text{TiCl}_6)$       (c)  $\text{VOSO}_4$       (d)  $\text{K}_3[\text{Cu}(\text{CN})_4]$  (1997)
- 14.** The complex ion which has no ‘d’ electrons in the central metal atom is  
 (a)  $[\text{MnO}_4]^-$       (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (c)  $[\text{Fe}(\text{CN})_6]^{3-}$       (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  (2001)
- 15.** The correct order of ionic radii of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  is  
 (a)  $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$       (b)  $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$   
 (c)  $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$       (d)  $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$  (2003)
- 16.** The fusion of  $\text{MnO}_2$  with  $\text{KOH}$  in air produces  
 (a) purple coloured  $\text{KMnO}_4$       (b) purple-green coloured  $\text{K}_2\text{MnO}_4$   
 (c) reddish-brown coloured  $\text{Mn}_2\text{O}_7$       (d) brown coloured  $\text{Mn}_2\text{O}_3$  (2003)
- 17.** A 2-L solution contains 0.04 mol of each of  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$  and  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ . To one litre of this solution, excess of  $\text{AgNO}_3$  is added. To the remaining solution, excess of  $\text{BaCl}_2$  is added. The amounts of precipitated salts respectively are  
 (a) 0.01 mol, 0.01 mol      (b) 0.02 mol, 0.01 mol  
 (c) 0.01 mol, 0.02 mol      (d) 0.02 mol, 0.02 mol (2003)
- 18.** The basic character of the transition metal monoxides follows the order  
 (a)  $\text{CrO} > \text{VO} > \text{FeO} > \text{TiO}$       (b)  $\text{TiO} > \text{FeO} > \text{VO} > \text{CrO}$   
 (c)  $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$       (d)  $\text{VO} > \text{CrO} > \text{TiO} > \text{FeO}$  (2003)
- Atomic numbers of Ti, V, Cr and Fe are 22, 23, 24 and 26, respectively.
- 19.** The species having tetrahedral shape is  
 (a)  $\text{Ni}(\text{CO})_4$       (b)  $[\text{Ni}(\text{CN})_4]^{2-}$       (c)  $[\text{PdCl}_4]^{2-}$       (d)  $[\text{Pd}(\text{CN})_4]^{2-}$  (2004)
- 20.** The spin magnetic moment of cobalt in the compound  $\text{K}_2[\text{Co}(\text{SCN})_4]$  is  
 (a)  $\sqrt{3}$  bohr magneton      (b)  $\sqrt{8}$  bohr magneton  
 (c)  $\sqrt{15}$  bohr magneton      (d)  $\sqrt{24}$  bohr magneton (2004)
- 21.** Which of the following pairs is expected to exhibit same colour in solution?  
 (a)  $\text{VOCl}_2, \text{MnCl}_2$       (b)  $\text{CuCl}_2, \text{VOCl}_2$       (c)  $\text{VOCl}_2, \text{FeCl}_2$       (d)  $\text{MnCl}_2, \text{FeCl}_2$  (2005)
- 22.** Which type of isomerism is shown by  $\text{Co}(\text{NH}_3)_4\text{Br}_2\text{Cl}$ ?  
 (a) Geometrical only      (b) Ionization only  
 (c) Geometrical and ionization      (d) Ionization and optical (2005)
- 23.** Excess of  $\text{KCN}$  is added to an aqueous solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . This causes  
 (a) the formation of  $\text{Cu}(\text{CN})_2$   
 (b) the formation of  $\text{Cu}(\text{OH})_2$   
 (c) the formation of complex ion  $[\text{Cu}(\text{CN})_4]^{2-}$   
 (d) the precipitation of  $\text{CuCN}$  which dissolves forming the complex ion  $[\text{Cu}(\text{CN})_4]^{3-}$  (2006)

24. Given:



The instability constant of the complex  $\text{Ag}(\text{NH}_3)_2^+$  is equal to

- (a)  $7.14 \times 10^3$     (b)  $2.33 \times 10^3$     (c)  $6.02 \times 10^{-8}$     (d)  $1.66 \times 10^7$     (2006)

25. The bond length of CO is 112.8 pm. Its bond length in  $\text{Fe}(\text{CO})_5$  will be about

- (a) 112.8 pm    (b) 110 pm    (c) 113 pm    (d) 120 pm    (2006)

26. Among the following metal carbonyls, the C—O bond order is lowest in

- (a)  $[\text{Mn}(\text{CO})_6]^+$     (b)  $[\text{Fe}(\text{CO})_5]$     (c)  $[\text{Cr}(\text{CO})_6]$     (d)  $[\text{V}(\text{CO})_6]^-$     (2007)

27. Both  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic. The hybridisations of nickel in these complexes, respectively, are

- (a)  $\text{sp}^3, \text{sp}^3$     (b)  $\text{sp}^3, \text{dsp}^2$     (c)  $\text{dsp}^2, \text{sp}^3$     (d)  $\text{dsp}^2, \text{dsp}^2$     (2008)

28. The IUPAC name of  $[\text{Ni}(\text{NH}_3)_4] [\text{NiCl}_4]$  is

- (a) Tetrachloronickel(II)—tetraamminenickel(II)  
 (b) Tetraamminenickel(II)—tetrachloronickel(II)  
 (c) Tetraamminenickel(II)—tetrachloronickelate(II)  
 (d) Tetrachloronickel(II)—tetraamminenickelate(0)    (2008)

29. Among the following, the coloured compound is

- (a)  $\text{CuCl}$     (b)  $\text{K}_3[\text{Cu}(\text{CN})_4]$     (c)  $\text{CuF}_2$     (d)  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$     (2008)

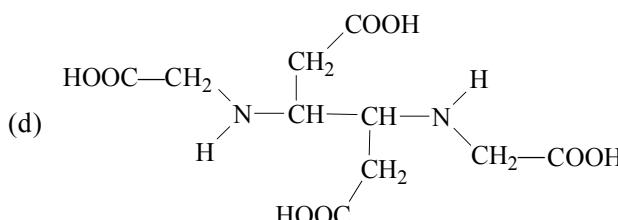
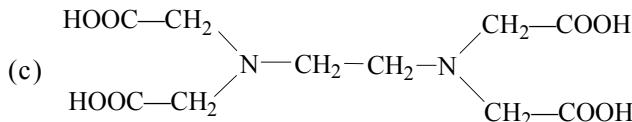
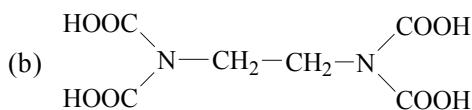
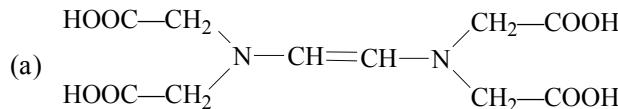
30. The spin only magnetic moment value (in Bohr magneton units) of  $\text{Cr}(\text{CO})_6$  is

- (a) 0    (b) 2.84    (c) 4.90    (d) 5.92    (2009)

31. The ionization isomer of  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$  is

- (a)  $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$     (b)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$   
 (c)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$     (d)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)]\text{H}_2\text{O}$     (2010)

32. The correct structure of ethylenediaminetetraacetic acid (EDTA) is



(2010)

33. The complex showing a spin-only magnetic moment of 2.82 B.M. is  
 (a)  $\text{Ni}(\text{CO})_4$       (b)  $[\text{NiCl}_4]^{2-}$       (c)  $\text{Ni}(\text{PPh}_3)_4$       (d)  $[\text{Ni}(\text{CN})_4]^{2-}$  (2010)
34. Geometrical shapes of the compounds formed by the reaction of  $\text{Ni}^{2+}$  with  $\text{Cl}^-$ ,  $\text{CN}^-$  and  $\text{H}_2\text{O}$ , respectively, are  
 (a) octahedral, tetrahedral and square planar      (b) tetrahedral, square planar and octahedral  
 (c) square planar, tetrahedral and octahedral      (d) octahedral, square planar and octahedral (2011)
35. Among the following complexes  
 $\text{K}_3[\text{Fe}(\text{CN})_6]$ ;  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ;  $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ ;  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ ;  $\text{K}_2[\text{Pt}(\text{CN})_4]$ ; and  $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$   
 (K)      (L)      (M)      (N)      (O)      (P)  
 the diamagnetic complexes are  
 (a) K, L, M, N      (b) K, M, O, P      (c) L, M, O, P      (d) L, M, N, O (2011)
36. As per IUPAC nomenclature, the name of the complex  $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$  is  
 (a) Tetraaquadiaminecobalt(III) chloride      (b) Tetraaquadiaminecobalt(III) chloride  
 (c) Diaminetetraaquacobalt(III) chloride      (d) Diamminetetraaquacobalt(III) chloride (2012)
37. The colour of light absorbed by an aqueous solution of  $\text{CuSO}_4$  is  
 (a) orange-red      (b) blue-green      (c) yellow      (d) violet (2012)
38.  $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of  $\text{Ni}^{2+}$  in the paramagnetic and diamagnetic states are respectively  
 (a) tetrahedral and tetrahedral      (b) square planar and square planar  
 (c) tetrahedral and square planar      (d) square planar and tetrahedral (2012)
39. Consider the following complex ions P, Q and R.  
 $\text{P} = [\text{FeF}_6]^{3-}$ ;       $\text{Q} = [\text{V}(\text{H}_2\text{O})_6]^{2+}$ ;       $\text{R} = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.), is  
 (a)  $\text{R} < \text{Q} < \text{P}$       (b)  $\text{Q} < \text{R} < \text{P}$       (c)  $\text{R} < \text{P} < \text{Q}$       (d)  $\text{Q} < \text{P} < \text{R}$  (2013)
- ### Multiple Correct-Choice Type
1. The aqueous solutions of the following salts will be coloured in the case of  
 (a)  $\text{Zn}(\text{NO}_3)_2$       (b)  $\text{LiNO}_3$       (c)  $\text{Co}(\text{NO}_3)_2$       (d)  $\text{CrCl}_3$  (1990)
2. Potassium manganate ( $\text{K}_2\text{MnO}_4$ ) is formed when  
 (a)  $\text{Cl}_2$  is passed into an aqueous  $\text{KMnO}_4$  solution  
 (b)  $\text{MnO}_2$  is fused with KOH in air  
 (c) formaldehyde reacts with  $\text{KMnO}_4$  in presence of strong alkali  
 (d)  $\text{KMnO}_4$  reacts with concentrated  $\text{H}_2\text{SO}_4$  (1988)
3. Identify the complexes which are expected to be coloured.  
 (a)  $\text{Ti}(\text{NO}_3)_4$       (b)  $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$   
 (c)  $[\text{Cr}(\text{NH}_3)_6]^{3+} (\text{Cl}^-)_3$       (d)  $\text{K}_3[\text{VF}_6]$  (1994)
4. Which of the following alloys contain(s) Cu and Zn?  
 (a) Bronze      (b) Brass      (c) Gun metal      (d) Type metal (1993)
5. Which of the following statements(s) is(are) correct with reference to the ferrous and ferric ions?  
 (a)  $\text{Fe}^{3+}$  gives brown colour with potassium ferricyanide.  
 (b)  $\text{Fe}^{2+}$  gives blue precipitate with potassium ferricyanide.  
 (c)  $\text{Fe}^{3+}$  gives red colour with potassium thiocyanate.  
 (d)  $\text{Fe}^{3+}$  gives brown colour with ammonium thiocyanate. (1998)

6. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese

  - (a) gives hardness to steel
  - (b) helps the formation of oxides of iron
  - (c) can remove oxygen and sulphur
  - (d) can show highest oxidation state of +7. (1998)

7. The compound(s) that exhibit(s) geometrical isomerism is(are)

  - (a)  $[\text{Pt}(\text{en})\text{Cl}_2]$
  - (b)  $[\text{Pt}(\text{en})_2]\text{Cl}_2$
  - (c)  $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$
  - (d)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  (2009)

8. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is (are)

  - (a)  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
  - (b)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  and  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$
  - (c)  $[\text{Co Br}_2\text{Cl}_2]^{2-}$  and  $[\text{PtBr}_2\text{Cl}_2]^{2-}$
  - (d)  $[\text{Pt}(\text{NH}_3)_3(\text{NO}_3)]\text{Cl}$  and  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Br}$  (2013)

9. The correct statement(s) about  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  is(are)  
 [Atomic numbers of Cr = 24 and Mn = 25]

  - (a)  $\text{Cr}^{2+}$  is a reducing agent
  - (b)  $\text{Mn}^{3+}$  is an oxidizing agent
  - (c) Both  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  exhibit  $d^4$  electronic configuration
  - (d) When  $\text{Cr}^{2+}$  is used as a reducing agent, the chromium ion attains  $d^5$  electronic configuration (2015)

## **Fill-in-the-Blanks Type**

1. The formula of the deep red liquid formed on warming dichromate with KCl in concentrated sulphuric acid is \_\_\_\_\_. (1993)
  2. The type of magnetism exhibited by  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  ion is \_\_\_\_\_. (1994)
  3. The IUPAC name of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is \_\_\_\_\_. (1994)
  4. The IUPAC name of  $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$  is \_\_\_\_\_. (1995)
  5. The IUPAC name of  $\text{K}_3[\text{Cr}(\text{CN})_6]$  is \_\_\_\_\_. (1995)
  6. Silver jewellery items tarnish slowly in the air due to their reaction with \_\_\_\_\_. (1997)

## **Integer Answer Type**

- The number of water molecules(s) directly bonded to the metal centre in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is \_\_\_\_\_. (2009)
  - Total number of geometrical isomers for the complex  $[\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{NH}_3)]$  is \_\_\_\_\_. (2010)
  - $\text{EDTA}^{4-}$  is ethylenediaminetetraacetate ion. The total number of N – Co – O bond angles in  $[\text{Co}(\text{EDTA})]^-$  complex ion is \_\_\_\_\_. (2013)
  - Consider the following list of reagents.  
Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$ , alkaline  $\text{KMnO}_4$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{HNO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . The total number of reagents that can oxidise aqueous iodide to iodine is \_\_\_\_\_. (2014)
  - For the octahedral complexes of  $\text{Fe}^{3+}$  in  $\text{SCN}^-$  (thiocyanato-S) and in  $\text{CN}^-$  ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is \_\_\_\_\_.  
[Atomic number of Fe = 26] (2015)
  - In the complex acetyl bromido dicarbonyl bis(triethylphosphine) iron(II), the number of Fe–C bond(s) is \_\_\_\_\_. (2015)
  - Among the complex ions,  $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^{+}$ ,  $[\text{CrCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]^{+}$ ,  $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ ,  $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{NH}_3)\text{Cl}]^{2+}$  and  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$ , the number of complex ion(s) that show(s) *cis-trans* isomerism is \_\_\_\_\_. (2015)

**True/False Type**

1. The outer electronic configuration of the ground state chromium atom is  $(3d)^4(4s)^2$ . (1982)
2. Diprotonic zinc exhibits paramagnetism due to loss of two electrons from 3d orbital of neutral atom. (1987)
3. Both potassium ferrocyanide and potassium ferricyanide are diamagnetic. (1989)
4. Most transition metal compounds are coloured (1986)
5. Dilute HCl oxidises metallic Fe to  $Fe^{2+}$  (1983)

**Reasoning Type**

The question below consists of an ‘Assertion’ in column 1 and the ‘Reason’ in column 2. Use the following key to choose the appropriate answer.

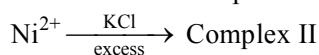
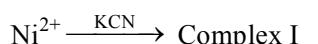
- (a) If both *assertion* and *reason* are CORRECT, and *reason* is the CORRECT explanation of the *assertion*.
- (b) If both *assertion* and *reason* are CORRECT, but *reason* is NOT the CORRECT explanation of the *assertion*.
- (c) If *assertion* is CORRECT, but *reason* is INCORRECT.
- (d) If *assertion* is INCORRECT, but *reason* is CORRECT.

**Assertion (column I)****Reason (column II)**

1.  $Zn^{2+}$  is diamagnetic. The electrons are lost from 4s orbital to form  $Zn^{2+}$ . (1998)
2. STATEMENT-1:  $[Fe(H_2O)_5NO]SO_4$  is paramagnetic.  
and  
STATEMENT-2: The Fe in  $[Fe(H_2O)_5NO]SO_4$  has three unpaired electrons.  
  - (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
  - (b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
  - (c) STATEMENT-1 is True, STATEMENT-2 is False
  - (d) STATEMENT-1 is False, STATEMENT-2 is True (2008)
3. STATEMENT-1: The geometrical isomers of the complex  $[M(NH_3)_4Cl_2]$  are optically inactive.  
and  
STATEMENT-2: Both geometrical isomers of the complex  $[M(NH_3)_4Cl_2]$  possess axis of symmetry.  
  - (a) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1
  - (b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
  - (c) STATEMENT-1 is True, STATEMENT-2 is False
  - (d) STATEMENT-1 is False, STATEMENT-2 is True (2008)

**Linked-Comprehension Type****Passage I**

$Ni^{2+}$  ions form the following complexes.



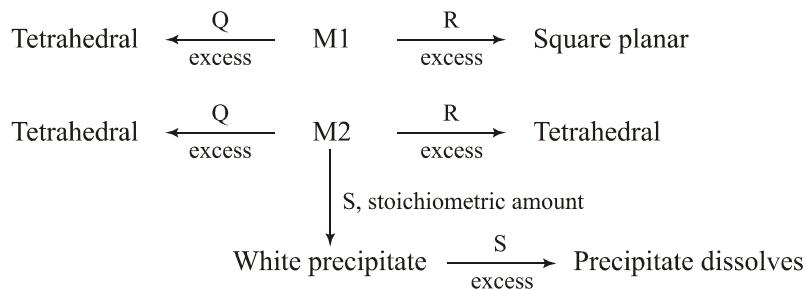
Both the complexes have coordination number 4.

1. The IUPAC names of the complexes respectively are
    - (a) potassium tetracyanonickel(II) and potassium tetrachloronickelate(II)
    - (b) potassium tetracyanonickelate(II) and potassium tetrachloronickel (II)
    - (c) potassium tetracyanonickel(II) and potassium tetrachlonickel(II)
    - (d) potassium tetracyanonickelate(II) and potassium tetrachloronickelate(II).
  2. Which of the following statements is correct?
    - (a) The cyano complex is diamagnetic and the chloro complex is paramagnetic
    - (b) The cyano complex is paramagnetic and the chloro complex is diamagnetic
    - (c) Both the complexes are diamagnetic
    - (d) Both the complexes are paramagnetic
  3. Nickel ion involves
    - (a)  $dsp^2$  hybridization in both complexes
    - (b)  $sp^3$  hybridization in both complexes
    - (c)  $dsp^2$  hybridization in cyano complex and  $sp^3$  hybridization in chloro complex
    - (d)  $sp^3$  hybridization in cyano complex and  $dsp^2$  hybridization in chloro complex
- (2006)

### Passage 2

An aqueous solution of metal ion **M1** reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion **M2** always forms tetrahedral complexes with these reagents. Aqueous solution of **M2** on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below.

#### SCHEME



1. M1, Q, R, respectively, are
 

(a) $\text{Zn}^{2+}$ , $\text{KCN}$ and $\text{HCl}$ (c) $\text{Cd}^{2+}$ , $\text{KCN}$ and $\text{HCl}$	(b) $\text{Ni}^{2+}$ , $\text{HCl}$ , $\text{HCN}$ (d) $\text{Co}^{2+}$ , $\text{HCl}$ , $\text{HCN}$
--	--
  2. The reagent S is:
 

(a) $\text{K}_4\text{Fe}(\text{CN})_6$ (c) $\text{K}_2\text{CrO}_4$	(b) $\text{Na}_2\text{HPO}_4$ (d) $\text{KOH}$
--	---
- (2014)

### Matrix Match Type

1. Match the complexes in **Column I** with their properties listed in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

**Column I**

- (a)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$   
 (b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$   
 (d)  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$

**Column II**

- (p) geometrical isomers  
 (q) paramagnetic  
 (r) diamagnetic  
 (s) metal ion with +2 oxidation state (2007)

2. Match each coordination compound in **List-I** with an appropriate pair of characteristics from **List-II** and select the correct answer using the code given below the lists.

(en =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ; atomic numbers: Ti = 22, Cr = 24, Co = 27, Pt = 78)

**List-I**

- P.  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 Q.  $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$   
 R.  $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$   
 S.  $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$

**List-II**

1. Paramagnetic and exhibits ionisation isomerism  
 2. Diamagnetic and exhibits *cis-trans* isomerism  
 3. Paramagnetic and exhibits *cis-trans* isomerism  
 4. Diamagnetic and exhibits ionisation isomerism

**Code:**

	P	Q	R	S
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

(2014)

**Short Answer Type**

- The species  $[\text{CuCl}_4]^{2-}$  exists while  $[\text{CuI}_4]^{2-}$  does not. (1992)
- Identify the complexes which are expected to be coloured. Explain. (1994)
 

(i) $[\text{Ti}(\text{NO}_3)_4]$	(ii) $[\text{Cu}(\text{NCCH}_3)_4]^+ \text{BF}_4^-$
(iii) $[\text{Cr}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	(iv) $\text{K}_3[\text{VF}_6]$ (1994)
- Write the IUPAC name for  $[\text{Cr}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ . (1996)
- Write the IUPAC name of the compound  $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$ . Is this compound coloured? (1997)
- Write the formulae of the following complexes:
 

(i) Pentamminechlorocobalt(III)	(ii) Lithium tetrahydroaluminate(III). (1997)
---------------------------------	---
- A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. (1997)
- A**, **B** and **C** are three complexes of chromium(III) with the empirical formula  $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$ . All the three complexes have water and chloride ion as ligands. Complex **A** does not react with concentrated  $\text{H}_2\text{SO}_4$ , whereas complexes **B** and **C** lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated  $\text{H}_2\text{SO}_4$ . Identify **A**, **B** and **C**. (1997)
- Draw the structures of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Ni}(\text{CO})_4]^{2-}$  and  $[\text{Ni}(\text{CO})_4]$ . Write the hybridisation of atomic orbitals of the transition metal in each case. (1999)
- A metal complex having composition  $\text{Cr}(\text{NH}_3)_4\text{Cl}_2\text{Br}$  has been isolated in two forms **A** and **B**. The form **A** reacts with  $\text{AgNO}_3$  to give a white precipitate readily soluble in dilute aqueous ammonia, whereas **B** gives a pale yellow precipitate soluble in concentrated ammonia. Write the formulae **A** and **B** and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). (2001)
- Deduce the structures of  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. (2002)
- The magnetic moment of the complex ion  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_6]^{2+}$  is found to be 3.9 Bohr magneton. Explain the structure of the complex ion. (2003)

12. Dimethylglyoxime is added to alcoholic solution of  $\text{NiCl}_2$ . When ammonium hydroxide is slowly added to it a precipitate of a complex appears. (a) Give the structure of complex showing hydrogen bonds. (b) What is the colour of the complex? (c) What is oxidation state of the central metal ion? (d) What is state of hybridisation of the central metal ion? (e) Is the complex paramagnetic or diamagnetic? (2004)

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (b)  | 3. (d)  | 4. (c)  | 5. (c)  | 6. (b)  | 7. (d)  |
| 8. (b)  | 9. (c)  | 10. (c) | 11. (d) | 12. (d) | 13. (c) | 14. (a) |
| 15. (a) | 16. (b) | 17. (d) | 18. (c) | 19. (a) | 20. (c) | 21. (b) |
| 22. (c) | 23. (d) | 24. (c) | 25. (c) | 26. (b) | 27. (b) | 28. (c) |
| 29. (c) | 30. (a) | 31. (b) | 32. (c) | 33. (b) | 34. (b) | 35. (c) |
| 36. (d) | 37. (a) | 38. (c) | 39. (b) |         |         |         |

### Multiple Correct-Choice Type

- |                  |             |             |                  |
|------------------|-------------|-------------|------------------|
| 1. (c), (d)      | 2. (b), (c) | 3. (c), (d) | 4. (a), (b), (c) |
| 5. (b), (c)      | 6. (a), (c) | 7. (c), (d) | 8. (b), (d)      |
| 9. (a), (b), (c) |             |             |                  |

### Fill-in-the-Blanks Type

- |                                     |  |
|-------------------------------------|--|
| 1. $\text{CrO}_2\text{Cl}_2$        | 2. Paramagnetism                       |
| 3. Hexamminecobalt(III) chloride    | 4. Pentamminenitrocobalt(III) chloride |
| 5. Potassium hexacyanochromate(III) | 6. $\text{H}_2\text{S}$                |

### Integer Answer Type

- |      |      |      |      |      |      |      |
|------|------|------|------|------|------|------|
| 1. 4 | 2. 3 | 3. 8 | 4. 7 | 5. 4 | 6. 3 | 7. 6 |
|------|------|------|------|------|------|------|

### True/False Type

- |          |          |          |         |         |
|----------|----------|----------|---------|---------|
| 1. False | 2. False | 3. False | 4. True | 5. True |
|----------|----------|----------|---------|---------|

### Reasoning Type

- |        |        |        |
|--------|--------|--------|
| 1. (b) | 2. (a) | 3. (b) |
|--------|--------|--------|

### Linked-Comprehension Type

#### Passage-1

- |        |        |        |
|--------|--------|--------|
| 1. (d) | 2. (a) | 3. (c) |
|--------|--------|--------|

#### Passage-2

- |        |        |
|--------|--------|
| 1. (b) | 2. (d) |
|--------|--------|

## **Matrix Match Type**

1. The correct-bubbled diagram is as follows.

	p	q	r	s
a	●	●	○	●
b	●	○	●	●
c	○	●	○	●
d	○	●	○	●

2. (b)

## **Short Answer Type**

1. The species  $\text{CuCl}_2$  is a stable one whereas  $\text{Cul}_2$  is unstable. The latter immediately breaks down into cuprous iodide.
  2. Only those complexes are coloured which contain the metal ions with incomplete d-subshell. If the metal ion involved completely filled or empty d-subshell, the complex will be colourless.

<i>Complex</i>	<i>Central metal ion</i>	<i>Outer electronic configuration</i>	<i>Colour</i>
Ti(NO <sub>3</sub> ) <sub>4</sub>	Ti <sup>4+</sup>	3d <sup>0</sup> 4s <sup>0</sup>	Colourless
[Cu(NCCH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	Cu <sup>+</sup>	3d <sup>0</sup> 4s <sup>0</sup>	Colourless
[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> 3Cl <sup>-</sup>	Cr <sup>3+</sup>	3d <sup>3</sup> 4s <sup>0</sup>	Coloured
K <sub>3</sub> [V F <sub>6</sub> ]	V <sup>3+</sup>	3d <sup>2</sup> 4s <sup>0</sup>	Coloured

3. Pentaamminecarbonatochromium(III) chloride  
4. The IUPAC name of  $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$  is Pentaammineisothiocyanochromium(III)-tetrachlorozincate(II).

The electronic configuration Cr(III) is  $3d^3$ . The compound is expected to be coloured.

5. (i)  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$  (ii)  $\text{Li}[\text{AlH}_4]$

6. The expression connecting magnetic moment with the number of unpaired electrons is

$$\mu = \sqrt{n(n+2)} \mu_B$$

For  $\mu = 1.73 \text{ } \mu_B$ ,  $n$  should be equal 1. Thus, vanadium ion has one unpaired electron. Its electronic configuration would be  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^1$ . Thus, vanadium ion carries  $4+$  charge (i.e,  $\text{V}^{4+}$ ).

7. The compound A does not react with concentrated  $\text{H}_2\text{SO}_4$  implying that all water molecules are coordinated with  $\text{Cr}^{3+}$  ion. Hence, its structure would be  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ .

The compound B loses 6.75% of its original mass when treated with concentrated  $\text{H}_2\text{SO}_4$ . This loss is due to the removal of water molecules which is/are not directly coordinated to  $\text{Cr}^{3+}$  ion.

The mass of water molecules removed per mole of the complex is

$$\frac{6.75}{100} \times \text{Molar mass of the complex} = \frac{6.75}{100} \times 266.5 \text{ g} = 17.98 \text{ g}$$

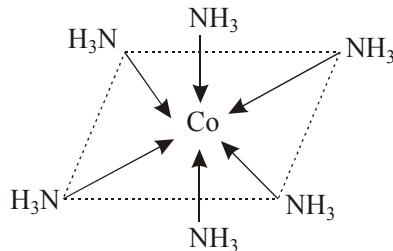
This corresponds to one mole of water. Hence, the structure of the compound B will be  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] (\text{H}_2\text{O})\text{Cl}_2$ .

The compound C loses 13.5% of its mass when treated with concentrated  $\text{H}_2\text{SO}_4$  which is twice of the mass lost by the compound B. Hence, the structure of the compound C will be  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{H}_2\text{O})_2\text{Cl}$ .

**8.  $[\text{Co}(\text{NH}_3)_6]^{3+}$** 

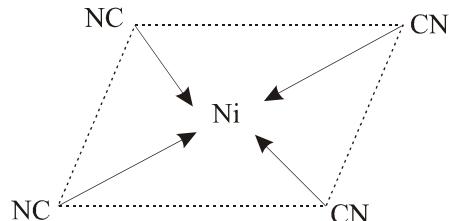
<i>Species</i>	<i>Electronic Configuration</i>		
	3d	4s	4p
Co atom			
$\text{Co}^{3+}$ ion			
$\text{Co}^{3+}$ in complex			

The structure of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is octahedral.

 **$[\text{Ni}(\text{CN})_6]^{2-}$** 

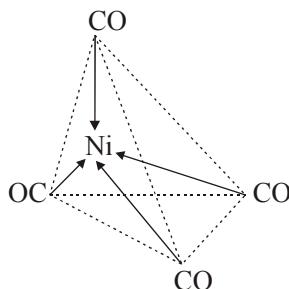
<i>Species</i>	<i>Electronic Configuration</i>		
	3d	4s	4p
Ni atom			
$\text{Ni}^{2+}$ ion			
$\text{Ni}^{2+}$ in complex			

The structure of  $[\text{Ni}(\text{CN})_6]^{2-}$  is a square planar:

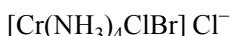
 **$[\text{Ni}(\text{CO})_4]$** 

<i>Species</i>	<i>Electronic Configuration</i>		
	3d	4s	4p
Ni atom			
Ni in complex			

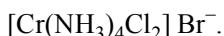
The structure of  $[\text{Ni}(\text{CO})_4]$  is tetrahedral.



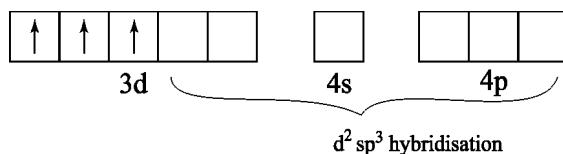
9. Since **A** gives white precipitate with  $\text{AgNO}_3$  which is soluble in dilute aqueous ammonia, **A** must be having  $\text{Cl}^-$  outside the coordination sphere. Hence, its formula is



Since **B** gives yellow precipitate with  $\text{AgNO}_3$  which is soluble in concentrated ammonia, **B** must be having  $\text{Br}^-$  outside the coordination sphere. Hence, its formula is



Both the compounds **A** and **B** have Cr in +3 oxidation state. Its electronic configuration is  $[\text{Ar}] (3d)^3$ .



Thus, Cr uses  $d^2sp^3$  hybrid orbitals in forming linkages with the atoms within the coordination sphere, forming octahedral arrangement.

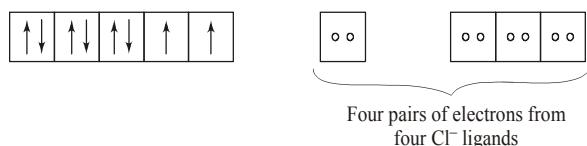
There are three unpaired electrons with Cr atom. Hence, its spin magnetic moment is

$$\mu = \sqrt{n(n+2)} \quad \mu_B = \sqrt{3(5)} \quad \mu_B = 3.87 \mu_B$$

10. The atomic number of Ni is 28. In both compounds  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ , Ni is present as  $\text{Ni}^{2+}$ . The outer electronic configuration of  $\text{Ni}^{2+}$  is



$\text{Ni}^{2+}$  in  $[\text{NiCl}_4]^{2-}$  is present as

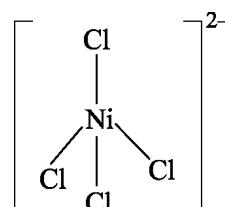


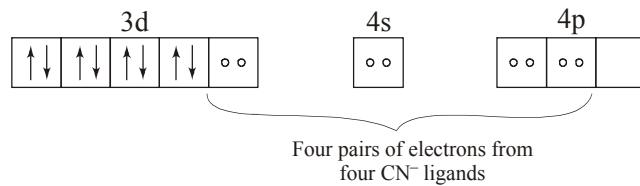
The  $\text{Cl}^-$  ligand is weak and it is unable to force the nickel electrons to pair up. The hybridisation present in  $[\text{NiCl}_4]^{2-}$  is  $sp^3$  and the structure is *tetrahedron*. The presence of two unpaired electrons makes the compound paramagnetic. Its magnetic moment is

$$\mu = \sqrt{n(n+2)} \quad \mu_B = \sqrt{2(2+2)} \quad \mu_B = 2\sqrt{2} \quad \mu_B$$

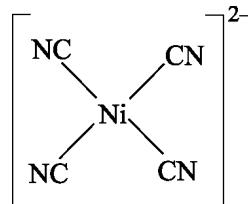
where  $\mu_B$  is Bohr magneton.

$\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$  is present as

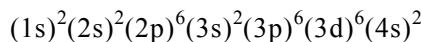




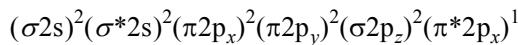
The  $\text{CN}^-$  ligand is strong and it is able to force the nickel electrons to pair up. The hybridisation present in  $[\text{Ni}(\text{CN})_4]^{2-}$  is  $\text{dsp}^2$  and the structure is square planar. There is no unpaired electrons. The compound is diamagnetic with zero magnetic moment.



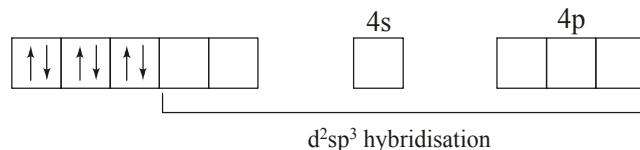
11. From the expression  $\mu_m = \sqrt{n(n+2)} \mu_B$ , we get  $n = 3$  for  $\mu_m = 3.9 \mu_B$ , i.e. the complex ion contains 3 unpaired electrons. The electronic configuration of Fe (atomic number = 26) is



The electronic configuration of NO (which carries 11 valence electrons) is



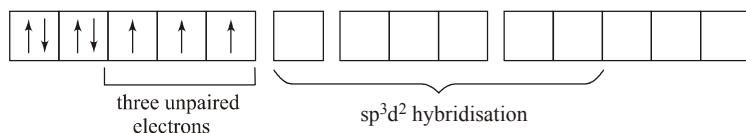
- (i) If 2+ charge of the complex may be formed by removing  $2e^-$  from Fe atom. The  $\text{Fe}^{2+}$  ion formed will have configuration  $3d^6$  with 4 unpaired electrons. If we propose  $\text{d}^2\text{sp}^3$  hybridisation in  $\text{Fe}^{2+}$  ion, then we will have



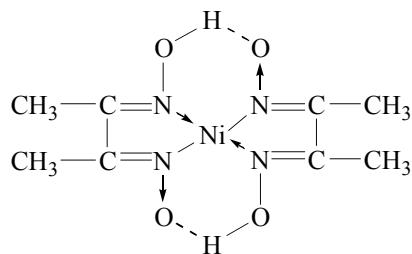
The complex will have only one unpaired electrons due to NO species. Hence, the above scheme of structure is excluded in the complex  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ .

- (ii) If we propose  $\text{sp}^3\text{d}^2$  hybridisation, then the complex ion will have 5 unpaired electrons (four from  $\text{Fe}^{2+}$  ion and one from NO). Hence, this scheme of structure is also excluded.
- (iii) If 2+ charge is generated by removing the unpaired electron of NO to give  $\text{NO}^+$  and one electron from Fe to yield  $\text{Fe}^+$  (electronic configuration  $3d^64s^1$ ), then there will also be 5 unpaired electrons. However, if  $(4s)^1$  electron in  $\text{Fe}^+$  is moved to 3d orbitals to give  $(3d)^7$ , then the complex will have three unpaired electrons.

Since the given complex also have 3 unpaired electrons, the state of hybridisation in the complex ion may be  $\text{sp}^3\text{d}^2$ . Hence, the actual structure of Fe in the complex ion is



12. (a) The structure of the complex is



- (b) The colour of the complex is rosy red.  
 (c) The oxidation state of the central metal ion is (II) in the complex.  
 (d) The state of hybridisation of Ni is  $d\sigma^2$ :

	3d	4s	4p
Ni atom	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$	$\uparrow\downarrow$	[ ] [ ] [ ]
$\text{Ni}^{2+}$ ion	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$	[ ]	[ ] [ ] [ ]
$\text{Ni}^{2+}$ ion in the complex	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \downarrow$	[ ]	[ ] [ ] [ ]

$d\sigma^2$  hybridisation

- (e) The complex is diamagnetic as there is no unpaired electrons in the central metal ion.

## HINTS AND SOLUTIONS

### Straight Objective Type

2. Electronic configuration of  $\text{Ni}^{2+}$ :

4. Electronic configurations are

$_{25}\text{Mn}^{2+}$

$_{29}\text{Cu}^{2+}$

$_{26}\text{Fe}^{2+}$

$_{28}\text{Ni}^{2+}$

Minimum upaired electrons is present in  $\text{Cu}^{2+}$ , hence, it has the lowest paramagnetism.

5. The configurations of Ni in the given complexes are as follows.

$[\text{Ni}(\text{CN})_4]^{2-}$    
 dsp<sup>2</sup> hybridisation

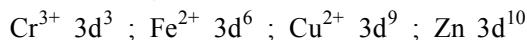
$[\text{NiCl}_4]^{2-}$    
 sp<sup>3</sup> hybridisation

$\text{Ni}(\text{CO})_4$    
 sp<sup>3</sup> hybridisation

$[\text{Ni}(\text{CN})_4]^{2-}$  and  $\text{Ni}(\text{CO})_4$  have no unpaired electrons, hence, are diamagnetic.

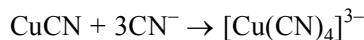
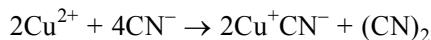
$[\text{NiCl}_4]^{2-}$  has two unpaired electrons, hence, is paramagnetic.

6. The electronic configurations of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  in the given complexes are



$\text{Fe}^{2+}$  contains highest number of unpaired electrons.

7. Adding  $\text{KCN}$  to  $\text{CuSO}_4$  solution first causes reduction and precipitation of cuprous cyanide. This reacts with excess  $\text{CN}^-$  forming a soluble complex  $[\text{Cu}(\text{CN})_4]^{3-}$ .



9. The magnetic moment ( $\mu_m$ ) of a species is related to its number of unpaired electrons ( $n$ ) by the expression

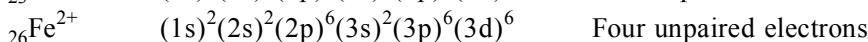
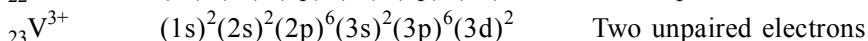
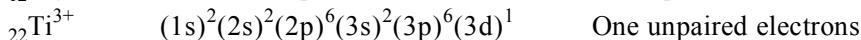
$$\mu_m = \sqrt{n(n+2)} \ \mu_B$$

where  $\mu_B$  is known as Bohr magneton. The number of unpaired electrons in the given pairs are as follows.



The given combinations differ in the number of unpaired electrons. Hence, these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion.

12. The electronic configuration of the given ions are as follows.



13. For a compound to be paramagnetic and coloured it must have unpaired electron(s) in 3d orbital(s) of the central atom.

Compound	Central atom	Electronic configuration
$\text{K}_2\text{Cr}_2\text{O}_7$	${}_{24}\text{Cr(VI)}$	$(3\text{s})^2(3\text{p})^6$
$(\text{NH}_4)_2(\text{TlCl}_6)$	${}_{22}\text{Tl(IV)}$	$(3\text{s})^2(3\text{p})^6$
$\text{VOSO}_4$	${}_{23}\text{V(IV)}$	$(3\text{s})^2(3\text{p})^6(3\text{d})^1$
$\text{K}_3[\text{Cu}(\text{CN})_4]$	${}_{29}\text{Cu(I)}$	$(3\text{s})^2(3\text{p})^6(3\text{d})^{10}$

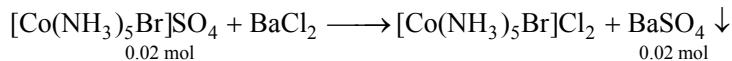
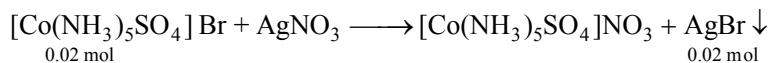
- 14.

Central atom	Oxidation state	Number of electrons	Configuration
Mn	+7	$25 - 7 = 18$	$(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^3(3\text{p})^6$
Co	+3	$27 - 3 = 24$	$1(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^2(3\text{p})^6(3\text{d})^6$
Fe	+3	$26 - 3 = 23$	$(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^2(3\text{p})^6(3\text{d})^5$
Cr	+3	$24 - 3 = 21$	$(1\text{s})^2(2\text{s})^2(2\text{p})^6(3\text{s})^2(3\text{p})^6(3\text{d})^3$

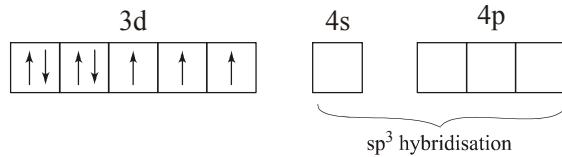
15. Eu and Lu are the members of lanthanide series. Due to the lanthanide contraction, the sizes of Eu, Lu and La will follow the order  $\text{Lu} < \text{Eu} < \text{La}$ . The element Y belongs to the fifth period while Lu belongs to the sixth period, we expect their sizes will follow the order  $\text{Y} < \text{Lu} < \text{Eu} < \text{La}$ .

16. The fusion reaction is  $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$

17. We will have



18. The size of given metals decreases whereas ionization energy increases from Ti, V, Cr to Fe. Hence, the metallic character of the metals decreases so is their basicity of oxides from Ti to V to Cr to Fe.
19. Ni in  $\text{Ni}(\text{CO})_4$  involves  $\text{sp}^3$  hybridisation while in the rest of the three species  $\text{dsp}^2$  hybridisation is involved. Hence,  $\text{Ni}(\text{CO})_4$  has tetrahedral structure while rest of the three species have square planar structure.
20. Cobalt in  $[\text{Co}(\text{SCN})_4]^{2-}$  is present as  $\text{Co}^{2+}$ . It involves the following hybridisation scheme in the complex.



Three unpaired electrons produce magnetic moment of

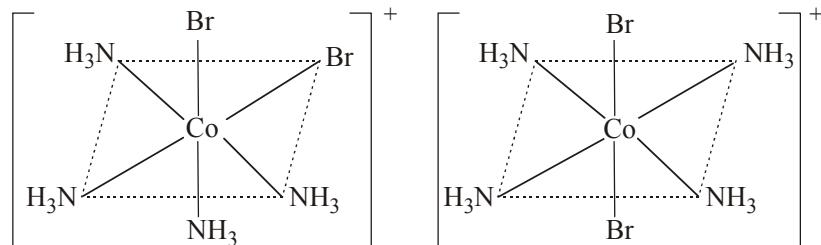
$$\mu = \sqrt{n(n+2)} \quad \mu_B = \sqrt{3(5)} \quad \mu_B = \sqrt{15} \quad \mu_B$$

21. The colour of a transition metal ion may be related to its number of unpaired d electrons. We have

Metal ion	Number of unpaired d electrons	Expected colour
$\text{V}^{4+}, \text{Cu}^{2+}$	1	Blue
$\text{Fe}^{2+}$	4	Green
$\text{Mn}^{2+}$	5	Pale pink

Hence,  $\text{CuCl}_2$  and  $\text{VOCl}_2$  are expected to have same colour.

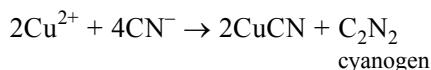
22. Geometrical isomers are



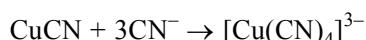
Ionization isomers are



23. The addition of KCN to a cupric salt solution causes the precipitation of cuprous cyanide.



The precipitate of cuprous cyanide dissolves in excess of potassium cyanide solution forming the complex ion

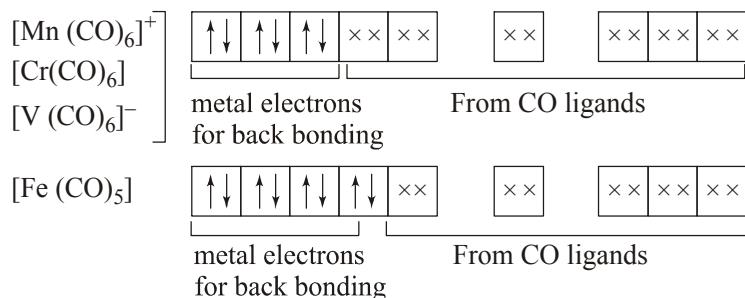


24. The standard instability constant refers to the reaction



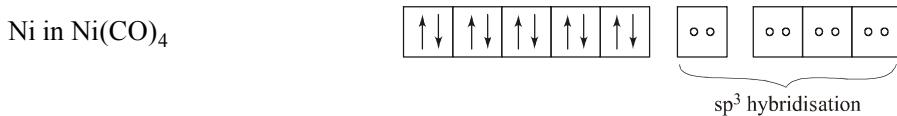
$$\begin{aligned} K_{\text{ins}}^{\circ} &= \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} \equiv \frac{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2^+]} \frac{[\text{Ag}^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)^+]} \\ &= K_1^{\circ} K_2^{\circ} = (1.4 \times 10^{-4})(4.3 \times 10^{-4}) \\ &= 6.02 \times 10^{-8} \end{aligned}$$

25. Bond length of CO in  $\text{Fe}(\text{CO})_5$  will be slightly larger than 112.8 pm due to decrease in bond order of CO because of  $d\pi-p\pi$  back bonding from metal to the ligand.
26. Metallic carbonyls involve both  $\sigma$  and  $\pi$  bonding.  $\sigma$ -Bond involves donation of the lone pair on carbon of the CO ligand into a hybridised vacant metal orbital.  $\pi$ -Bond involves back donation of metal d electrons into vacant antibonding  $\pi^*2p$  orbital on CO. The larger the electrons involved in back bonding, lesser the bond order of CO ligand. The following schemes of bonding exist in the given carbonyls.

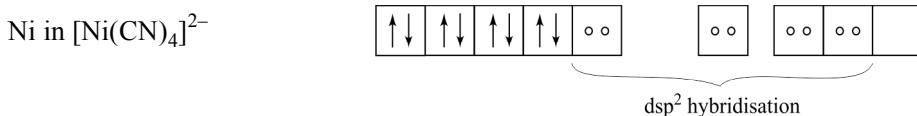


Since Fe complex involves largest metal electrons for back bonding, the CO in  $\text{Fe}(\text{CO})_5$  will have lowest bond order.

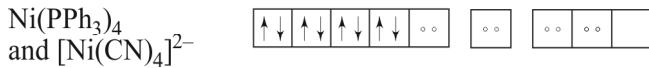
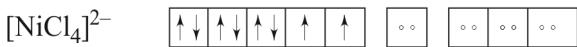
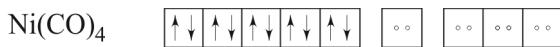
27. For  $[\text{Ni}(\text{CO})_4]$ , we have



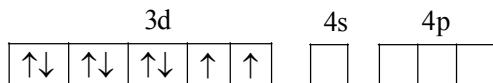
For  $[\text{Ni}(\text{CN})_4]^{2-}$ , we have



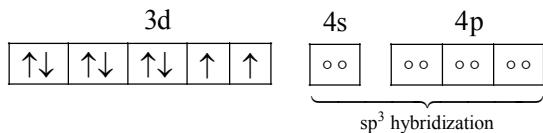
28. The positive ion is named first followed by the negative ion. The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the name. The complex negative ion ends in ‘-ate’. Thus, the IUPAC name of the given compound is tetraamminenickel(II)-tetrachloronickelate(II).
29. Only in  $\text{CuF}_2$ , copper exists as  $\text{Cu}^{2+}$  with one unpaired electron. Its colour is blue. In other choices, copper exists as  $\text{Cu}^+$  with no unpaired electrons and thus are colourless.
30. The electronic configuration of Cr is  $[\text{Ar}] (3d)^5 (4s)^1$ . In order to accommodate six ligands and the fact that CO is strong ligand, the electrons in Cr are paired to provide two unfilled 3d orbitals which are involved in  $d^2\text{sp}^3$  hybridisation. Thus, there are no unpaired electrons in  $\text{Cr}(\text{CO})_6$ . Hence, its spin magnetic moment will be zero.
31. The ionization isomers involve the interchange of ions inside and outside the coordination sphere.
32. The structure given by the choice (c) represents ethylenediaminetetraacetic acid.
33. We have  $\sqrt{n(n+2)} = 2.82 \Rightarrow n = 2$  (two unpaired electrons) The nickel configuration in the given compounds are as follows.



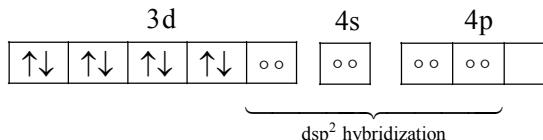
34. The electronic configuration of  ${}_{28}\text{Ni}^{2+}$  is  $(1\text{s})^2 (2\text{s})^2 (2\text{p})^6 (3\text{s})^2 (3\text{p})^6 (3\text{d})^8$ . Its valence electronic configuration is



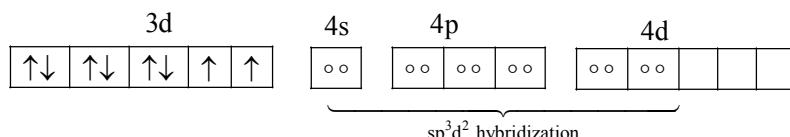
$\text{Cl}^-$  ligand is a weak ligand. It has no effect in pairing 3d electrons. Hence, 4s and 4p<sup>3</sup> orbitals with the hybridization sp<sup>3</sup> are used in forming the complex  $[\text{NiCl}_4]^{2-}$ . Its geometry is tetrahedral.



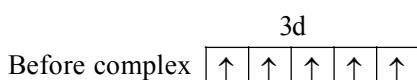
$\text{CN}^-$  ligand is a strong ligand. Its effect is to pair 3d electrons. Hence, 3d, 4s and 4p<sup>2</sup> orbitals with the hybridization dsp<sup>2</sup> are used in forming the complex  $[\text{Ni}(\text{CN})_4]^{2-}$ . Its geometry is square planar.



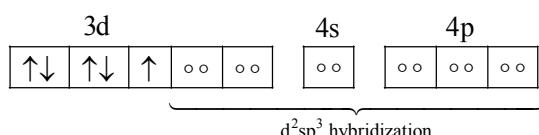
With  $\text{H}_2\text{O}$ ,  $\text{Ni}^{2+}$  forms  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  complex.  $\text{H}_2\text{O}$  also has no effect on 3d electrons. Hence 4s, 4p<sup>3</sup> and 4d<sup>2</sup> orbitals with sp<sup>3</sup>d<sup>2</sup> hybridization are used in forming the complex. Its geometry is octahedral.



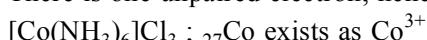
35. The electronic configurations of metallic ions in the given complexes are as follows.

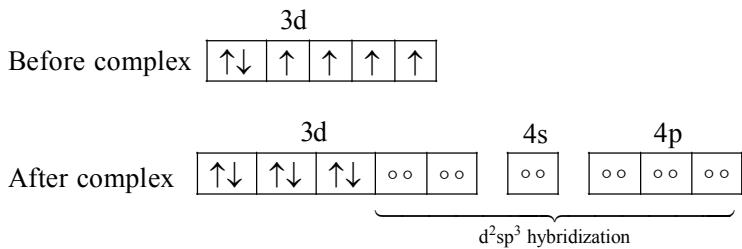


After complex



There is one unpaired electron, hence it is paramagnetic.

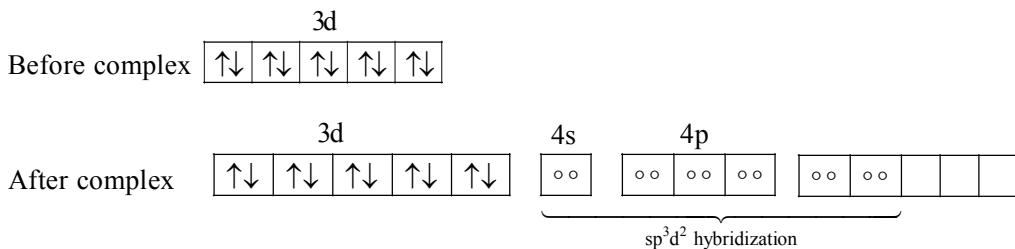




There is no unpaired electron, hence it is diamagnetic.

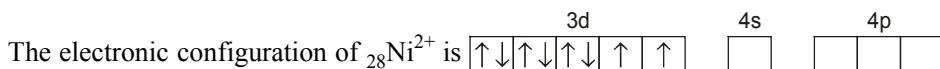
**(Note:** From the above two cases, it is obvious that the choices (a) and (b) are incorrect whereas the choices (c) and (d) contain one correct choice. In the latter choices, the complexes N and P are different, so these need to be examined.)

The complex P is  $[Zn(H_2O)_6](NO_3)_2$  in which  $^{30}Zn$  exists as  $Zn^{2+}$ .



There is no unpaired electron and hence it is diamagnetic.

36. While naming a complex, the ligands are quoted in alphabetical order, regardless of their charges (followed by the metal). The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the metal name without any intervening blank.  $NH_3$  is named as ammine and not as amine. Hence, the IUPAC name of the given compound is Diamminetetraaquacobalt(III) chloride.
37. An aqueous solution of  $CuSO_4$  is blue. The colour of light absorbed by this solution is that of complimentary colour which is orange-red.
38. In the paramagnetic state, the complex will have unpaired 3d electrons in  $Ni^{2+}$  ion, whereas no such electrons (i.e. all the 3d electrons will be paired) are present in the diamagnetic state.



If the two unpaired electrons remain present in the ion, it will undergo  $sp^3$  hybridization to accommodate ligands and the geometry of the complex ion will be tetrahedral.

If the two unpaired electrons are coupled, the ion will be diamagnetic and it can undergo  $dsp^2$  hybridization to accommodate ligands leading to the square planar geometry to the complex ion.

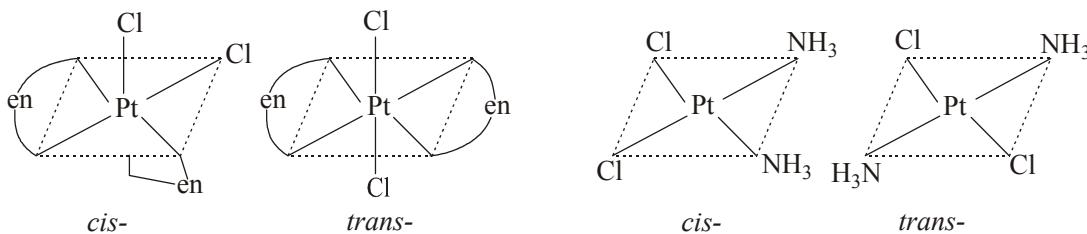
39. The electronic configurations of  $^{23}V^{2+}$ ,  $^{26}Fe^{2+}$  and  $^{26}Fe^{3+}$  are  $(3d)^3$ ,  $(3d)^6$  and  $(3d)^5$ , respectively. Since  $F^-$  and  $H_2O$  are weak ligands, there occurs no rearrangement of d electrons in the formation of the given complex ions. Thus, the number of unpaired electrons of  $V^{2+}$ ,  $Fe^{2+}$  and  $Fe^{3+}$  ions in the complex ions are 3, 4 and 5, respectively. The expression of magnetic moment is  $\sqrt{n(n+2)} \mu_B$ , where  $n$  is the number of unpaired electrons and  $\mu_B$  is the Bohr magneton. Hence, the magnetic moment of the given complexes follows the order Q < R < P.

### Multiple Correct-Choice Type

5. The blue precipitate of  $Fe^{2+}$  ions with potassium ferricyanide is due to the formation of Turnbull's blue,  $KFe^{II}[Fe^{III}(CN)_6]$ .

The red colouration of  $\text{Fe}^{3+}$  ions with potassium thiocyanate is due to the formation of  $[\text{Fe}(\text{CNS})]^{2+}$

7. The compounds c and d show geometrical isomerism as depicted in the following structures.



8. The complex  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  in the choice (a) will not show either structural or stereoisomerism whereas  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  exhibits geometrical (*cis-trans*) isomerism.

In the choice (b), the complex  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is octahedral whereas  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$  is a square planar. Both these complexes will exhibit geometrical (*cis-trans*) isomerism.

In the choice (c),  $[\text{CoBr}_2\text{Cl}_2]^{2-}$  is tetrahedral while  $[\text{PtBr}_2\text{Cl}_2]^{2-}$  is square planar. There is no isomerism of the same type in these complexes.

In the choice (d), both are square planar and can exhibit ionization isomerism.

9. The electronic configurations of Cr and Mn are  $(3d)^5(4s)^1$  and  $(3d)^5(4s)^2$ , respectively, and those of  $\text{Cr}^{2+}$  and  $\text{Mn}^{3+}$  are  $(3d)^4$  and  $(3d)^4$ , respectively (Choice c).

$\text{Cr}^{2+}$  acts as a reducing agent and its electronic configuration changes from  $(3d)^4$  to  $(3d)^3$ .

$\text{Mn}^{3+}$  is an oxidizing agent and its electronic configuration changes from  $(3d)^4$  to  $(3d)^5$  – a more stable electronic configuration.

Thus, the choices (a), (b) and (c) are correct.

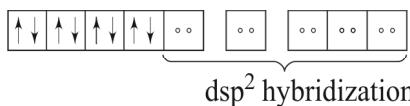
## Fill-in-the-Blanks Type

### Integer Answer Type

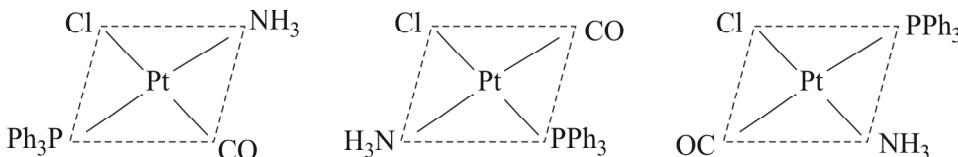
1. The correct formula of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

2. The electronic configuration of  ${}_{45}\text{Rh}$  is  $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (3d)^{10} (4s)^2 (4p)^6 (4d)^8 (5s)^1$

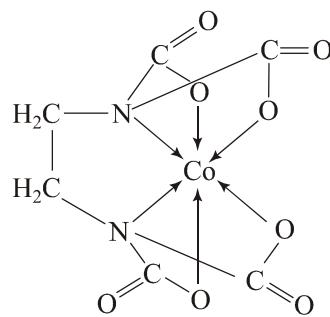
In the complex, Rh exists as  $\text{Rh}^+$ . Thus, its configuration is  $\boxed{\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \quad \uparrow \quad \uparrow}$ . In the complex, it exists as



Thus, the complex is square planar. Its isomers are

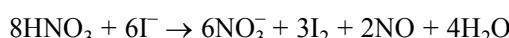
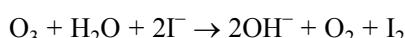
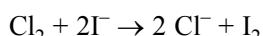
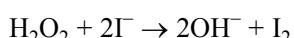
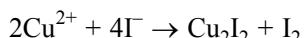
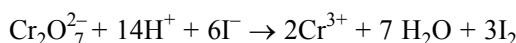


3. Ethylenediaminetetraacetate ion is a hexadentate. It is linked to the central Co(III) ion via two nitrogen atoms of amines and four oxygen atoms of acetate ions. Hence, there will be eight ( $= 2 \times 4$ ) N – Co – O bond angles. The structure for the complex ion is



Therefore, there are **8 N – Co – O bonds.**

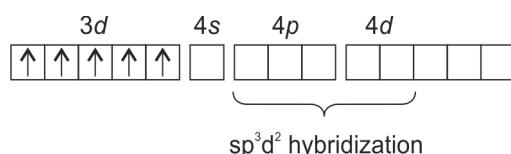
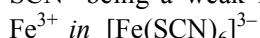
- 4.** The reagents  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CuSO}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_3$ ,  $\text{FeCl}_3$  and  $\text{HNO}_3$  can oxidize  $\text{I}^-$  to  $\text{I}_2$ . The reactions are:



The total number of reagents are **seven**.

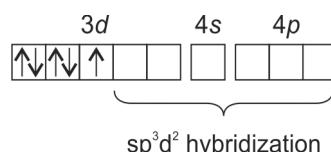
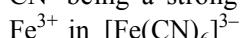
Alkaline  $\text{KMnO}_4$  (undergoing reaction  $\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$ ) cannot oxidise  $\text{I}^-$  to  $\text{I}_2$  because  $E^\circ(\text{MnO}_4^-, \text{MnO}_4^{2-}, \text{OH}^- | \text{Pt}) < E^\circ(\text{I}^-, \text{I}_2 | \text{Pt})$ .

- 5.**  $\text{SCN}^-$  being a weak ligand, it will form high-spin complex with  $\text{Fe}^{3+}$  ( $3d^5$ ) ion.



Its spin only magnetic moment will be  $\mu = \sqrt{n(n+2)} \mu_B = \sqrt{5(7)} \mu_B = 5.92 \mu_B$

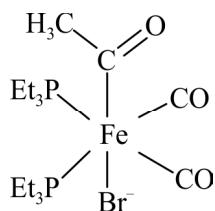
$\text{CN}^-$  being a strong ligand, it will form low-spin complex with  $\text{Fe}^{3+}$  ion.



Its spin-only magnetic moment will be  $\mu = \sqrt{n(n+2)} \mu_B = \sqrt{1(3)} \mu_B = 1.73 \mu_B$

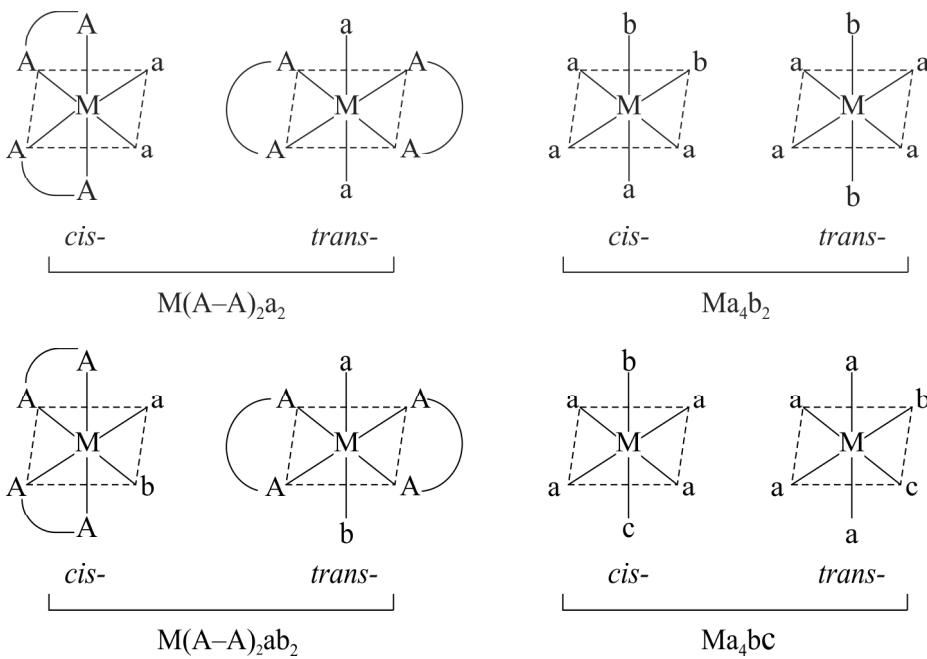
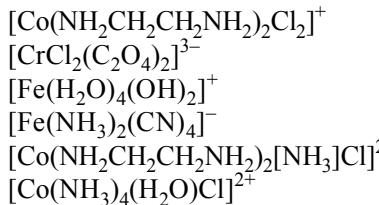
The difference between the two magnetic moment is  $\Delta\mu = (5.92 - 1.73) \mu_B = 4.19 \mu_B \approx 4 \mu_B$  (nearest integer)

6. The given complex is



The number of Fe—C bonds is **three**.

7. Complex



The number of complex ions is **6**.

### True/False type

1. The correct configuration is  $(3d)^5 (4s)^1$  as half-filled d orbitals is more stable configuration.
2. The electronic configurations of  $\text{Zn}^{2+}$  is  $(1s)^2 (2s)^6 (2p)^6 (3s)^2 (3p)^6 (3d)^{10}$   
It is diamagnetic as no unpaired electrons are present.
3. Potassium ferrocyanide is diamagnetic (no unpaired electron) while potassium ferricyanide is paramagnetic (one unpaired electron)
4. It is due to d-d transition in the metallic ion of the compound.

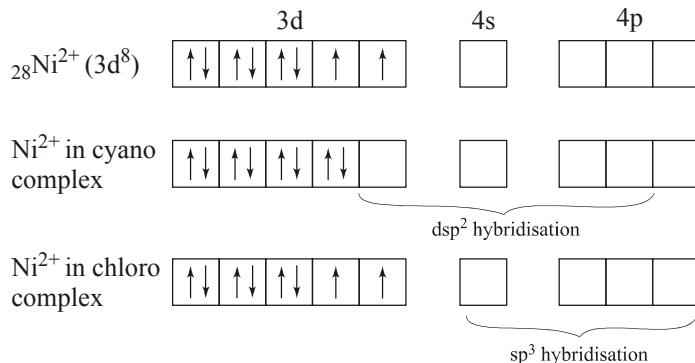
## Reasoning Type

2. Iron in  $[\text{Fe}(\text{H}_2\text{O})_5 \text{NO}]^+$  should exist in +II oxidation state with electronic configuration  $(3d)^6$ . In the complex,  $\text{sp}^3\text{d}^2$  hybridisation exists. However, the unpaired electron of NO is shifted to  $\text{Fe}^{2+}$  changing it to  $\text{Fe}^+$  and also changes NO to  $\text{NO}^+$ . The electronic configuration of iron in the complex becomes  $(3d)^7$  with three unpaired electrons.

## Linked-Comprehension Type

### Passage-1

- The complexes are  $\text{K}_2[\text{Ni}(\text{CN})_4]$  and  $\text{K}_2[\text{Ni}(\text{Cl})_4]$ . Hence, their names are potassium tetracyanonickelate(II) and potassium tetrachloronickelate(II)
- and
- The configurations of free  $\text{Ni}^{2+}$  ions and those in the complexes are as follows.



### Passage-2

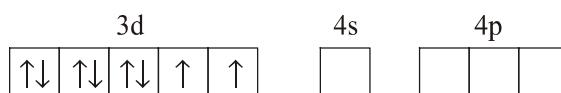
- The electronic configurations of the given ions in the choices of Q.1 are:



From these choices, the metal ion M1 cannot be  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  as their d orbitals are completely filled and thus cannot form square planar complexes which require  $\text{dsp}^2$  hybridization of orbitals.

The ion  $\text{Co}^{2+}$  generally forms 6-coordinated complexes.

The ion  $\text{Ni}^{2+}$  does form 4-coordinated complexes. Its electronic configuration is



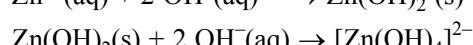
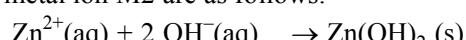
It can form tetrahedral complex (involving  $\text{sp}^3$  hybridization) with weak ligand such as  $\text{Cl}^-$  (from HCl)

It can form square planar complex (involving  $\text{dsp}^2$  hybridization) with strong ligand such  $\text{CN}^-$  (from HCN). The latter is able to pair 3d electrons making a vacant 3d orbital for  $\text{dsp}^2$  hybridization.

Hence, the choice (b) is correct.

- The reaction of M2 with S indicates the amphoteric nature of metal ion.

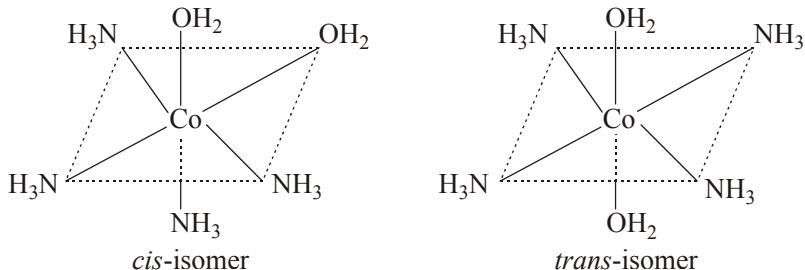
This ion may be  $\text{Zn}^{2+}$  ions as it form only tetrahedral complexes. The reagent S seems to be KOH. Its reaction with metal ion M2 are as follows.



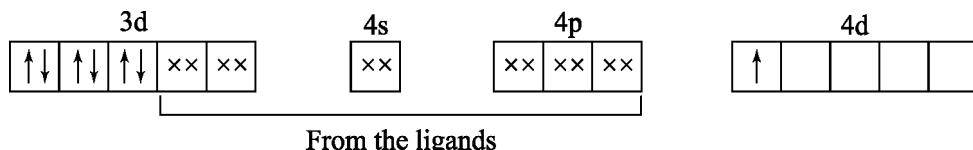
Hence, the choice (d) is correct.

**Matrix Match Type**

1. (a)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$  can show geometrical isomers (choices p)

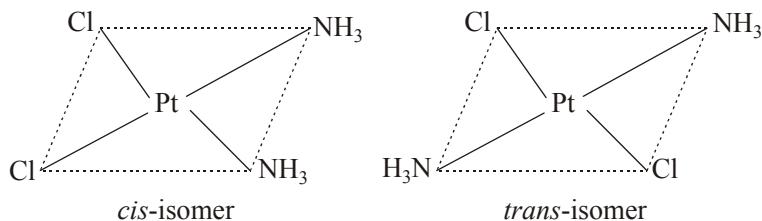


It is also paramagnetic (choice q) because the metal ion is Co(II) with the following electronic configuration.



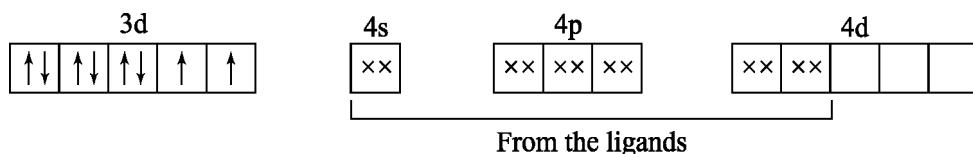
In the complex, Co(II) contains one unpaired electron. (choice s).

- (b)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  involves square planar geometry. It can exhibit geometrical isomers (choice p).



Pt in this complex has +2 oxidation state (choice s). Its electronic configuration in the complex is  $(5\text{d})^3$  with no unpaired electron and thus the complex is diamagnetic (choice r).

- (c)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$  has metal in +2 oxidation state (choice s) and thus also will have one unpaired electron which makes the complex paramagnetic (choice q).  
 (d)  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  has metal in +2 oxidation state (choice s). Its configuration in the complex is



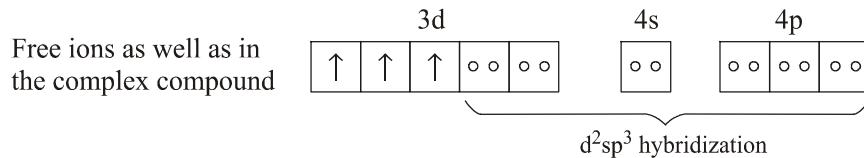
It has two unpaired electrons and is thus paramagnetic (choice q).

2. In the choices (a) to (d) of the given code, none of the choices (1) to (4) of List II is repeated for the compound P. Therefore, it is sufficient to pick up the correct choice from the List II for the compound P in the List I. Rest of matchings follow automatically. (However, these may be checked for the correctness.)

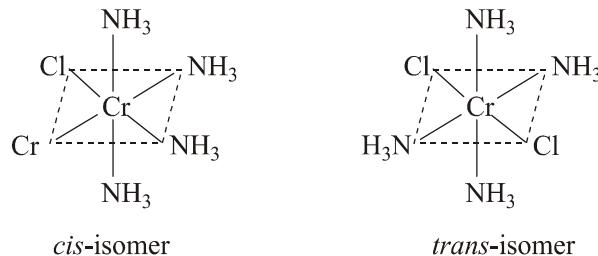
The coordination compound P is  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .

The chromium ion in the complex is  $^{24}\text{Cr}^{3+}$ .

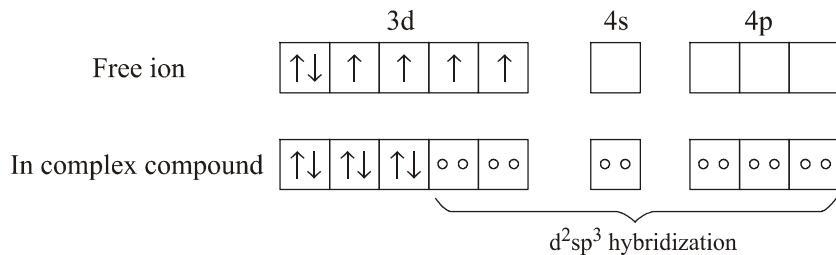
Its electronic configuration is  $3\text{d}^3$ .



$Cr^{3+}$  involves  $d^2sp^3$  hybridization to give six equivalent orbitals for the accommodation of ligands. Since  $Cr^{3+}$  involves 3 unpaired electrons, the complex will be paramagnetic. The complex  $[Cr(NH_3)_4Cl_2]^+$  will exhibit *cis-trans* isomerisation as depicted in the following.



Thus, the item P of List-I matches with item 3 of List-II. This match is given by the choice (b) of the given code. Rest of matching follows automatically. For example, the complex  $[Co(NH_3)_4(NO_3)_2]NO_3$  involves the following electronic configuration of  $_{24}Co^{3+}$  ( $3d^6$ )



The complex will be diamagnetic and also exhibits *cis-trans* isomerism. Thus, the item S in List-I matches with item 2 in the List-II. This is exactly the same in the **choice (b)** in the given code.



# **ORES/MINERALS AND EXTRACTIVE METALLURGY**

**17**

## **Straight Objective Type**

1. Copper can be extracted from
  - (a) Kupfernickel
  - (b) Dolomite
  - (c) Cinnabar
  - (d) Galena
  - (e) Malachite(1978)
2. In the manufacture of iron from haematite, the function of lime stone is as
  - (a) a reducing agent
  - (b) slag
  - (c) flux
  - (d) gangue
  - (e) None of these(1978)
3. Calcium is obtained by
  - (a) Electrolysis of molten  $\text{CaCl}_2$
  - (b) Electrolysis of aqueous solution of  $\text{CaCl}_2$
  - (c) Reduction of  $\text{CaCl}_2$  with carbon
  - (d) Roasting of lime stone(1980)
4. In the metallurgy of iron, when limestone is added to the blast furnace, the calcium ions ends up in
  - (a) slag
  - (b) gangue
  - (c) metallic Ca
  - (d) calcium carbonate(1982)
5. The major role of fluorspar ( $\text{CaF}_2$ ) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite ( $\text{Na}_3\text{AlF}_6$ ) is
  - (a) that of a catalyst
  - (b) to make the fused mixture very conducting
  - (c) to lower the temperature of the melt
  - (d) to decrease the rate of oxidation of carbon at the anode(1993)
6. In the commercial electrochemical process for aluminium extraction the electrolyte used is
  - (a)  $\text{Al(OH)}_3$  in  $\text{NaOH}$  solution
  - (b) an aqueous solution of  $\text{Al}_2(\text{SO}_4)_3$
  - (c) a molten mixture of  $\text{AlO(OH)}$  and  $\text{Al(OH)}_3$
  - (d) a molten mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3\text{AlF}_6$(1999)
7. The chemical processes in the production of steel from haematite ore involve
  - (a) reduction
  - (b) oxidation
  - (c) reduction followed by oxidation
  - (d) oxidation followed by reduction(2000)
8. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out
  - (a) in the presence of  $\text{NaCl}$
  - (b) in the presence of fluorite
  - (c) in the presence of cryolite which forms a melt with lower melting temperature
  - (d) in the presence of cryolite which forms a melt with higher melting point(2000)

9. In the aluminothermite process, aluminium acts as
  - (a) an oxidizing agent
  - (b) a flux
  - (c) a reducing agent
  - (d) a solder(1983)
10. Among the following statements, the incorrect one is
  - (a) calamine and siderite are carbonates;
  - (b) argentite and cuprite are oxides;
  - (c) zinc blende and pyrites are sulphides;
  - (d) malachite and azurite are ores of copper.(1997)
11. In the commercial electrochemical process for aluminium extraction the electrolyte used is
  - (a)  $\text{Al}(\text{OH})_3$  in  $\text{NaOH}$  solution
  - (b) an aqueous solution of  $\text{Al}_2(\text{SO}_4)_3$
  - (c) a molten mixture of  $\text{Al}_2\text{O}_3$  and  $\text{Na}_3\text{AlF}_6$
  - (d) a molten mixture of  $\text{AlO}(\text{OH})$  and  $\text{Al}(\text{OH})_3$(1999)
12. The chemical composition of 'slag' formed during the smelting process in the extraction of copper is
  - (a)  $\text{Cu}_2\text{O} + \text{FeS}$
  - (b)  $\text{FeSiO}_3$
  - (c)  $\text{CuFeS}_2$
  - (d)  $\text{Cu}_2\text{S} + \text{FeO}$(2001)
13. Which of the following processes is used in the extractive metallurgy of magnesium?
  - (a) fused salt electrolysis
  - (b) self reduction
  - (c) aqueous solution electrolysis
  - (d) thermite reduction(2002)
14. In the extraction of silver, the reactions involved are
 
$$\text{Roasted silver ore} + \text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} \text{X} + \text{OH}^-;$$

$$\text{X} + \text{Zn} \longrightarrow \text{Y} + \text{Ag}$$

The species X and Y, respectively, are

  - (a)  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Zn}(\text{CN})_4]^{2-}$
  - (b)  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Zn}(\text{CN})_6]^{2-}$
  - (c)  $[\text{Ag}(\text{CN})_4]^{3-}$ ,  $[\text{Zn}(\text{CN})_4]^{2-}$
  - (d)  $[\text{Ag}(\text{CN})_4]^-$ ,  $[\text{Zn}(\text{CN})_4]^{2-}$(2003)
15. Lead and tin are, respectively, extracted from their chief ore by
  - (a) carbon reduction and self reduction
  - (b) carbon reduction and electrolytic reduction
  - (c) self reduction and carbon reduction
  - (d) electrolytic reduction and carbon reduction(2004)
16. Which of the following ores contains both iron and copper?
  - (a) Malachite
  - (b) Azurite
  - (c) Dolomite
  - (d) Chalcopyrite(2005)
17. Extraction of zinc from zinc blende is achieved by
  - (a) electrolytic reduction
  - (b) roasting followed by reduction with carbon
  - (c) roasting followed by reduction with another metal
  - (d) roasting followed by self-reduction(2007)
18. Native silver metal forms a water soluble complex with a dilute aqueous solution of  $\text{NaCN}$  in the presence of
  - (a) nitrogen
  - (b) oxygen
  - (c) carbon dioxide
  - (d) argon(2008)
19. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are
  - (a)  $\text{O}_2$  and  $\text{CO}$ , respectively
  - (b)  $\text{O}_2$  and  $\text{Zn}$  dust, respectively
  - (c)  $\text{HNO}_3$  and  $\text{Zn}$ , respectively
  - (d)  $\text{HNO}_3$  and  $\text{CO}$ , respectively(2012)
20. Sulphides ores are common for the metals
  - (a) Ag, Cu and Pb
  - (b) Ag, Cu and Sn
  - (c) Ag, Mg and Pb
  - (d) Al, Cu and Pb(2013)

## Multiple Correct-Choice Type

1. In the electrolysis of alumina, cryolite is added to
 

(a) lower the melting point of alumina	(b) increase the electrical conductivity
(c) minimise the anode effect	(d) remove impurities from alumina

(1986)
2. Of the following, the metals that cannot be obtained by electrolysis of the aqueous solution of their salts are
 

(a) Ag	(b) Mg	(c) Cu	(d) Al
--------	--------	--------	--------

(1990)
3. Extraction of metal from the ore cassiterite involves
 

(a) carbon reduction of an oxide ore	(b) self reduction of a sulphide ore
(c) removal of copper impurity	(d) removal of iron impurity

(2011)
4. The carbon-based reduction method is **NOT** used for the extraction of
 

(a) tin from $\text{SnO}_2$	(b) iron from $\text{Fe}_2\text{O}_3$
(c) aluminium from $\text{Al}_2\text{O}_3$	(d) magnesium from $\text{MgCO}_3 \cdot \text{CaCO}_3$

(2013)
5. Upon heating with  $\text{Cu}_2\text{S}$ , the reagent(s) that give copper metal is/are
 

(a) $\text{CuFeS}_2$	(b) $\text{CuO}$	(c) $\text{Cu}_2\text{O}$	(d) $\text{CuSO}_4$
----------------------	------------------	---------------------------	---------------------

(2014)
6. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is(are)
 

(a) Impure Cu strip is used as cathode	(b) Acidified aqueous $\text{CuSO}_4$ is used as electrolyte
(c) Pure Cu deposits at cathode	(d) Impurities settle as anode-mud

(2015)

## Fill-in-the-Blanks Type

1. In the basic Bessemer process for the manufacture of steel, the lining of the converter is made of \_\_\_\_\_. The slag formed consists of \_\_\_\_\_. (1980)
2. In the thermit process \_\_\_\_\_ is used as a reducing agent. (1980)
3. Cassiterite is an ore of \_\_\_\_\_. (1980)
4.  $\text{AgCl}$  dissolves in excess  $\text{KCN}$  solution to give the complex compound \_\_\_\_\_. (1980)
5. In extractive metallurgy of zinc partial fusion of  $\text{ZnO}$  with coke is called \_\_\_\_\_ and reduction of the ore to the molten metal is called \_\_\_\_\_. (1988)

## Linked Comprehension Type

### Paragraph for Questions 1 to 3

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), cuprite ( $\text{Cu}_2\text{O}$ ), copper glance ( $\text{Cu}_2\text{S}$ ) and malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ). However, 80% of the world copper production comes from the ore chalcopyrite ( $\text{CuFeS}_2$ ). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction.

1. Partial roasting of chalcopyrite produces
 

(a) $\text{Cu}_2\text{S}$ and $\text{FeO}$	(b) $\text{Cu}_2\text{O}$ and $\text{FeO}$	(c) $\text{CuS}$ and $\text{Fe}_2\text{O}_3$	(d) $\text{Cu}_2\text{O}$ and $\text{Fe}_2\text{O}_3$
--	--	--	---
2. Iron is removed from chalcopyrite as
 

(a) $\text{FeO}$	(b) $\text{FeS}$	(c) $\text{Fe}_2\text{O}_3$	(d) $\text{FeSiO}_3$
------------------	------------------	-----------------------------	----------------------
3. In self-reduction, the reducing species is
 

(a) S	(b) $\text{O}^{2-}$	(c) $\text{S}^{2-}$	(d) $\text{SO}_2$
-------	---------------------	---------------------	-------------------

(2010)

## Matching Type

1. Match the following extraction process with the appropriate metals listed below.

- |             |                               |
|-------------|-------------------------------|
| (a) Silver  | (p) Fused-salt electrolysis   |
| (b) Calcium | (q) Carbon reduction          |
| (c) Zinc    | (r) Carbon monoxide reduction |
| (d) Iron    | (s) Amalgamation              |
| (e) Copper  | (t) Self reduction            |

(1979)

2. Write the matching pairs

- |                     |                        |
|---------------------|------------------------|
| (a) Bleaching agent | (p) Aluminium          |
| (b) Smelting salt   | (q) Carbon             |
| (c) Cryolite        | (r) Tin                |
| (d) Bell metal      | (s) Ammonium carbonate |
| (e) Fluorspar       | (t) Ammonium phosphate |
| (f) Fertilizer      | (u) Calcium            |
| (g) Anthracite      | (v) Chlorine           |

(1980)

3. (a) Welding  
 (b) Production of ammonia  
 (c) Ore purification  
 (d) Production of nitric acid
- |                      |
|----------------------|
| (p) Baeyer's process |
| (q) Thermit          |
| (r) Ostwald process  |
| (s) Cyanamide        |

(1981)

4. (a) Al  
 (b) Cu  
 (c) Mg  
 (d) Zn
- |                |
|----------------|
| (p) Calamine   |
| (q) Cryolite   |
| (r) Malachite  |
| (s) Carnallite |

(1983)

5. (a) Haber  
 (b) Graham  
 (c) Arrhenius  
 (d) Lewis
- |                        |
|------------------------|
| (p) Activation energy  |
| (q) Diffusion of gases |
| (r) Oclet rule         |
| (s) Ammonia synthesis  |

(1983)

6. (a) Spinel  
 (b) Felspar  
 (c) Cerussite  
 (d) Malachite  
 (e) Kissnerite
- |  |
|--|
| (p) $\text{MgAl}_2\text{O}_4$                    |
| (q) $\text{PbCO}_3$                              |
| (r) $\text{KAlSi}_2\text{O}_3$                   |
| (s) $\text{MgSO}_4 \cdot \text{H}_2\text{O}$     |
| (t) $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ |

(1985)

7. Match the entries on the left with those given on the right

- |   |                       |
|---|-----------------------|
| (a) Self reduction                              | (p) Copper extraction |
| (b) Carbon reduction                            | (q) Lead extraction   |
| (c) Reduction by heating its trihalide          | (r) Silver extraction |
| (d) Complex formation followed by precipitation | (s) Boron extraction  |

(2006)

## Matrix Match Type

1. Match the conversions in **Column I** with the type(s) of reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS

<b>Column I</b>	<b>Column II</b>	
(a) $\text{PbS} \rightarrow \text{PbO}$	(p) roasting	
(b) $\text{CaCO}_3 \rightarrow \text{CaO}$	(q) calcination	
(c) $\text{ZnS} \rightarrow \text{Zn}$	(r) carbon reduction	
(d) $\text{Cu}_2\text{S} \rightarrow \text{Cu}$	(s) self reduction	(2008)
<b>2.</b> Match the anionic species given in Column I that are present in the ore(s) given in Column II		
<b>Column I</b>	<b>Column II</b>	
(a) Carbonate	(p) Siderite	
(b) Sulphide	(q) Malachite	
(c) Hydroxide	(r) Bauxite	
(d) Oxide	(s) Calamine	
	(t) Argentite	(2015)

### Short Answer Type

- Distinguish between the following (limit your answer to two sentences).
  - Amalgam and alloy
  - Slag and flux
  - Smelting and roasting(1978)
- Two metals X and Y have the following characteristics.  
 X-Low melting point; forms only one chloride and occurs only as chloride. The oxide reacts with water to form hydroxide  
 Y-High melting point; forms chlorides; but occurs only as oxide. The oxide is stable  
 Briefly outline a method by which the elements X and Y can be obtained from their ores, in not more than two sentences each.
 (1978)
- Write the chemical equations involved in the extraction of lead from galena, by the self-reduction process.
 (1979)
- Give balanced equations:
  - Extraction of silver from its sulphide ore
  - Extraction of aluminium from bauxite by electrolysis.(1982)
- Fluorine cannot be prepared from fluoride by chemical oxidation. Explain.
 (1985)
- Answer the following questions briefly.
  - What is the actual reducing agent of haematite in blast furnace?
  - Give the equations for the recovery of lead from galena by air reduction.
  - Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride?
  - Zinc and not copper is used for the recovery of metallic silver from complex  $[\text{Ag}(\text{CN})_2]^-$ . Explain.
  - Why is chalcocite roasted and not calcinated during recovery of copper?(1987)
- Write balanced equations for the extraction of copper from copper pyrites by self-reduction.
 (1990)
- Give briefly the process of isolation of magnesium from sea water by the Dow process. Give equations for the steps involved.
 (1993)
- Write a balanced equation for the reaction of argentite with KCN and name the products in solution.
 (1996)
- When the ore haematite is burnt in air with coke around  $2000^\circ\text{C}$  along with lime, the process not only produces steel but also produces a silicate slag that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equations.
 (1998)
- Write the chemical reactions involved in the extraction of metallic silver from argenite.
 (2000)
- Write down the reactions involved in the extraction of Pb.
 (2003)

**ANSWERS****Straight Objective Type**

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (e)  | 2. (c)  | 3. (a)  | 4. (a)  | 5. (c)  | 6. (d)  | 7. (d)  |
| 8. (c)  | 9. (c)  | 10. (b) | 11. (c) | 12. (b) | 13. (a) | 14. (a) |
| 15. (c) | 16. (d) | 17. (b) | 18. (b) | 19. (b) | 20. (a) |         |

**Multiple Correct-Choice Type**

- |                  |             |             |             |                  |
|------------------|-------------|-------------|-------------|------------------|
| 1. (a), (b)      | 2. (b), (d) | 3. (a), (d) | 4. (c), (d) | 5. (b), (c), (d) |
| 6. (b), (c), (d) |             |             |             |                  |

**Fill-in-the-Blanks Type**

- |                              |                        |        |
|------------------------------|------------------------|--------|
| 1. magnesia, lime            | 2. aluminium           | 3. Tin |
| 4. $\text{KAg}(\text{CN})_2$ | 5. sintering, smelting |        |

**Linked Comprehension Type**

- |        |        |        |
|--------|--------|--------|
| 1. (a) | 2. (d) | 3. (c) |
|--------|--------|--------|

**Matching Type**

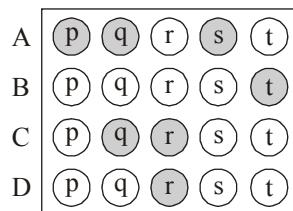
1. (a) – (s); (b) – (p); (c) – (q); (d) – (r); (e) – (t)
2. (a) – (v); (b) – (s); (c) – (p); (d) – (r); (e) – (u); (f) – (t); (g) – (q)
3. (a) – (q); (b) – (s); (c) – (p); (d) – (r)
4. (a) – (q); (b) – (r); (c) – (s); (d) – (p)
5. (a) – (s); (b) – (q); (c) – (p); (d) – (r)
6. (a) – (p); (b) – (r); (c) – (q); (d) – (t); (e) – (s)
7. (a) – (p); (b) – (q); (c) – (s); (d) – (r);

**Matrix Match Type**

1. The correct-bubbled diagram is as follows.

	p	q	r	s
A	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
B	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>
C	<input checked="" type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
D	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>

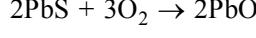
2. The correct-bubbled diagram is as follows.



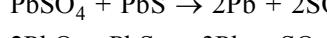
### Short Answer Type

- (i) An alloy is a homogenous mixture of a metal with other metal(s) or with nonmetal(s), having metallic properties  
An amalgam is an alloy containing mercury.
  - (ii) The chemical which reacts with the unwanted siliceous material (called gangue) to form a substance (having low melting point) is called flux. The product formed is called slag.
  - (iii) Smelting is the process by which the metal oxide gets reduced to the metal in its fused state.  
Roasting is the process by which the ore gets converted to its oxide by heating it in excess of air.
2. The list of properties indicate that X corresponds to a highly electropositive metal belonging to either alkali or alkaline-earth metals. The extraction of such a metal is carried out by an electrolytic process. The list of properties indicate that Y is metallic. The extraction of metal is carried out by reduction of its oxide using reducing agent like C, CO and aluminium.
3. The chemical equations involved in the extraction of lead from galena are:

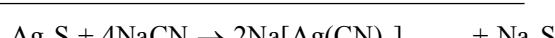
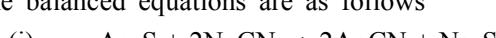
#### Heating in excess of air



#### Heating with excess of PbS



4. The balanced equations are as follows

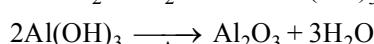
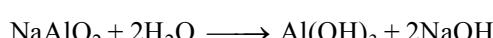
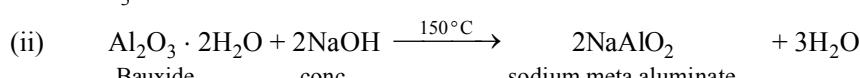


Sodium argentocyanide

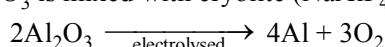
Sodium argentocyanide is treated with Zn to get silver.



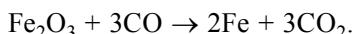
Silver obtained is porous in character. To get it in compressed form, it is fused with either borax or  $\text{KNO}_3$ .



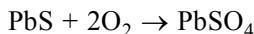
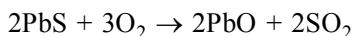
$\text{Al}_2\text{O}_3$  is mixed with cryolite ( $\text{NaAlF}_4$ ) and electrolysed:



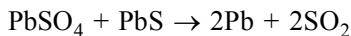
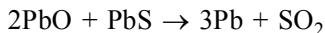
5. Fluorine is highly electronegative element. It cannot be prepared by chemical oxidation of fluorides.  
 6. (i) The actual reducing agent of haematite in blast furnace is CO.



(ii) Galena ore( $\text{PbS}$ ) is roasted at moderately temperature in excess of air on the hearth of a reverberatory furnace. The ore is oxidised partly to oxide and partly to sulphate.

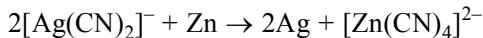


Now, the air supply is stopped and more of galena is added and the temperature is raised. Both  $\text{PbO}$  and  $\text{PbSO}_4$  get converted to  $\text{Pb}$ .

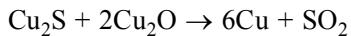
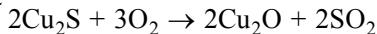


(iii) Sodium chloride prevents hydrolysis of magnesium chloride and increases the conductivity of the fused mass

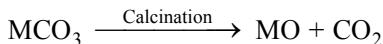
(iv) Zinc is more reducing than copper and is also cheaper.



(v) Chalcocite ( $\text{Cu}_2\text{S}$ ) is roasted and not calcined because free supply of air is needed to convert  $\text{Cu}_2\text{S}$  into  $\text{Cu}_2\text{O}$ .



In calcination, heating is done without free supply of air as in case of carbonates.



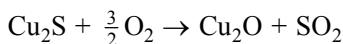
7. The required balanced equations are as follows.

(i) Extraction of copper from copper pyrites by self reduction:

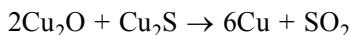
Roasting in a limited supply of air



Partial conversion of  $\text{Cu}_2\text{S}$  to  $\text{Cu}_2\text{O}$

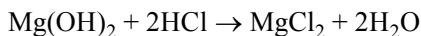
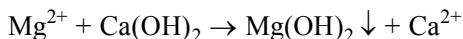


Self-reduction of oxide and sulphide



8. In the Dow process, magnesium is recovered from sea water as magnesium chloride which is then electrolysed using an iron cathode and a graphite anode.

First of all slaked lime,  $\text{Ca}(\text{OH})_2$  is added to sea water to precipitate magnesium hydroxide which is subsequently dissolved in hydrochloric acid.



Hydrated magnesium chloride,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , thus obtained is partially dehydrated by dry hydrogen chloride gas. The resulting chloride is mixed with a fused mixture of sodium chloride and calcium chloride. Magnesium chloride melts in the fused mixture (975–1025 K) and becomes completely anhydrous. The molten mixture of three chlorides is then electrolysed and magnesium is obtained at the cathode and chlorine is liberated at the anode

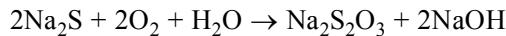


Upper portion (675 K – 975 K)	$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ This reaction occurs in stages. $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$ $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
Middle portion (1000 K – 1500 K)	$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ $\text{FeO} + \text{CO} \rightarrow \text{Fe(s)} + \text{CO}_2$
Upper lower portion (1500 K – 1800 K)	Impure iron melts $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$ (slag)
Lower portion (1800 K – 2000 K)	Phosphates and silicates are reduced P and S pass into molten iron $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

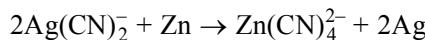
11. After the preliminary crushing and concentration, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated by current of air.  
Silver passes into solution as argentocyanide:



The air blown in remove  $\text{Na}_2\text{S}$  as  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  causing the above reaction to proceed to completion.

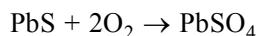
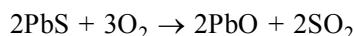


The solution obtained above is filtered and treated with scrap iron or zinc when silver gets precipitated.

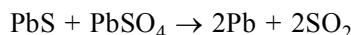
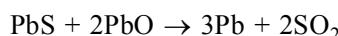


The obtained silver is purified electrolytically (electrolyte: silver nitrate solution containing 1% nitric acid, anode: impure silver and cathode: pure silver).

12. Lead is mainly extracted from galena. After the concentration of the ore by froth flotation process, the ore is roasted in a reverberatory furnace for about six hours. Part of PbS undergoes the following reactions.



The supply of air is stopped and temperature is increased, where the following reactions occur.

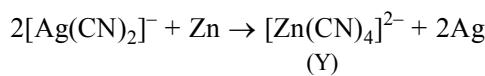
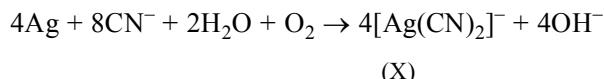


## HINTS AND SOLUTIONS

## **Straight Objective Type**

7. Firstly, carbon which is added along with crushed haematite ore is oxidised to CO (and  $\text{CO}_2$ ). The produced CO acts as chief reducing agent for the reduction of haematite to steel.

14. The reactions involved are



15. Lead is extracted by self-reduction method and tin by carbon-reduction method.

16. Chalcopyrites is copper pyrites ( $\text{CuFeS}_2$ ).

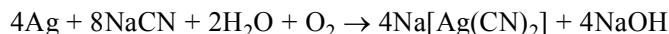
Malachite is  $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ .

Azurite is  $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$ .

Dolomite is  $\text{MgCO}_3 \cdot \text{CaCO}_3$ .

17. Zinc from zinc blende is achieved by roasting followed by reduction with carbon.

18. The reaction is



19. The argentite ore contains  $\text{Ag}_2\text{S}$ . After crushing and concentration by froth flotation process, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated with a current of air.

Silver passes into the solution as argentocyanide.  $\text{Ag}_2\text{S} + 4\text{NaCN} \rightleftharpoons 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$

The air blown removes  $\text{Na}_2\text{S}$  as  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$  causing the above reaction to proceed to completion. Silver

is recovered by adding zinc into argentocyanide.  $2\text{Ag}(\text{CN})_2^- + \text{Zn} \rightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag}$

Thus, oxidizing agent is  $\text{O}_2$  (from air) and the reducing agent is Zn.

20. Ag, Cu and Pb occur as sulphide ores while Sn, Mg and Al occur in non-sulphide ores.

### Multiple Correct-Choice type

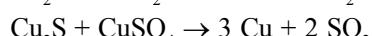
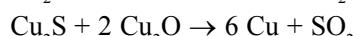
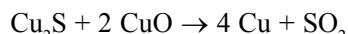
3. Cassiterite is an ore of tin which contains  $\text{SnO}_2$  and impurities of Fe, Cu and As as tungstates.  $\text{SnO}_2$  is reduced by carbon:



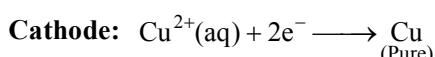
The molten metal is collected from the bottom of blast furnace. The product contains traces of Fe which is removed by blowing air through the molten mixture as  $\text{FeO}$  (which floats on the surface of molten metal).

4. Tin and iron are extracted by carbon-based reduction method whereas aluminium and magnesium are extracted by electrolytic method.

5. The reagents  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{CuSO}_4$  give the metal Cu on heating with  $\text{Cu}_2\text{S}$ .



6. In the electrolytic refining of blister copper, the electrodic reactions are:



Impurities settle as anode-mud.

The choice (b), (c) and (d) are correct.

### Linked Comprehension Type

1. Partial roasting of the ore chalcopyrite ( $\text{CuFeS}_2$ ) produces  $\text{Cu}_2\text{S}$  and  $\text{FeO}$  as per equations given below.
  - (i)  $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2 \uparrow$  (major)
  - (ii)  $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2$  (minor)
  - (iii)  $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$  (minor)
2. Iron is removed as  $\text{FeSiO}_3$ .  $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
3. The basic reaction is  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$   
Here  $\text{S}^{2-}$  in  $\text{Cu}_2\text{S}$  is changed to  $\overset{4+}{\text{S}}$  in  $\text{SO}_2$ . Thus, reducing species is  $\text{S}^{2-}$  as it undergoes the reaction  
 $\text{S}^{2-} \longrightarrow \overset{4+}{\text{S}} + 6\text{e}^-$ .

### Matrix Match Type

1. (a) The conversion of  $\text{PbS}$  into  $\text{PbO}$  is the phenomenon of roasting (choice p)  
 (b) The conversion of  $\text{CaCO}_3$  to  $\text{CaO}$  is calcination (choice q)  
 (c)  $\text{ZnS}$  is reduced to  $\text{Zn}$  by first roasting to  $\text{ZnO}$  followed by reduction by carbon (choices p and r)  
 (d)  $\text{Cu}_2\text{S}$  is roasted to  $\text{Cu}_2\text{O}$  followed by self-reduction to give  $\text{Cu}$  (choices p and s).
2. (p) Siderite is  $\text{FeCO}_3$   
 (q) Malachite is  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$   
 (r) Bauxite is  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$   
 (s) Calamine is  $\text{ZnCO}_3$   
 (t) Argentite is  $\text{Ag}_2\text{S}$   
 Thus, matchings go as follows:  
 (a)  $\rightarrow$  (p), (q), (s); (b)  $\rightarrow$  (t); (c)  $\rightarrow$  (q), (r); (d)  $\rightarrow$  (r)



# EXERCISES IN INORGANIC CHEMISTRY

18

## Straight Objective Type

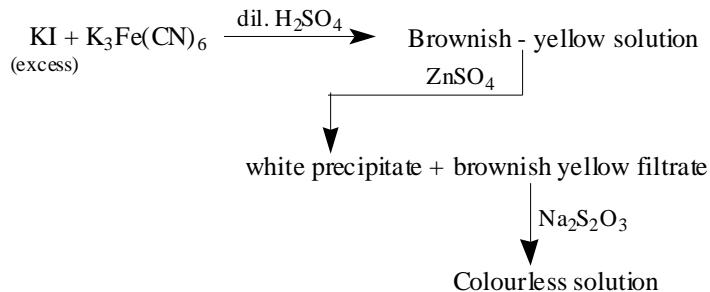
1. A solution of KBr is treated with each of the following. Which one would liberate bromine?  
(a) Cl<sub>2</sub>      (b) HI      (c) I<sub>2</sub>      (d) SO<sub>2</sub>      (1980)
2. Which of the following is the most stable to heat?  
(a) HCl      (b) HOCl      (c) HBr      (d) HI      (1980)
3. The pairs of compounds which cannot exist together in solution is  
(a) NaHCO<sub>3</sub> and NaOH      (b) Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>  
(c) Na<sub>2</sub>CO<sub>3</sub> and NaOH      (d) NaHCO<sub>3</sub> and NaCl      (1986)
4. Which compound does dissolve in hot, dilute HNO<sub>3</sub>?  
(a) HgS      (b) PbS      (c) CuS      (d) CdS      (1996)
5. An aqueous solution of FeSO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and chrome alum is heated with excess of Na<sub>2</sub>O<sub>2</sub> and filtered. The materials obtained are:  
(a) a colourless filtrate and a green residue  
(b) a yellow filtrate and a green residue  
(c) a yellow filtrate and a brown residue  
(d) a green filtrate and a brown residue      (1996)
6. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.  
ClOH (I)      BrOH (II)      IOH (III)  
(a) I > II > III      (b) II > I > III      (c) III > II > I      (d) I > III > II      (1996)
7. The only cations present in a slightly acidic solution are Fe<sup>3+</sup>, Zn<sup>2+</sup> and Cu<sup>2+</sup>. The reagent that when added in excess to this solution would identify and separate Fe<sup>3+</sup> in one step is  
(a) 2 M HCl      (b) 6 M NH<sub>3</sub>      (c) 6 M NaOH      (d) H<sub>2</sub>S gas      (1997)
8. Ammonium dichromate is used in some fireworks. The green coloured powder blown in the air is  
(a) CrO<sub>3</sub>      (b) Cr<sub>2</sub>O<sub>3</sub>      (c) Cr      (d) CrO(O<sub>2</sub>)      (1997)
9. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a  
(a) Hg<sup>2+</sup> salt      (b) Cu<sup>2+</sup> salt      (c) Ag<sup>+</sup> salt      (d) Pb<sup>2+</sup> salt      (2002)
10. From the following information  
$$X + H_2SO_4 \rightarrow Y \text{ (a colourless and irritating gas)}$$
$$Y + K_2Cr_2O_7 + H_2SO_4 \rightarrow \text{green solution}$$
Identify the pair X and Y from the list given below.  
(a) Cl<sup>-</sup>, HCl      (b) S<sup>2-</sup>, H<sub>2</sub>S      (c) CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub>      (d) SO<sub>3</sub><sup>2-</sup>, SO<sub>2</sub>      (2003)

## 18.2 IIT Chemistry: Topic-wise Solved Questions

11.  $\text{NH}_4\text{NO}_2$  on heating produces a gas which can also be obtained on heating  
 (a)  $\text{AgNO}_3$       (b)  $\text{Ag}_2\text{CO}_3$       (c)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$       (d)  $\text{NH}_4\text{NO}_3$  (2004)
12. A metallic nitrate gives black precipitates with KI solution. On adding excess of KI, an orange-coloured solution is obtained. The metallic ion in the metallic nitrate is  
 (a)  $\text{Hg}^{2+}$       (b)  $\text{Sn}^{2+}$       (c)  $\text{Bi}^{3+}$       (d)  $\text{Pb}^{2+}$  (2005)
13. A colourless aqueous solution on adding water and on heating gave a white precipitate. This precipitate when reacted with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  in excess resulted in dissolution of some of the precipitate and a gelatious precipitate is obtained. The hydroxide formed in aqueous solution is  
 (a)  $\text{Zn}(\text{OH})_2$       (b)  $\text{Al}(\text{OH})_3$       (c)  $\text{Ca}(\text{OH})_2$       (d)  $\text{Mg}(\text{OH})_2$  (2006)
14. Heating an ammoniacal solution of  $\text{MgSO}_4$  in the presence of  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{HPO}_4$  causes the precipitation of  
 (a)  $\text{Mg}(\text{HPO}_4)$       (b)  $\text{Mg}(\text{NH}_4)\text{PO}_4$       (c)  $\text{MgCl}_2$       (d)  $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$  (2006)
15. A solution of a metal ion when treated with KI gives a red precipitate which dissolves in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt(II) thiocyanate gives rise to a deep blue crystalline precipitate. The metal ion is  
 (a)  $\text{Pb}^{2+}$       (b)  $\text{Hg}^{2+}$       (c)  $\text{Cu}^{2+}$       (d)  $\text{Co}^{2+}$  (2007)
16. Passing  $\text{H}_2\text{S}$  gas into a mixture of  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions in an acidified aqueous solution precipitates  
 (a)  $\text{CuS}$  and  $\text{HgS}$       (b)  $\text{MnS}$  and  $\text{CuS}$       (c)  $\text{MnS}$  and  $\text{NiS}$       (d)  $\text{NiS}$  and  $\text{HgS}$  (2011)
17. Upon treatment with ammoniacal  $\text{H}_2\text{S}$ , the metal ion that precipitates as sulphide is  
 (a)  $\text{Fe}(\text{III})$       (b)  $\text{Al}(\text{III})$       (c)  $\text{Mg}(\text{II})$       (d)  $\text{Zn}(\text{II})$  (2013)

### Multiple Correct-Choice Type

1. For the given aqueous solutions, which of the following statement(s) is(are) correct?



- (a) The first reaction is a redox reaction.  
 (b) White precipitate is  $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ .  
 (c) Addition of filtrate to starch solution gives blue coloration.  
 (d) White precipitate is soluble in NaOH solution. (2012)
2. The pair(s) of ions where **BOTH** the ions are precipitated upon passing  $\text{H}_2\text{S}$  gas in presence of dilute HCl, is(are)  
 (a)  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$       (b)  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$       (c)  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$       (d)  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$  (2015)

### Integer Answer Type

1. Among  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{SnS}_2$ , the total number of **BLACK**-coloured sulphides is \_\_\_\_\_. (2014)
2. A list of species having the formula  $\text{XZ}_4$  is given below.  
 $\text{XeF}_4$ ,  $\text{SF}_4$ ,  $\text{SiF}_4$ ,  $\text{BrF}_4^-$ ,  $\text{BF}_4^-$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{FeCl}_4]^{2-}$ ,  $[\text{CoCl}_4]^{2-}$  and  $[\text{PtCl}_4]^{2-}$   
 Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is \_\_\_\_\_. (2014)

**True/False Type**

1. From the solution containing copper(+2) and zinc(+2) ions, copper can be selectively precipitated using sodium sulphide. (1987)

**Reasoning Type**

1. In the question below a statement (S) is given which may be correct or wrong. For each statement an explanation (E) is given which may be correct or wrong. Choose the correct answer from the code a, b, c, d given for each subquestion.

*Statement (S):* If a strong acid is added to a solution of potassium chromate it changes its colour from yellow to orange.

*Explanation (E):* The colour change is due to the oxidation of potassium chromate.

*Code:*

- (a) Both (S) and (E) are correct and (E) is the correct explanation of (S)
- (b) Both (S) and (E) are correct but (E) is not the correct explanation of (S)
- (c) (S) is correct but (E) is wrong.
- (d) (S) is wrong but (E) is correct. (1988)

2. In the question below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subquestion.

*Code*

- (a) If both assertion and statement are true and statement is an explanation of assertion.
- (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
- (c) If assertion is wrong and statement is correct, statement is not an explanation of assertion.
- (d) If both assertion and statement are wrong and statement is not explanation of assertion.

*Assertion*

A very dilute acidic solution of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  gives yellow precipitate of  $\text{CdS}$  on passing hydrogen sulphide.

*Statement*

Solubility product of  $\text{CdS}$  is more than that of  $\text{NiS}$ .

(1989)

3. In each sub-question below are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code from among a, b, c and d which are defined below—

*Code*

- (a) Both S and E are true, E is the correct explanation of S.
- (b) Both S and E are true, but E is not the correct explanation of S.
- (c) S is true but E is false.
- (d) S is false but E is true.

*STATEMENT (S)*

- (i) Although  $\text{PF}_5$ ,  $\text{PCl}_5$  and  $\text{PBr}_5$  are known, the pentahalides of nitrogen have not been observed.
- (ii) The alkali metals can form ionic hydrides which contain the hydride ion,  $\text{H}^-$ .

*EXPLANATION (E)*

Phosphorus has lower electronegativity than nitrogen.

(1994)

The alkali metals have low electronegativity; their hydrides conduct electricity when fused and liberate hydrogen at the anode

(1994)

4. STATEMENT-1: Alkali metals dissolve in liquid ammonia to give blue solutions.  
because

## **18.4** IIT Chemistry: Topic-wise Solved Questions

**STATEMENT-2:** Alkali metals in liquid ammonia give solvated species of the type  $[M(NH_3)_n]^+$  ( $M$  = alkali metals).

- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1  
(b) Statement-1 is True, Statement-2 is True Statement-2 is Not a correct explanation for Statement-1  
(c) Statement-1 is True, Statement-2 is False  
(d) Statement-1 is False, Statement-2 is True

(2007)

### **Linked-Comprehension Type**

#### **Passage-1**

*p*-Amino-N, N-dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate(II) leads to the formation of an intense blue precipitate. The precipitate dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate(II) leads to a brown coloration due to the formation of Z.

1. The compound X is  
(a)  $NaNO_3$       (b)  $NaCl$       (c)  $NaSO_4$       (d)  $Na_2S$
2. The compound Y is  
(a)  $MgCl_2$       (b)  $FeCl_2$       (c)  $FeCl_3$       (d)  $ZnCl_2$
3. The compound Z is  
(a)  $Mg_2[Fe(CN)_6]$       (b)  $Fe[Fe(CN)_6]$       (c)  $Fe_4[Fe(CN)_6]_3$       (d)  $K_2Zn_3[Fe(CN)_6]_2$

(2009)

#### **Passage-2**

When a metal M is dipped into an aqueous colourless concentrated solution of compound N, the solution turns light blue. Addition of aqueous  $NaCl$  to the blue solution gives a white precipitate O. Addition of aqueous  $NH_3$  dissolves O and gives an intense blue solution.

1. The metal rod M is  
(a) Fe      (b) Cu      (c) Ni      (d) Co
2. The compound N is  
(a)  $AgNO_3$       (b)  $Zn(NO_3)_2$       (c)  $Al(NO_3)_3$       (d)  $Pb(NO_3)_2$
3. The final solution contains  
(a)  $[Pb(NH_3)_4]^{2+}$  and  $[CoCl_4]^{2-}$       (b)  $[Al(NH_3)_4]^{3+}$  and  $[Cu(NH_3)_4]^{2+}$   
(c)  $[Ag(NH_3)_2]^+$  and  $[Cu(NH_3)_4]^{2+}$       (d)  $[Ag(NH_3)_2]^+$  and  $[Ni(NH_3)_6]^{2+}$

(2011)

#### **Passage-3**

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry.

1. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N  $Na_2S_2O_3$  was used to reach the end point. The molarity of the household bleach solution is  
(a) 0.48 M      (b) 0.96 M      (c) 0.24 M      (d) 0.024 M
2. Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is  
(a)  $Cl_2O$       (b)  $Cl_2O_7$       (c)  $ClO_2$       (d)  $Cl_2O_6$

(2012)

## Passage-4

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (**P**) and a filtrate (**Q**). The precipitate **P** was found to dissolve in hot water. The filtrate (**Q**) remained unchanged, when treated with H<sub>2</sub>S in a dilute mineral acid medium. However, it gave a precipitate (**R**) with H<sub>2</sub>S in an ammoniacal medium. The precipitate **R** gave a coloured solution (**S**) when treated with H<sub>2</sub>O<sub>2</sub> in an aqueous NaOH medium.

1. The precipitate P contains

- (a)  $\text{Pb}^{2+}$       (b)  $\text{Hg}_2^{2+}$       (c)  $\text{Ag}^+$       (d)  $1 + \text{Hg}^{2+}$

2. The coloured solution S contains

- (a)  $\text{Fe}_2(\text{SO}_4)_3$       (b)  $\text{Cu SO}_4$       (c)  $\text{Zn SO}_4$       (d)  $\text{Na}_2\text{Cr O}_4$       (2013)

## **Passage-5**

The reaction of  $\text{Cl}_2$  gas with cold-dilute and hot-concentrated  $\text{NaOH}$  in water give sodium salts of two (different) oxoacids of chlorine, P and Q, respectively. The  $\text{Cl}_2$  gas reacts with  $\text{SO}_2$  gas in presence of charcoal to give a product R. The product R reacts with white phosphorus to give a compound S. On hydrolysis, S gives an oxoacid of phosphorous, T.

1. P and Q, respectively, are the sodium salts of



- 2.** R, S and T, respectively, are

- (a)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_5$  and  $\text{H}_3\text{PO}_4$       (b)  $\text{SO}_2\text{Cl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_3$   
 (c)  $\text{SOCl}_2$ ,  $\text{PCl}_3$  and  $\text{H}_3\text{PO}_2$       (d)  $\text{SOCl}_2$ ,  $\text{PCl}_5$  and  $\text{H}_3\text{PO}_4$       (2013)

## Matching Type

1. (a)  $\text{HgCl}_2$  (p) Cassiterite  
 (b)  $(\text{NaPO}_3)_n$  (q) Lunar caustic  
 (c)  $\text{NO}_3^-$  (r) Producer gas  
 (d)  $\text{SnO}_2$  (s) Water softner  
 (e)  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (t) Brown ring test  
 (f)  $\text{AgNO}_3$  (u) Carnallite  
 (g)  $\text{CO} + \text{N}_2$  (v) Calomel

(1981)

**Each entry in column X is in some way related to the entries in columns Y and Z. Match the appropriate entries.**

- | 2.                | X                    | Y                 | Z |
|-------------------|----------------------|-------------------|---|
| (a) Asbestors     | molecular sieve      | air pollutant     |   |
| (b) Fluorocarbons | paramagnetic         | carcinogen        |   |
| (c) Lithium metal | refrigeration        | fluorescent paint |   |
| (d) Nitric oxide  | reducing agent       | electron donor    |   |
| (e) Zeolites      | semiconductor        | ion exchanger     |   |
| (f) Zinc oxide    | silicates of Ca + Mg | propellent        |   |

- | 3.                  | X                  | Y                        | Z |
|---------------------|--------------------|--------------------------|---|
| (a) Animal charcoal | $\text{kJ K}^{-1}$ | watch spring             |   |
| (b) Invar           | $\text{cm}^{-1}$   | $1.3805 \times 10^{-26}$ |   |
| (c) Nichrome        | Co, Ni             | sugar refining           |   |
| (d) Rydberg         | Fe, Ni             | cutlery                  |   |

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(e) Stainless steel	Fe, Cr, Ni, C	109677	
(f) Boltzmann	C, Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	heating element	(1988)

**Match the entries on the left with most appropriate choice(s) given on the right.**

- |    |   |   |        |
|----|---|---|--------|
| 4. | (a) Liquid air<br>(b) Na <sub>2</sub> CO <sub>3</sub><br>(c) Nitric Oxide<br>(d) Silver<br>(e) Chlorine   | (p) Deacon's process<br>(q) Parke's process<br>(r) Claude's process<br>(s) Ostwald's process<br>(t) Solvay's process  | (1985) |
| 5. | (a) Phenol<br>(b) Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub><br>(c) Salicylic acid<br>(d) Quick lime<br>(e) CuO  | (p) coloured glass<br>(q) antichlor<br>(r) refractory material<br>(s) antiseptic<br>(t) analgesic   | (1985) |
| 6. | (a) Aston<br>(b) Priestley<br>(c) Ramsay<br>(d) Marie Curie<br>(e) Becquerel  | (p) radium<br>(q) radioactivity<br>(r) oxygen<br>(s) inert gas<br>(t) mass spectrum   | (1985) |
| 7. | 1. Lewis acid<br>2. Philospher's wool<br>3. Electrophile<br>4. Preservative<br>5. Electron emission<br>6. Bronsted acid<br>7. Black Jack<br>8. X-ray emission | (a) K electron capture<br>(b) Zinc ore<br>(c) HCHO<br>(d) NH <sub>4</sub> <sup>+</sup><br>(e) small portion to neutron ratio<br>(f) SO <sub>2</sub><br>(g) BF <sub>3</sub><br>(h) ZnO | (1986) |

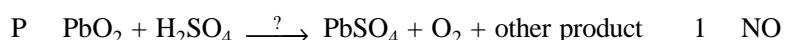
X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Graphite crystalline	Abrasive
Superphosphate	Cubic	Insulator
Carbon fibres	Layer structure	Fertilizer
Rock salt	Diamond structure	Reinforced plastics
Caborundum	Bone ash	Preservative

9. Match the entries on the left with most appropriate choice(s) given on the right.

- |   |                         |
|---|-------------------------|
| (a) Bi <sub>2</sub> O <sub>3</sub> → BiO <sup>+</sup>                             | (p) Hydrolysis          |
| (b) AlO <sub>2</sub> <sup>-</sup> → Al(OH) <sub>3</sub>                           | (q) Dilution with water |
| (c) SiO <sub>4</sub> <sup>4-</sup> → Si <sub>2</sub> O <sub>7</sub> <sup>2-</sup> | (r) Acidification       |
| (d) B <sub>4</sub> O <sub>7</sub> <sup>2-</sup> → B(OH) <sub>3</sub>              | (s) Heating             |

10. The unbalanced chemical reactions given in List I show missing reagent or condition(?) which are provided in List II. Match List I with List II and select the correct answer using the code given below the lists:

**List I**

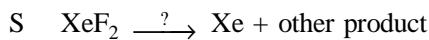


**List II**





3 warm



4  $\text{Cl}_2$

### Codes

	P	Q	R	S
(a)	4	2	3	1
(b)	3	2	1	4
(c)	1	4	2	3
(d)	3	4	2	1

(2013)

### Matrix Match Type

1. Match the reactions in **Column I** with nature of the reactions/type of the products in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

#### Column I

- (a)  $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$
- (b)  $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow \dots$
- (c)  $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow \dots$  metal ion
- (d)  $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow \dots$

- (p) redox reaction
- (q) one of the products has trigonal planar structure
- (r) dimeric bridged tetrahedral
- (s) disproportionation

(2008)

### Short Answer Type

#### I. Descriptive

- Account for the following. Limit your answer to one sentence for each.
  - $\text{H}_2\text{O}$  is a liquid while  $\text{H}_2\text{S}$  is a gas at ordinary temperature
  - Although the molecules in a gas are moving about rapidly, a closed vessel of negligible mass, containing the gas, still does not move.
  - Aqueous solution of  $\text{AlCl}_3$  behaves acidic towards litmus while that of  $\text{NaCl}$  does not.
  - Nitric oxide becomes brown when exposed to air.
  - A few drops of concentrated  $\text{HNO}_3$  is added before precipitating the hydroxides of the third group in qualitative analysis
  - Bleaching of flowers by  $\text{Cl}_2$  is permanent, while after bleaching with  $\text{SO}_2$ , the colour returns. (1978)
- Name the reagents used to distinguish between the following pairs of ions and state what happens. No equations need be given.
 

(i) Mercuric from mercurous	(ii) Cupric from cuprous
(iii) Ferrous from ferric	(iv) Sulphite from sulphate

(1978)
- Sulphuric acid acts as an acid, an oxidising agent or as a dehydrating agent. In which way does it react when it acts on
 

(i) sugar	(ii) sulphur
(iii) Calcium carbonate	(iv) Copper

(1978)
- Give reasons for the following in not more than two sentences.
  - Sodium is kept under kerosene
  - A small amount of acid or alkali is added before the electrolysis of water

- (iii) A standard solution of NaOH is not prepared by dissolving its mass in water
- (iv) A small quantity of H<sub>2</sub>SO<sub>4</sub> is added while preparing a standard solution of ferrous ammonium sulphate
- (v) Borax is used in qualitative analysis

5. Account for the following. Limit your answer to two sentences:

- (i) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on sodium bromide.
- (ii) When a blue litmus paper is dipped into a solution of hypochlorous acid, it first turns red and then latter gets decolourised.
- (iii) The precipitation of second group sulphides in qualitative analysis is carried out with hydrogen sulphide in presence of hydrochloric acid, and not nitric acid.
- (iv) Atomic masses of most of the elements are fractional.

6. Suggest a simple qualitative test to distinguish between each of the following pairs.

- (i) PbCO<sub>3</sub> and PbSO<sub>4</sub>
- (ii) CaCl<sub>2</sub> and MgCl<sub>2</sub>
- (iii) Na<sub>2</sub>SO<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

7. Explain the following in not more than two sentences.

- (i) Concentrated HNO<sub>3</sub> turns yellow in sunlight
- (ii) CO<sub>2</sub> does not burn in air and does not support combustion, but a burning Mg wire continues to burn in it.
- (iii) A solution of FeCl<sub>3</sub> in water gives brown precipitate on standing.
- (iv) Bleaching powder loses its bleaching property when it is kept in an open bottle for a long time
- (v) Chloroform is stored in dark-coloured bottles

8. Give reasons for the following.

- (i) Carbon acts as an abrasive and also as a lubricant.
- (ii) Sulphur melts to a clear, mobile liquid at 119 °C but on further heating above 160 °C it becomes viscous
- (iii) Sodium carbonate is made by the Solvay's process but the same process is not extended to the manufacture of potassium carbonate

9. In the preparation of hydrogen iodide from alkali iodides, phosphoric acid is preferred to sulphuric acid. (1982)

10. Show with equations, how the following compounds are prepared.

- (i) Sodium thiosulphate from sodium sulphite
- (ii) Bleaching powder from slaked lime.

11. Give reasons for the following in one or two sentences.

- (i) A bottle of liquor ammonia should be cooled before opening the stopper.
- (ii) Silver bromide is used in photography.
- (iii) Solid carbon dioxide is known as dry ice.

12. Each of the following statements is true only under some specific conditions. Write the condition for each sub-question in not more than two sentences.

- (i) Two volatile and miscible liquids can be separated by fractional distillation into pure components
- (ii) The heat energy,  $q$ , absorbed by a gas is  $\Delta H$ .
- (iii) Metals can be recovered from their ores by chemical methods
- (iv) High purity metals can be obtained by zone refining.
- (v) Equal volumes of gases contain equal amount (in moles) of gases.

13. Explain the following in one or two sentences only.

- (i) Magnesium oxide is used for the lining of steel making furnace.
- (ii) The mixture of hydrazine and hydrogen peroxide with a copper(II) catalyst is used as a rocket propellant.
- (iii) Orthophosphorous acid is not tribasic acid.

- (iv) Phenol is an acid but it does not react with sodium bicarbonate.
- (v) The molecule of magnesium chloride is linear whereas that of stannous chloride is angular. (1987)
14. Give reasons for
- The colour of mercurous chloride,  $Hg_2Cl_2$ , changes from white to black when treated with ammonia
  - Valecy of oxygen is generally two whereas sulphur shows valency of two, four and six (1988)
15. The hydroxides of aluminium and iron are insoluble in water. However, NaOH is used to separate one from the other. (1991)
16. In the following reactions, identify the compounds A, B, C and D.
- $$PCl_5 + SO_2 \rightarrow A + B$$
- $$A + CH_3COOH \rightarrow C + SO_2 + HCl$$
- $$2C + (CH_3)_2Cd \rightarrow 2D + CdCl_2 \quad (1994)$$
17. Account for the following: (Write the answers in four or five sentences only.)
- The experimentally determined N—F bond-length in  $NF_3$  is greater than the sum of the single bond covalent radii of N and F.
  - $Mg_3N_2$  when reacted with water gives off  $NH_3$  but HCl is not obtained from  $MgCl_2$  on reaction with water at room temperature.
  - $(SiH_3)_3N$  is a weaker base (1995)
18. Gradual addition of KI solution to  $Bi(NO_3)_3$  solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write chemical equations for the above reactions. (1996)
19. Aluminium sulphide gives a foul odour when it become damp. Write a balanced chemical equation for the reaction. (1997)
20. An aqueous solution containing one mole of  $HgI_2$  and two moles of NaI is orange in colour. On addition of excess NaI the solution becomes colourless. The orange colour reappears on subsequent addition of NaOCl. Explain with equations. (1999)
21. Write the chemical reactions associated with the ‘brown ring test’. (2000)
22. An aqueous blue coloured solution of a transition metal sulphate reacts with  $H_2S$  in acidic medium to give a black precipitate A, which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium, turns yellow and produces a white precipitate B. Identify the transition metal ion. Write the chemical reactions involved in the formation of A and B. (2000)
23. The gas liberated, on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of  $K_2HgI_4$ . The aqueous solution of the mixture on treatment with  $BaCl_2$  gives a white precipitate which is sparingly soluble in concentrated HCl, On heating the mixture with  $K_2Cr_2O_7$  and concentrated  $H_2SO_4$ , red vapours A are produced. The aqueous solution of the mixture gives a deep blue colouration B with potassium ferricyanide solution. Identify the ions in the given mixture and write the balanced chemical equations for the formation of A and B. (1991)

## II. Increasing/Decreasing Characteristics

- Arrange the following in the order of increasing acidity (write the weakest acid first).
  - $HOCl$ ,  $HOI$ ,  $HOBr$
  - $HOCl$ ,  $HOClO_2$ ,  $HOClO_3$ ,  $HOClO$  (1978)
- Decreasing ionic size  $Mg^{2+}$ ,  $O^{2-}$ ,  $Na^+$ ,  $F^-$  (1985)
- Increasing acidic property  $ZnO$ ,  $Na_2O_2$ ,  $P_2O_5$ ,  $MgO$  (1985)
- Increasing first ionization potential  $Mg$ ,  $Al$ ,  $Si$ ,  $Na$  (1985)
- Increasing bond length  $F_2$ ,  $N_2$ ,  $Cl_2$ ,  $O_2$  (1985)
- Increasing size  $Cl^-$ ,  $S^{2-}$ ,  $Ca^{2+}$ ,  $Ar$  (1986)
- Increasing acid strength  $HClO_3$ ,  $HClO_4$ ,  $HClO_2$ ,  $HClO$  (1986)
- Increasing bond strength  $HCl$ ,  $HBr$ ,  $HF$ ,  $HI$  (1986)

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9.	Increasing oxidation number of iodine	I <sub>2</sub> , HI, HIO <sub>4</sub> , ICl	(1986)
10.	Increasing thermal stability	HOCl, HOClO <sub>2</sub> , HOClO <sub>3</sub> , HOClO	(1988)
11.	Increasing bond enthalpy	N <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub> , Cl <sub>2</sub>	(1988)
12.	Increasing acidic character	CO <sub>2</sub> , N <sub>2</sub> O <sub>5</sub> , SiO <sub>2</sub> , SO <sub>3</sub>	(1988)
13.	Increasing ionic size	N <sup>3-</sup> , Na <sup>+</sup> , F <sup>-</sup> , O <sup>2-</sup> , Mg <sup>2+</sup>	(1991)
14.	Increasing basic character	MgO, SrO, K <sub>2</sub> O, NiO, Cs <sub>2</sub> O	(1991)
15.	Increasing extent of hydrolysis	CCl <sub>4</sub> , MgCl <sub>2</sub> , AlCl <sub>3</sub> , PCl <sub>5</sub> , SiCl <sub>4</sub>	(1991)
16.	Increasing strength of hydrogen bonding (X ... H - X)	O, S, F, Cl, N	(1991)
17.	Increasing basicity	H <sub>2</sub> O, OH <sup>-</sup> , CH <sub>3</sub> OH, CH <sub>3</sub> O <sup>-</sup>	(1992)

**III. Predicting Chemical Reactions**

1. Give balanced equations for
  - (i) Reaction of chlorine on aqueous sodium sulphite
  - (ii) Reaction of HCl on bleaching powder
  - (iii) Action of heat on ammonium nitrate
  - (iv) Reaction of calcium oxide with coke at 2000 °C
  - (v) Reaction of H<sub>2</sub>S with acidified potassium dichromate
  - (vi) Reaction of Cl<sub>2</sub> with hot concentrated KOH

(1978)
2. State, with balanced equations, what happens when:
  - (i) Tin is treated with moderately concentrated nitric acid
  - (ii) Silver is treated with hot, concentrated sulphuric acid
  - (iii) Aluminium is reacted with hot, concentrated caustic soda solution
  - (iv) Ammonium dichromate is heated
  - (v) Hydrogen sulphide is passed through a solution of potassium permanganate acidified with dilute sulphuric acid.

(1979)
3. Write balanced equations involved in the preparation of:
  - (i) Anhydrous aluminium chloride from alumina
  - (ii) Bleaching power from staked lime
  - (iii) Tin metal from cassiterite
  - (iv) Chlorine from sodium chloride
  - (v) Nitric oxide from nitric acid.

(1979)

**IV. Writing Balanced Chemical Equations**

1. White phosphorus (P<sub>4</sub>) is boiled with a strong solution of sodium hydroxide in an inert atmosphere.  
(1982, 1987)
2. Sodium iodate is treated with sodium bisulphite solution.  
(1982)
3. Sulphur dioxide gas is bubbled through an aqueous solution of copper sulphate in presence of potassium thiocyanate.  
(1982)
4. An alkaline solution of potassium ferricyanide is reacted with hydrogen peroxide.  
(1982, 1989)
5. Propene is bubbled through a hot aqueous solution of potassium permanganate.  
(1982)
6. Mixing of aqueous solution of ferric sulphate and potassium iodide.  
(1984)
7. Aqueous solution of potassium manganate and acid.  
(1984)
8. Aqueous solution of potassium chromate and acid.  
(1984)

9. A mixture of potassium chlorate, oxalic acid and sulphuric acid is heated. (1985)
10. Potassium permanganate reacts with manganese dioxide in presence of potassium hydroxide. (1985)
11. Calcium phosphate is heated with a mixture of sand and carbon. (1985)
12. Potassium ferrocyanide is heated with concentrated sulphuric acid. (1985)
13. Ammonium sulphate is heated with a mixture of nitric oxide and nitrogen dioxide. (1985)
14. Hydrogen sulphide is bubbled through an aqueous solution of sulphur dioxide. (1985)
15. Aqueous ammonia is added drop-wise to a solution of copper sulphate till it is in excess. (1985)
16. Tin is heated with concentrated nitric acid. (1985)
17.  $\text{CrCl}_3$  solution is treated with sodium hydroxide and then with hydrogen peroxide. (1985)
18.  $\text{Pb}_3\text{O}_4$  is treated with nitric acid. (1985)
19. Chlorine gas is bubbled through a solution of ferrous bromide. (1986)
20. Zinc oxide is treated with excess of sodium hydroxide solution. (1986)
21. Iodine is added to a solution of stannous chloride. (1986)
22. Sulphur dioxide gas, water vapour and air are passed over heated sodium chloride. (1986)
23. Dilute nitric acid is slowly reacted with metallic tin. (1987)
24. Potassium permanganate is reacted with warm solution of oxalic acid in the presence of sulphuric acid. (1987)
25. Gold is dissolved in aqua regia. (1987)
26. Iodate ion reacts with bisulphite ion to liberate iodine. (1988)
27. Extraction of silver from silver glance by cyanide process. (1988)
28. Phosphorus reacts with nitric acid to give equimolar ratio of nitric oxide and nitrogen dioxide. (1988)
29. Carbon dioxide is passed through a concentrated aqueous solution of sodium chloride saturated with ammonia. (1988)
30. Hypophosphorous acid is heated. (1989)
31. Sodium bromate reacts with fluorine in the presence of an alkali. (1989)
32. Silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium. (1989)
33. Cobalt(II) solution reacts with  $\text{KNO}_2$  in acetic acid medium. (1989)
34. Sodium chlorate reacts with sulphur dioxide in dilute sulphuric acid medium. (1989)
35. A mixture of potassium dichromate and sodium chloride is heated with concentrated  $\text{H}_2\text{SO}_4$ . (1990)
36. An aqueous solution of sodium nitrate is heated with zinc dust and caustic soda solution. (1990)
37. Sodium iodate is added to a solution of sodium bisulphite. (1990)
38. Iron reacts with cold dilute nitric acid. (1990)
39. Potassium permanganate is added to a hot solution of manganous sulphate. (1990)
40. Sodium nitrite is produced by absorbing the oxides of nitrogen in aqueous solution of washing soda. (1991)
41. Nitrogen is obtained in the reaction of aqueous ammonia with potassium permanganate. (1991)
42. Elemental phosphorus reacts with concentrated  $\text{HNO}_3$  to give phosphoric acid. (1991)
43. Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate. (1991)
44. Sulphur is precipitated in the reaction of hydrogen sulphide with sodium bisulphite solution. (1991)
45. Carbon dioxide is passed through a suspension of lime stone in water. (1991)
46. Copper reacts with  $\text{HNO}_3$  to give NO and  $\text{NO}_2$  in molar ratio of 2:1. (1992)
47. Sodium carbonate is added to a solution of copper sulphate. (1992)
48. Red phosphorus is reacted with iodine in presence of water. (1992)
49. Anhydrous potassium nitrate is heated with excess of metallic potassium. (1992)

**18.12** IIT Chemistry: Topic-wise Solved Questions

50. Potassium dichromate and concentrated hydrochloric acid are heated together. (1992)
51. Manufacture of triple superphosphate from fluorapatite. (1997)
52. Oxidation of cuprous oxide to cupric hydroxide by alkaline  $\text{KMnO}_4$ . (1997)
53. Reaction of alkaline perbromate with zinc giving tetrahydroxozincate. (1997)
54. Silver bromide with hypo in photographic process. (1997)
55. Cobaltous chloride with excess  $\text{KNO}_2$  in aqueous acidic solution. (1997)
56. Phosphorus is treated with concentrated nitric acid. (1997)
57. Oxidation of hydrogen peroxide with potassium permanganate in acidic medium. (1997)
58. Manufacture of phosphoric acid from phosphorus. (1997)
59. Reaction of aluminium with aqueous sodium hydroxide. (1997)
60. Reaction of zinc with dilute nitric acid. (1997)
61. In moist air copper corrodes to produce a green layer on the surface. (1998)
62. Chlorination of calcium hydroxide produces bleaching powder. (1998)
63. Write balanced equations for the reactions of the following compounds with water:
  - (i)  $\text{Al}_4\text{C}_3$
  - (ii)  $\text{CaNCN}$
  - (iii)  $\text{BF}_3$
  - (iv)  $\text{NCl}_3$
  - (v)  $\text{XeF}_4$  (2002)

**Completing and Balancing Chemical Equations**

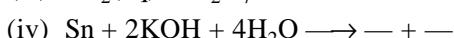
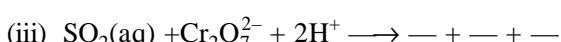
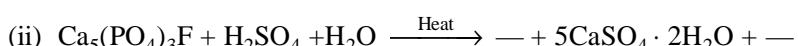
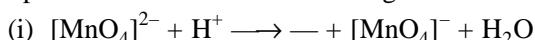
Complete and balance the following equations:

1.  $\text{SO}_2 + \text{MnO}_4^- \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} + \text{_____}$  (1981)
2.  $\text{HCO}_3^- + \text{Al}^{3+} \rightarrow \text{Al}(\text{OH})_3 + \text{_____}$  (1981)
3.  $\text{AlBr}_3 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_3\text{PO}_4 \rightarrow \text{K}_3\text{PO}_4 + \text{AlPO}_4 + \text{H}_2\text{O} + \text{_____} + \text{_____}$  (1981)
4.  $\text{Cu}_2\text{O} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O} + \text{_____}$  (1981)
5.  $\text{K}_4\text{Fe}(\text{CN})_6 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{_____}$  (1981)
6.  $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- + \text{I}^- + \text{H}_2\text{O} + \text{_____}$  (1981)
7.  $\text{Zn} + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NH}_4^+ + \text{_____}$  (1983)
8.  $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{H}_4\text{O} \rightarrow \text{C}_2\text{H}_4\text{O}_2 + \text{Cr}^{3+} + \text{_____}$  (1983)
9.  $\text{HNO}_3 + \text{HCl} \rightarrow \text{NO} + \text{Cl}_2 + \text{_____}$  (1983)
10.  $\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{Ce}^{4+}$  (1983)
11.  $\text{Cl}_2 + \text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{_____}$  (1983)
12.  $\text{NH}_3 + \text{NaOCl} \rightarrow \text{_____} + \text{_____} + \text{_____}$  (1993)
13.  $\text{AgBr} + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{_____} + \text{_____}$  (1993)
14.  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} + \text{MnSO}_4 \rightarrow \text{_____} + \text{_____} + \text{_____}$  (1993)
15.  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO}_3^- + \text{H}^+ \rightarrow \text{_____} + [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O}$   
 $\text{Fe}(\text{H}_2\text{O})_6^{2+} + \text{_____} \rightarrow \text{_____} + \text{H}_2\text{O}$  (1993)

16. In the following subquestions, identify the COMPOUNDS/REACTION CONDITIONS represented by alphabets, **A**, **B**.

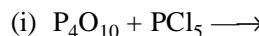


17. Complete and balance the following reactions.



(1994)

18. Complete and balance the following chemical equations.



(1998)

### Subjective Type

- A mixture of  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  when heated in air to a constant weight, gains 5% in its mass. Determine the initial composition of the mixture. (1978)
- Igniting  $\text{MnO}_2$  in air converts it quantitatively to  $\text{Mn}_3\text{O}_4$ . A sample of pyrolusite is of the following composition:  $\text{MnO}_2$ , 80%;  $\text{SiO}_2$  and other inert constituents, 15% ; rest being water. The sample is ignited into constant weight. What is the percentage of Mn in the ignited sample. (1978)
- Compound A is a greenish crystalline salt which gives the following results when treated;
  - Addition of  $\text{BaCl}_2$  solution to a solution of A results in the formation of a white precipitate B, which is insoluble in dilute HCl.
  - On heating, water vapour and two oxides of sulphur, C and D, are liberated, leaving a red brown residue E.
  - E dissolves in warm concentrated HCl to give a yellow solution F.
  - With  $\text{H}_2\text{S}$ , the solution F yields a yellow-white precipitate G, which when filtered leaves a greenish filtrate H. Identify the substances A to H. (1978)
- One gram of an alloy of aluminium and magnesium when treated with excess of dilute HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen, collected over mercury at  $0^\circ\text{C}$  has a volume of 1.20 L at 0.92 atm pressure. Calculate the composition of the alloy. (1978)
- In the analysis of a 0.50 g sample of feldspar, a mixture of the chlorides of sodium and potassium is obtained, which weighs 0.118 g. Subsequent treatment of the mixed chlorides with silver nitrate gives 0.2451 g of silver chloride. What is the percentage of sodium oxide and potassium oxide in feldspar. (1979)
- A white amorphous powder A when heated gives a colourless gas B, which turns lime water milky and the residue C which is yellow when hot but white when cold. The residue C dissolves in dilute HCl and the resulting solution gives a white precipitate on addition of potassium ferrocyanide solution. A dissolves in dilute HCl with the evolution of a gas which is identical in all respects with B. The solution of A as obtained above gives a white precipitate D on addition of excess of  $\text{NH}_4\text{OH}$  and on passing  $\text{H}_2\text{S}$ . Another portion of this solution gives initially a white precipitate E on addition of NaOH solution, which dissolves on further addition of the base. Identify the compounds A to E. (1979)
- A solution contains  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . 10 mL of the solution requires 2.5 mL of 0.1 M  $\text{H}_2\text{SO}_4$  for neutralization using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M  $\text{H}_2\text{SO}_4$  was required. Calculate the masses of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  per litre of the solution. (1979)
- 5.5 g of a mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  requires 5.4 mL of 0.1N  $\text{KMnO}_4$  solution for complete oxidation. Calculate the amount of hydrated ferric sulphate in the mixture. (1979)
- Compound A is a light green crystalline solid. It gives the following tests.
  - It dissolves in dilute sulphuric acid. No gas is produced.
  - A drop of  $\text{KMnO}_4$  is added to the above solution. The pink colour disappears.
  - Compound A is heated strongly. Gases B and C with pungent smell came out. A brown residue D is left behind.
  - The gas mixture (B and C) is passed into a dichromate solution. The solution turns green.
  - The green solution from step (iv) gives a white precipitate E with a solution of barium nitrate.
  - Residue D from (v) is heated on charcoal in reducing flame. It gives a magnetic substance.

Identify the compounds A to E. (1980)

10. A mixture contains NaCl and an unknown chloride MCl.
    - (i) 1 g of this is dissolved in water. Excess of acidified AgNO<sub>3</sub> solution is added to it. 2.567 g of a white precipitate is formed.
    - (ii) 1 g of the original mixture is heated to 300 °C. Some vapours come out which are absorbed in acidified AgNO<sub>3</sub> solution. 1.341 g of a white precipitate is obtained. Find the molar mass of the unknown chloride. (1980)
  11. One litre of a sample of hard water contains 1 mg of CaCl<sub>2</sub> and 1 mg of MgCl<sub>2</sub>. Find the total hardness in terms of parts of CaCO<sub>3</sub> per 10<sup>6</sup> parts of water by mass. (1980)
  12. A sample of hard water contains 20 mg Ca<sup>2+</sup> ions per litre. How many milli-equivalents of Na<sub>2</sub>CO<sub>3</sub> would be required to soften 1 L of the sample. (1980)
  13. (i) A sample of MnSO<sub>4</sub>·4H<sub>2</sub>O is strongly heated in air. The residue is Mn<sub>3</sub>O<sub>4</sub>.
  - (ii) The residue is dissolved in 100 mL of 0.1 M FeSO<sub>4</sub> containing dilute H<sub>2</sub>SO<sub>4</sub>.
  - (iii) The solution reacts completely with 50 mL of KMnO<sub>4</sub> solution.
  - (iv) 25 mL of the KMnO<sub>4</sub> solution used in step (iii) requires 30 mL of 0.1 M FeSO<sub>4</sub> solution for complete reaction.
- Find the mass of MnSO<sub>4</sub>·4H<sub>2</sub>O in the sample. (1980)
14. One litre of a mixture of CO and CO<sub>2</sub> is taken. The mixture is passed through a tube containing red-hot charcoal. The volume now becomes 1.6 L. The volumes are measured under the same conditions. Find the composition of the mixture by volume. (1980)
  15. A compound contains 28% of nitrogen and 72% of a metal by mass. 3 atoms of the metal combine with 2 atoms of nitrogen. Find the atomic mass of the metal. (1980)
  16. An aqueous solution of salt A gives a white crystalline precipitate B with NaCl solution. The filtrate gives a black precipitate C when H<sub>2</sub>S is passed through it. Compound B dissolves in hot water and the solution gives yellow precipitate D on treatment with potassium iodide and cooling. The compound A does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify the compounds A to D giving the involved equations. (1976)
  17. An unknown solid mixture contains one or two of the following.  
 CaCO<sub>3</sub>, BaCl<sub>2</sub>, AgNO<sub>3</sub>, ZnSO<sub>4</sub> and NaOH.  
 The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is formed which dissolves with further addition of the acid. What components is/are present in the solid? Give the involved chemical equations. (1981)
  18. When 16.8 g of white solid X was heated, 4.4 g of acid gas A that turned lime water milky was driven off together with 1.8 g of a gas B which condenses to a colourless liquid. The solid Y that remained is dissolved in water to give an alkaline solution, with which excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X. (1984)
  19. A mixture of two salts was treated as follows.
    - (i) The mixture was heated with MnO<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub> when yellowish-green gas was liberated.
    - (ii) The mixture on heating with NaOH solution gave a gas which turned red litmus blue.
    - (iii) Its solution in water gave blue precipitate with potassium ferricyanide and red colouration with ammonium thiocyanate.
    - (iv) The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K<sub>2</sub>HgI<sub>4</sub> to give brown precipitate. Identify the two salts. Give ionic equations for the reactions involved. (1987)
  20. A hydrated metallic salt A, light green in colour, gives a white anhydrous residue B after being heated gradually. B is soluble in water and its aqueous solution reacts with NO to give a dark brown compound C. B on strong heating gives a brown residue and a mixture of two gases E and F. The gaseous mixture, when passed through acidified permanganate, discharges the pink colour and when passed through acidified BaCl<sub>2</sub> solution, gives a white precipitate. Identify A, B, C, D, E and F. (1988)

21. When 20.02 g of a white solid X is heated, 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue of mass 1.38 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z. (1989)
22. A light bluish green crystalline compound responds to the following tests.
- Its aqueous solution gives a brown precipitate or colouration with alkaline  $K_2[HgI_4]$  solution.
  - Its aqueous solution gives a blue colour with  $K_3[Fe(CN)_6]$  solution.
  - Its solution in hydrochloric acid gives a white precipitate with  $BaCl_2$  solution. Identify the ions present and suggest the formula of the compound. (1992)
23. An orange solid A on heating gave a green residue B, a colourless gas C and water vapour. The dry gas C on passing over heated Mg gave a white solid D. D on reaction with water gave a gas E which formed dense white fumes with HCl. Identify A to E and give the reactions involved. (1993)
24. A is a binary compound of a univalent metal. 1.422 g of A reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid B that forms a hydrated double salt, C with  $Al_2(SO_4)_3$ . Identify A, B and C. (1994)
25. When the gas A is passed through dry KOH at low temperature, a deep red-coloured compound, B and a gas C are obtained. The gas A on reaction with but-2-ene, followed by treatment with  $Zn/H_2O$  yields acetaldehyde. Identify A, B and C. (1994)
26. A scarlet compound A is treated with concentrated  $HNO_3$  to give chocolate brown precipitate B. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate C. The precipitate B on warming with concentrated  $HNO_3$  in the presence of  $Mn(NO_3)_2$  produces a pink-coloured solution due to the formation of D. Identify A, B, C and D. Write the reaction sequence. (1995)
27. A  $5.0\text{ cm}^3$  solution of  $H_2O_2$  liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of  $H_2O_2$  solution in terms of volume strength at STP. (1995)
28. An equal volume of a reducing agent is titrated separately with 1 M  $KMnO_4$  in acid, neutral and alkaline media. The volumes of  $KMnO_4$  required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reduction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M  $K_2Cr_2O_7$  consumed, if the same volume of the reducing agent is titrated in an acid medium. (1989)
29. The composition of a sample of wüstite is  $Fe_{0.93}O_{1.00}$ . What percentage of the iron is present in the form of Fe(III)? (1994)
30. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B. (1996)
31. A colourless inorganic salt (A) decomposes completely at about  $250^\circ C$  to give only two products, (B) and (C), leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is a neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations of the reactions involved in the above process. (1966)
32. A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with sulphuric acid and distillation produces the liquid A again. Identify A, B and C and write the equations involved. (1997)
33. To a 25 mL  $H_2O_2$  solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 mL of 0.3 N sodium thiosulphate solution. Calculate the volume strength of  $H_2O_2$  solution. (1997)
34. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide. Identify A, B, C and D. (1997)
35. A soluble compound of a poisonous element M, when heated with  $Zn/H_2SO_4$  gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silvery mirror of element M. Identify M and N. (1997)

36. Compound **X** on reduction with  $\text{LiAlH}_4$  gives a hydride **Y** containing 21.72% hydrogen along with other products. The compound **Y** reacts with air explosively resulting in boron trioxide. Give balanced reactions involved in the formation of **Y** and its reaction with air. Draw the structure of **Y**. (2001)
37. A white substance **A** reacts with dilute  $\text{H}_2\text{SO}_4$  to produce a colourless gas **B** and a colourless solution **C**. The reaction between **B** and acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution produces a green solution and a slightly coloured precipitate **D**. The substance **D** burns in air to produce a gas **E** which reacts with **B** to yield **D** and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous  $\text{NH}_3$  or  $\text{NaOH}$  to **C** produces first a precipitate, which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify **A**, **B**, **C**, **D** and **E**. Write the equations of the reactions involved. (2001)
38. When a white crystalline compound **X** is heated with  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$ , a reddish brown gas **A** is evolved. On passing **A** into caustic soda solution, a yellow coloured solution of **B** is obtained. Neutralizing the solution of **B** with acetic acid and on subsequent addition of lead acetate, a yellow precipitate **C** is obtained. When **X** is heated with  $\text{NaOH}$  solution, a colourless gas is evolved and on passing this gas into  $\text{K}_2\text{HgI}_4$  solution, a reddish brown precipitate **D** is formed. Identify **A**, **B**, **C**, **D** and **X**. Write the equations of reaction involved. (2002)
39. A mixture consists of **A** (yellow solid) and **B** (colourless solid) which gives lilac colour in flame  
(a) Mixture gives black precipitate **C** on passing  $\text{H}_2\text{S(g)}$   
(b) **C** is soluble in aqua-regia and on evaporation of aqua-regia and adding  $\text{SnCl}_2$  gives grayish black precipitate **D**.  
(c) The salt solution with  $\text{NH}_4\text{OH}$  gives a brown precipitate.  
(d) The sodium extract of the salt with  $\text{CCl}_4/\text{FeCl}_3$  gives a violet layer.  
(e) The sodium extract gives yellow precipitate with  $\text{AgNO}_3$  which is insoluble in ammonia. Identify **A** and **B**, and the precipitates **C** and **D**. (2003)
40. There are two ores **A**<sub>1</sub> and **A**<sub>2</sub> of a metal **M**. (i) When the ore **A**<sub>1</sub> is calcined a black solid **S** is obtained alongwith the evolution of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . (ii) The ore **A**<sub>1</sub> on treatment with  $\text{HCl}$  and  $\text{KI}$  gives a precipitate **P** and iodine is liberated. (iii) The ore **A**<sub>2</sub> on roasting gives a gas **G** and metal **M** is free. (iv) When the gas **G** is passed through  $\text{K}_2\text{Cr}_2\text{O}_7$  it turns green. Identify **M**, **A**<sub>1</sub>, **A**<sub>2</sub>, **S**, **P** and **G**. (2004)

## ANSWERS

### Straight Objective Type

1. (a)      2. (a)      3. (a)      4. (a)      5. (c)      6. (a)      7. (b)  
8. (b)      9. (d)      10. (d)     11. (c)     12. (c)     13. (b)     14. (b)  
15. (b)     16. (a)     17. (d)

### Multiple Correct-Choice Type

1. (a), (c), (d)    2. (c), (d)

### Integer Answer Type

1. (7)      2. (4)

### True / False Type

1. True

**Reasoning Type**

1. (c)      2. (b)      3. (i) (b) (ii) (a)      4. (b)

**Linked-Comprehension Type****Passage-1**

1. (d)      2. (c)      3. (b)

**Passage-2**

1. (b)      2. (a)      3. (c)

**Passage-3**

1. (c)      2. (a)

**Passage-4**

1. (a)      2. (d)

**Passage-5**

1. (a)      2. (a)

**Matching Type**

1. (a)–(v) ; (b)–(s); (c)–(t); (d)–(p); (e)–(u); (f)–(q); (g)–(r)
2. (a)–(f)–(b); (b)–(c)–(f); (c)–(d)–(d); (d)–(b)–(a); (e)–(a)–(e); (f)–(e)–(c)
3. (a)–(f)–(c); (b)–(d)–(a); (c)–(c)–(f); (d)–(b)–(e); (e)–(e)–(d); (f)–(a)–(b)
4. (a)–(r); (b)–(t); (c)–(s); (d)–(b); (e)–(a)
5. (a)–(s); (b)–(q); (c)–(t); (d)–(r); (e)–(p)
6. (a)–(t); (b)–(r); (c)–(s); (d)–(p); (e)–(q)
7. (1)–(f); (2)–(h); (3)–(g); (4)–(c); (5)–(e); (6)–(d); (7)–(b); (8)–(a)
8. Mica–Layer structure–Insulator  
Superphosphate–Bone ash–Fertilizer.  
Carbon fibres–Graphite–Reinforced plastics  
Rock salt–Cubic–Preservative  
Carborundum–Diamond structure–Abrasives
9. (a)–(p); (b)–(q); (c)–(s); (d)–(r)
10. **Code (d):** (P)–(3); (Q)–4; (R)–(2); (S)–(1)

**Matrix Match Type**

1. The correct-bubbled diagram is as follows.

	p	q	r	s
a	●	○	○	●
b	○	○	●	○
c	●	●	○	○
d	●	○	○	○

## Short Answer Type

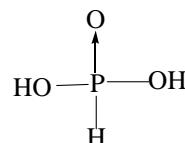
### I. Descriptive

1. (i) There exists hydrogen bondings in water which leads it to liquid while no such hydrogen bonding exists in  $\text{H}_2\text{S}$  which leads it to gas.  
(ii) The motion of molecules are random and the net force in any direction is zero.  
(iii)  $\text{Al}^{3+}$  hydrolyses water giving free  $\text{H}^+$  ions while no hydrolysis exits with  $\text{NaCl}$   
(iv) NO is converted to brown  $\text{NO}_2$  when it comes in contact with air  
(v) With  $\text{HNO}_3$ ,  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$   
(vi)  $\text{Cl}_2$  causes oxidative bleaching while  $\text{SO}_2$  causes reductive bleaching.
2. (i) Stannous chloride: It gives a silky white precipitate with mercuric ions only.  
(ii) Potassium iodide: It gives iodine only with cupric ions.  
(iii) Potassium permanganate solution: It is decolourised only by ferrous ions.  
(iv)  $\text{BaCl}_2$  solution with conc.  $\text{HCl}$ : It gives white precipitate only with sulphate.
3. (i) With sugar, sulphuric acid acts as a dehydrating agent  
(ii) With sulphur, sulphuric acid acts as an oxidising agent  
(iii) With  $\text{CaCO}_3$ , sulphuric acid acts as an acid.  
(iv) With copper, sulphuric acid acts as an oxidising agent.
4. (i) Because sodium reacts with air and moisture of the atmosphere.  
(ii) Addition of acid or base makes the water electrically conducting.  
(iii) Sodium hydroxide is a hygroscopic material and also absorbs  $\text{CO}_2$  from atmosphere. It is not a primary standard.  
(iv) Addition of dilute sulphuric acid prevents the hydrolysis and aerial oxidation of  $\text{Fe}^{2+}$  ions.  
(v) It forms characteristic coloured beads with coloured salts when fused together.
5. (i) Concentrated  $\text{H}_2\text{SO}_4$  converts  $\text{HBr}$  to  $\text{Br}_2$   
(ii)  $\text{HClO}$  is acidic in nature and is also a strong oxidising agent. It turns blue litmus to red followed by its oxidation.  
(iii)  $\text{HNO}_3$  acid will also cause the precipitation of S from  $\text{H}_2\text{S}$   
(iv) Atomic mass of an element is the weighted average of atomic masses of naturally occurring isotopes of the element.
6. (i) On adding dilute  $\text{HCl}$ ,  $\text{PbCO}_3$  gives out  $\text{CO}_2$  while  $\text{PbSO}_4$  remains unaffected.  
(ii)  $\text{CaCl}_2$  gives dull red colour to flame while  $\text{MgCl}_2$  does not impart any colour  
(iii)  $\text{AgNO}_3$  gives white precipitate with  $\text{Na}_2\text{S}_2\text{O}_3$  which are turned to brown and ultimately black. No such precipitates are formed with  $\text{Na}_2\text{SO}_3$ .
7. (i) Concentrated  $\text{HNO}_3$  decomposes to give  $\text{NO}_2$  which on dissolving in acid imparts yellow colour.  
(ii) Mg wire burns in the atmosphere of  $\text{CO}_2$  resulting into the reaction  $2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C}$   
(iii) Brown precipitates result from the hydrolysis of ferric salt ( $\text{FeCl}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3 + 3\text{HCl}$ ).  
(iv) With moist acid, bleaching property is lost due to libration of  $\text{Cl}_2$   

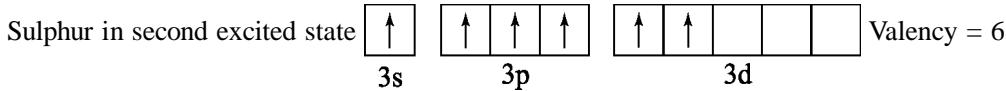
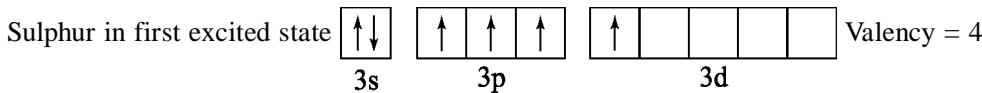
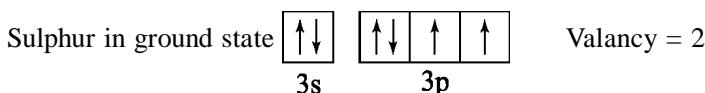
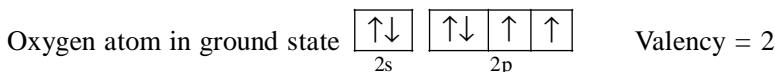
$$\text{CaOCl}_2 + \text{H}_2\text{O} \xrightarrow{\text{libration}} \text{Ca}(\text{OH})_2 + \text{Cl}_2$$
.  
(v)  $\text{CHCl}_3$  reacts with moisture in the presence of sunlight to give phosgene  

$$\text{CHCl}_3 + \text{H}_2\text{O} \xrightarrow{\text{h}\nu} \text{COCl}_2 + 2\text{HCl}$$
8. (i) Among the two allotropes of carbon, diamond is an abravise while graphite is a lubricant.  
(ii) Heating beyond  $160^\circ\text{C}$ , sulphur becomes viscous because  $\text{S}_8$  rings break up to form long chains  
(iii)  $\text{KHCO}_3$  being more soluble than  $\text{NaHCO}_3$  is not easily precipitated out.

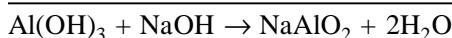
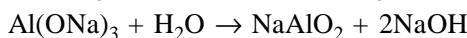
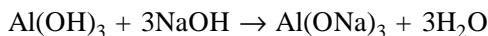
9. Sulphuric acid is a strong oxidising agent, it oxidises HI to I<sub>2</sub>. Because of this, phosphoric acid is preferred.
10. (i) Sodium sulphite is boiled with S.  $\text{Na}_2\text{SO}_3 + \text{S} \rightarrow \text{Na}_2\text{S}_2\text{O}_3$ .
- (ii) Slaked lime is treated with Cl<sub>2</sub>  $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \rightarrow \text{Ca}(\text{OCl})\text{Cl} + \text{H}_2\text{O}$ .
11. (i) Cooling liquor ammonia reduces its vapour pressure
- (ii) AgBr is converted into metallic silver grains when light falls on it.
- (iii) Solid CO<sub>2</sub> is directly converted into gaseous state
12. (i) Provided azeotropic mixture is not formed.
- (ii) Provided pressure is kept constant.
- (iii) Provided the metal is not of high electropositivity
- (iv) Provided the melting points of impurities are low
- (v) Provided  $T$  and  $P$  of the gases are identical.
13. (i) MgO is used for the lining of steel making furnace as it facilitates the removal of impurities of silicon, phosphorus and sulphur through slag formation.
- (ii) The mixture of N<sub>2</sub>H<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> with a Cu(II) catalyst is used as a rocket propellant because the reaction is highly exothermic and is accompanied with a large increase in volume.
- $$\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$$
- (iii) H<sub>3</sub>PO<sub>3</sub> is not a tribasic acid as only two hydrogen atoms are bonded to two oxygens.

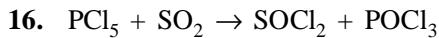


- (iv) Phenol is a very weak acid (weaker than carboxylic acid or even carbonic acid), and, therefore, does not react with NaHCO<sub>3</sub>.
- (v) The molecule of MgCl<sub>2</sub> is linear as sp hybrid orbitals of Mg are involved in bonding SnCl<sub>2</sub> is angular because sp<sup>2</sup> hybrid orbitals of Sn are involved in bonding.
14. (i) This is due to the formation of metallic mercury
- $$\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{Hg}(\text{NH}_2)\text{Cl} + \text{Hg} + \text{NH}_4\text{Cl}$$
- (ii) In contrast to oxygen, the octet can be expanded in sulphur using d orbitals.

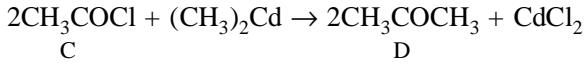
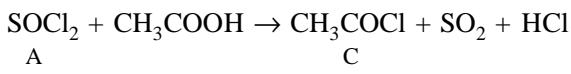


15. The precipitate of Al(OH)<sub>3</sub> dissolves in NaOH whereas that of Fe(OH)<sub>3</sub> does not. The solubility of Al(OH)<sub>3</sub> is due to the formation of meta-aluminates.





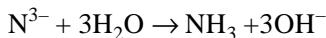
A                    B



Thus      A is  $\text{SOCl}_2$     :    B is  $\text{POCl}_3$   
           C is  $\text{CH}_3\text{COCl}$     :    D is  $\text{CH}_3\text{COCH}_3$

17. (a) Lone-pair-lone pair repulsion in N—F bond make this bond longer than the sum of the single bond covalent radii of N and F.

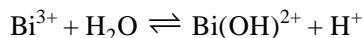
- (b)  $\text{N}^{3-}$  being smaller size and high charge make it more susceptible to hydrolysis:



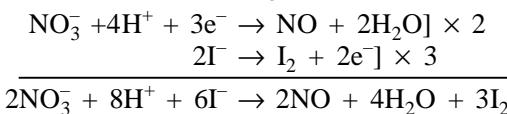
$\text{Cl}^-$  being a weak conjugate base does not undergo hydrolysis.

- (c) Back bonding in  $(\text{SiH}_3)_3\text{N}$  (lone pair on nitrogen sharing with the empty d orbital of Si) make the availability of lone pair on N less than that in  $(\text{CH}_3)_3\text{N}$ .

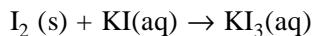
18.  $\text{Bi}^{3+}$  ions hydrolyse and give free  $\text{H}^+$  in solution



The liberated  $\text{H}^+$  along with  $\text{NO}_3^-$  ions oxidises  $\text{I}^-$  to  $\text{I}_2$  giving dark brown precipitate.

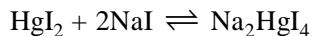


The dark brown precipitate of  $\text{I}_2$  dissolves in excess KI.



19.  $\text{Al}_2\text{S}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{S} + 2\text{Al}(\text{OH})_3$

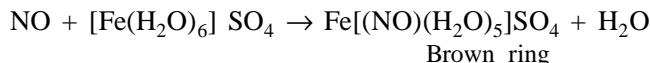
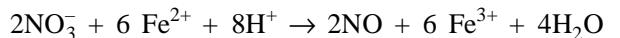
20. The reaction between  $\text{HgI}_2$  and NaI is reversible in nature:



The orange colour is due to the uncombined  $\text{HgI}_2$ . The addition of excess of NaI causes the reaction to proceed in the forward direction giving only colourless  $\text{Na}_2\text{HgI}_4$ .

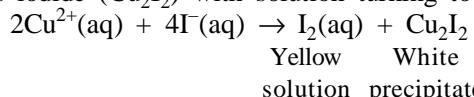
The addition of NaOCl causes the oxidation of  $\text{I}^-$  to  $\text{I}_2$  causing the above reaction to proceed to the left side with the appearance of orange colour.

21. To a nitrate solution in a test tube, ferrous sulphate is added. This is followed by the addition of concentrated sulphuric acid along the side of the test tube. A dark brown ring is obtained at the junction of the two liquids. Nitrate is reduced to NO, which combines with ferrous sulphate to give brown ring.



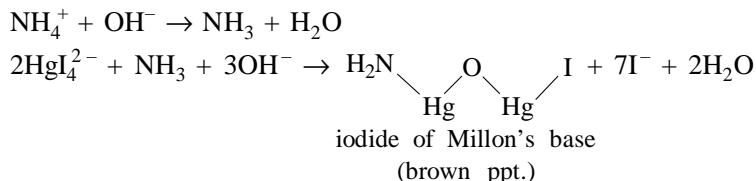
22. The transition metal ion is  $\text{Cu}^{2+}$ .

The compound is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . It dissolves in water to give blue-coloured solution. With  $\text{H}_2\text{S}$  in acidic medium, the black precipitate is due to the formation of  $\text{CuS}$ , which is soluble in acidic medium but not in alkaline medium. The addition of KI in aqueous solution of  $\text{CuSO}_4$  causes the precipitation of white precipitate of cuprous iodide ( $\text{Cu}_2\text{I}_2$ ) with solution turning to yellow due to the appearance of iodine. The reaction is



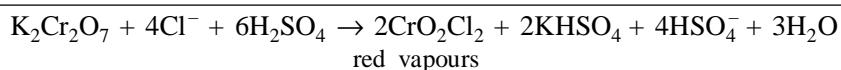
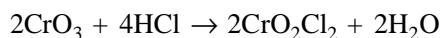
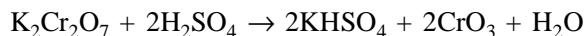
23. The observation

Mixture +  $\text{NaOH} \rightarrow$  gas which gives reddish-brown precipitate with an alkaline solution of  $\text{K}_2\text{HgI}_4$  indicates that the gas liberated is  $\text{NH}_3$  and the mixture contains  $\text{NH}_4^+$  ions.



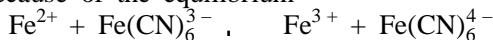
The white precipitate obtained by mixing  $\text{BaCl}_2$  with aqueous solution of the mixture indicates the presence of  $\text{SO}_4^{2-}$  ions. This is also indicated by the fact that  $\text{BaSO}_4$  is sparingly soluble in concentrated HCl.

On heating the mixture with  $\text{K}_2\text{Cr}_2\text{O}_7$  and concentrated  $\text{H}_2\text{SO}_4$ , red vapours (A) are produced. This indicates the presence of  $\text{Cl}^-$  ions. The reactions involved are as follows.



The reddish vapours are due to  $\text{CrO}_2\text{Cl}_2$ .

The deep blue colouration produced by mixing aqueous solution of the mixture and potassium ferricyanide solution indicates the presence of  $\text{Fe}^{2+}$  ions. The deep blue colouration is due to the formation of Turnbull's blue. In fact, because of the equilibrium



The solution contains

Chief products	$\left[ \begin{array}{l} \text{Ferric potassium ferrocyanide, } \text{Fe K}[\text{Fe}(\text{CN})_6] \\ \text{Ferro ferricyanide, } \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 \end{array} \right]$
Minor products	$\left[ \begin{array}{l} \text{Ferric ferrocyanide, } \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \\ \text{Ferro ferricyanide, } \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 \end{array} \right]$

## II. Increasing / Decreasing Characteristics

1. (i) HOI, HOBr, HOCl  
(ii) HOCl, HOClO, HOClO<sub>2</sub>, HOClO<sub>3</sub>

The larger the number of oxygen atoms attached to chlorine, greater the electron pull towards oxygen, hence, more easy to remove hydrogen from the acid.

2.  $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+}$

All the four species are isoelectronic ( $1s^2 2s^2 2p^6$ ). The number of positive charges in the nucleus decreases in the order  $_{12}\text{Mg} > _{11}\text{Na} > _9\text{F} > _8\text{O}$ . Hence,  $\text{O}^{2-}$  involved minimum nucleus-electrons attraction and maximum electron-electron repulsion while  $\text{Mg}^{2+}$  involves maximum nucleus-electrons attraction and minimum electron-electron repulsion. These factors make the size of anion greater than the corresponding neutral atom and that of cation lesser than the corresponding atom.

3.  $\text{Na}_2\text{O}_2 < \text{MgO} < \text{ZnO} < \text{P}_2\text{O}_5$

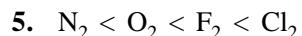
Oxides of electropositive elements are alkaline while those of electronegative elements are acidic. Alkaline property will increase with increase in electropositive character of metal and acidic characteristics increase with increase in electronegative characteristics of nonmetals. Since the electronegativity increases in the order Na < Mg < Zn < P, the acidic character of oxide will also increase in the same order.

4. Na < Al < Mg < Si

The electronic configurations of given elements are

$_{11}\text{Na}$	$(1s)^2(2s)^2(2p)^6(3s)^1$	$_{13}\text{Al}$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^1$
$_{12}\text{Mg}$	$(1s)^2(2s)^2(2p)^6(3s)^2$	$_{14}\text{Si}$	$(1s)^2(2s)^2(2p)^6(3s)^2(3p)^2$

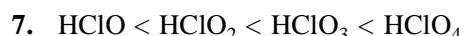
Aluminium will have lower ionization potential than magnesium as the removal of one electron leads to the formation of stable completely filled orbital configuration. So it is loosely held and can be removed more easily than to remove electron from filled 3s orbital of magnesium atom.

**18.22** IIT Chemistry: Topic-wise Solved Questions

Nitrogen contains triple bond, oxygen contains double bond and fluorine and chlorine contain a single bond each. Chlorine involves bonding of 3p orbitals while fluorine involves 2p orbitals.



The given species are isoelectronic. The size of cation will be the smallest. The mononegative anion will have smaller size than the dinegative anion. The size of the noble gas Ar will be maximum.

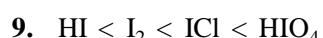


These acids are better represented as  $\text{Cl} - \text{OH}$ ,  $\text{OCl} - \text{OH}$ ,  $\text{O}_2\text{Cl} - \text{OH}$ ,  $\text{O}_3\text{Cl} - \text{OH}$ .

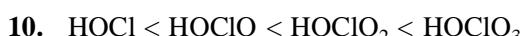
The larger the number of oxygen atoms attached to chlorine, greater the electron pull towards oxygen, hence, more easy to remove hydrogen from the acid.



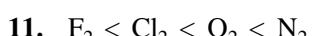
As the size of the halogen atom increases, the strength of HX bond decreases. Besides this, decreasing per cent ionic character from HF to HI makes the bond less stable.



The oxidation states of iodine in HI,  $\text{I}_2$ ,  $\text{ICl}$  and  $\text{HIO}_4$  are  $-1$ ,  $0$ ,  $+1$  and  $+7$ , respectively.



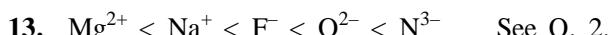
The stability is explained by the increasing number of electrons involved in the formation of s and p bonds in going from HOCl to HOClO<sub>3</sub>. In ClO<sub>4</sub><sup>-</sup> ion all the valence orbitals and electrons of chlorine are involved in the formation of bonds.



$\text{N}_2$  involves a triple bond,  $\text{O}_2$  involves a double bond,  $\text{F}_2$  and  $\text{Cl}_2$  involve a single bond each.  $\text{F}_2$  has a lower bond enthalpy than  $\text{Cl}_2$ . This is due to more repulsion of nonbonding electrons in  $\text{F}_2$ . Besides this, there is a possibility of multiple bonding in  $\text{Cl}_2$  involving d orbitals.



Increasing electronegativity of an element makes its oxide more acidic.



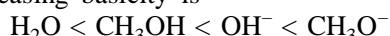
Increasing electropositive nature of the element makes its oxide more basic.



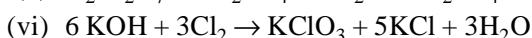
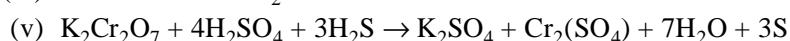
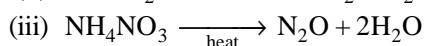
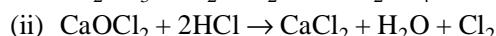
In covalent halides, hydrolysis occurs as a result of coordination of a water molecule to the less electronegative element. CCl<sub>4</sub> does not undergo hydrolysis as carbon cannot expand its octet to accommodate water molecules.



The negative charge on X in HX increases with increasing electronegativity of X. This makes the hydrogen bonding more strong.

**III. Predicting Chemical Reactions**

1. The balanced equations are



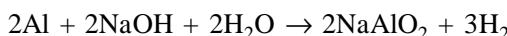
2. (i) There is evolution of  $\text{NO}_2$  gas.



- (ii) There is evolution of  $\text{SO}_2$  gas.



- (iii) There is evolution of  $\text{H}_2$  gas.



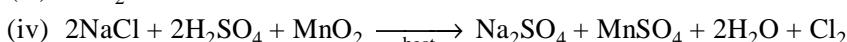
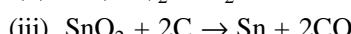
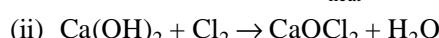
- (iv) There is evolution of  $\text{N}_2$  gas.



- (v) There is evolution of S.



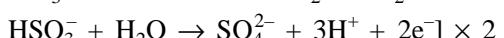
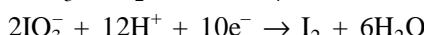
3. (i)  $\text{Al}_2\text{O}_3 + 3\text{Cl}_2 + 3\text{C} \xrightarrow{\text{heat}} 2\text{AlCl}_3 + 3\text{CO}$



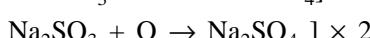
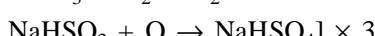
### Writing Balanced Chemical Equations



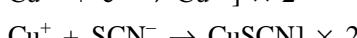
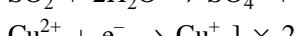
2. This is a redox reaction where  $\text{HSO}_3^-$  is a reducing agent and  $\text{IO}_3^-$  is an oxidising agent.



The third reaction namely the oxidation of  $\text{HSO}_3^-$  to  $\text{SO}_4^{2-}$  is written so as to have no  $\text{H}^+$  in the final reaction.  
Molecular reaction may be derived either from the above expression or as follows.

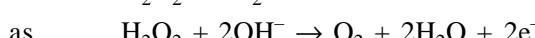


3. This is a composite reaction, where  $\text{SO}_2$  reduces copper(II) to copper(I) followed by the formation of  $\text{CuSCN}$ .



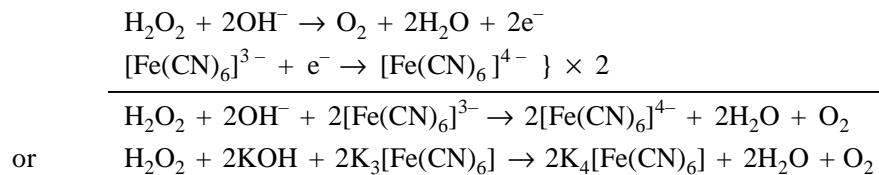
or  $\text{SO}_2 + 2\text{H}_2\text{O} + 2\text{CuSO}_4 + 2\text{KSCN} \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4 + 2\text{CuSCN}$

4. This is redox reaction where  $\text{H}_2\text{O}_2$  acts as a reducing agent. It reduces ferricyanide to ferrocyanide. Since the reaction is carried out in alkaline medium, we write

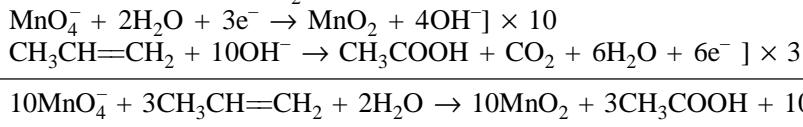


Hence, the reactions occurring are

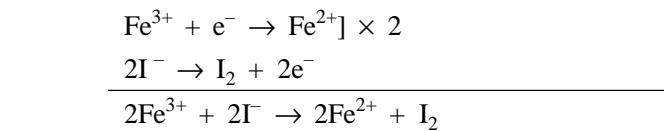
**18.24** IIT Chemistry: Topic-wise Solved Questions



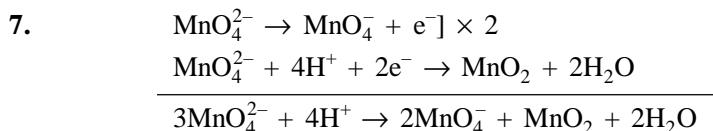
5. Since the reaction is carried out in hot aqueous medium, permanganate oxidises propene to propanoic acid and itself is reduced to  $\text{MnO}_2$ .



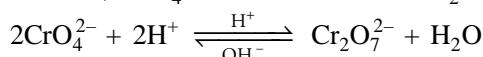
6. This is redox reaction where ferric oxidises  $\text{I}^-$  to  $\text{I}_2$



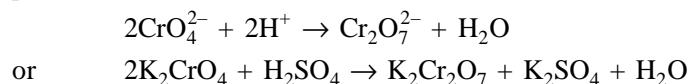
or  $\text{Fe}_2(\text{SO}_4)_3 + 2\text{KI} \rightarrow 2\text{FeSO}_4 + \text{I}_2 + \text{K}_2\text{SO}_4$



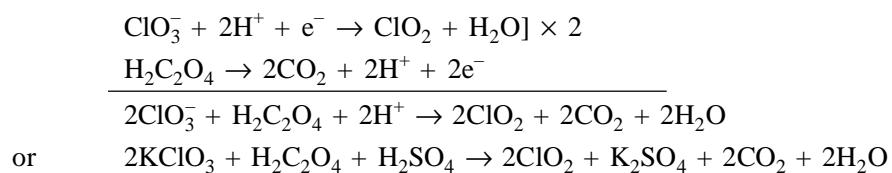
8. In acidic medium,  $\text{CrO}_4^{2-}$  is transformed to  $\text{Cr}_2\text{O}_7^{2-}$ , as the reaction



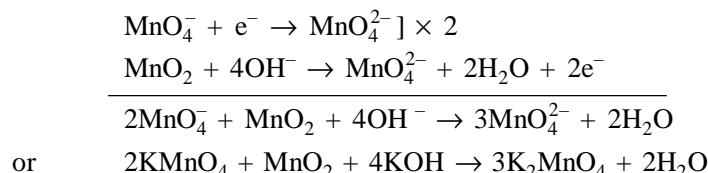
proceeds to the forward direction. Thus, the reaction is



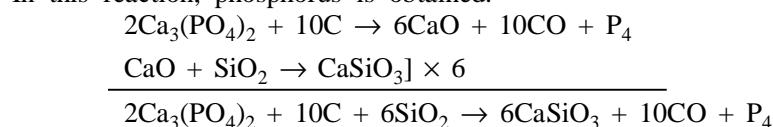
9. In this reaction, chlorate ion oxidises oxalic acid to  $\text{CO}_2$  and itself is reduced to  $\text{ClO}_2$ .



10. In this reaction, permanganate oxidises  $\text{MnO}_2$  to manganate and itself is reduced to manganate.



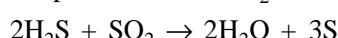
11. In this reaction, phosphorus is obtained.



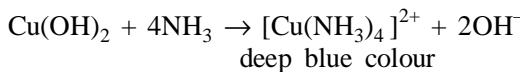
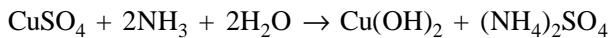
12.  $\text{K}_4\text{Fe}(\text{CN})_6 + 6\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{K}_2\text{SO}_4 + \text{FeSO}_4 + 6\text{CO} + 3(\text{NH}_4)_2\text{SO}_4$

13.  $(\text{NH}_4)_2\text{SO}_4 + \text{NO} + \text{NO}_2 \rightarrow \text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} + 2\text{N}_2$

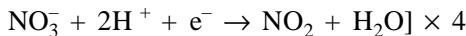
14. Hydrogen sulphide reduces  $\text{SO}_2$  to S and itself is oxidised to S. There is a formation of colloidal sulphur.



15. There is first formation of green precipitate of  $\text{Cu}(\text{OH})_2$  which dissolves in excess of  $\text{NH}_3$  forming blue tetramminecopper complex.

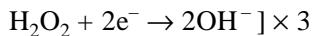
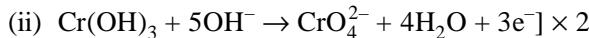
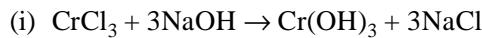


16. With concentrated nitric acid, hydrated stannic oxide (metastannic acid) is formed.

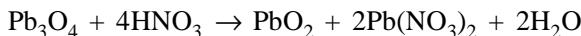


The exact formula of metastannic acid is  $(\text{SnO}_2 \cdot \text{H}_2\text{O})_5$ .

17. With  $\text{NaOH}$ , green coloured precipitate of  $\text{Cr}(\text{OH})_3$  is formed which is dissolved as chromate due to the oxidation by  $\text{H}_2\text{O}_2$ .



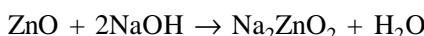
18.  $\text{Pb}_3\text{O}_4$  is a mixed oxide,  $2\text{PbO} \cdot \text{PbO}_2$ . With nitric acid,  $\text{PbO}$  is converted to  $\text{Pb}(\text{NO}_3)_2$  while  $\text{PbO}_2$  remains as such.



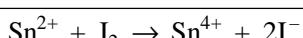
19. Chlorine displaces bromide as bromine and it is reduced to  $\text{Cl}^-$



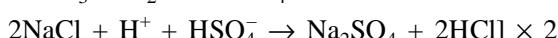
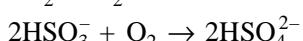
20.  $\text{ZnO}$  is dissolved as zincate ion.



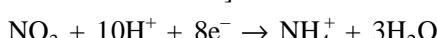
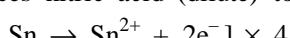
21.  $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2\text{e}^-$



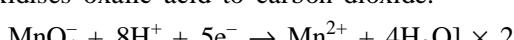
22. The products are sodium sulphate and  $\text{HCl}$ .



23. Tin reduces nitric acid (dilute) to ammonia.

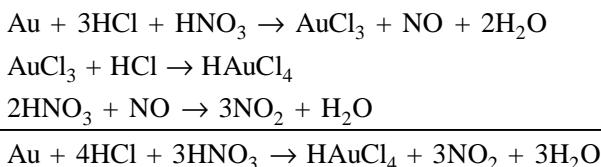


24.  $\text{MnO}_4^-$  oxidises oxalic acid to carbon dioxide.



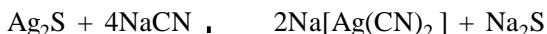
or  $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5(\text{COOH})_2 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 10\text{CO}_2 + 8\text{H}_2\text{O}$

25. Gold dissolves in aqua regia as  $\text{HAuCl}_4$ .

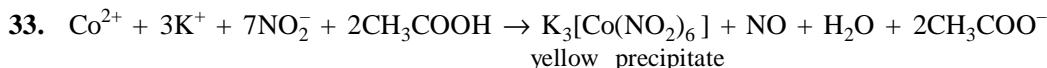
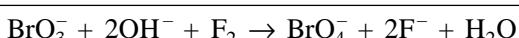
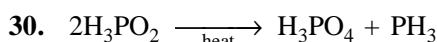
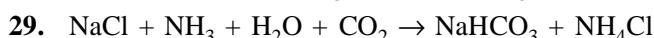
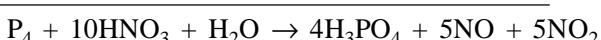
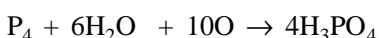
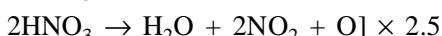
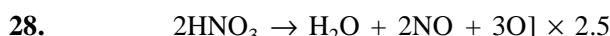
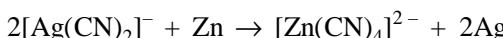


26. Same as reaction (2).

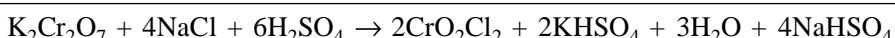
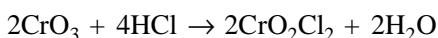
27. After the concentration of ore, it is treated with dilute solution of sodium cyanide.



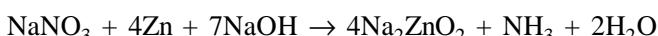
A current of air is simultaneously passed through the solution so as to oxidise  $\text{Na}_2\text{S}$  to  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{Na}_2\text{SO}_4$ , thus the reaction proceeds to completion. The addition of Zn replaces Ag from the complex.



35. This produces chromyl chloride.



36. Nitrate is reduced to ammonia.

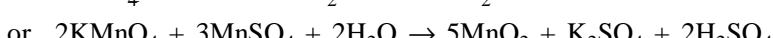
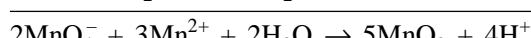
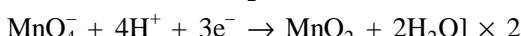


37. Same as reaction (2).

38. With cold dilute acid, iron produces ferrous nitrate and ammonium nitrate.

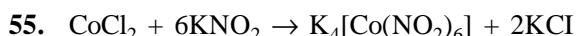
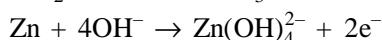
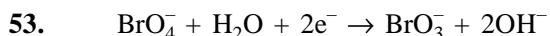
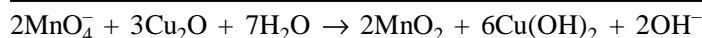
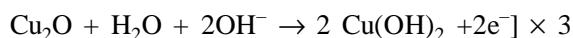
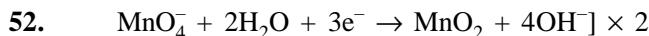


39.  $\text{MnO}_4^-$  oxidises  $\text{Mn}^{2+}$  to  $\text{MnO}_2$  and is itself reduced to  $\text{MnO}_2$ .

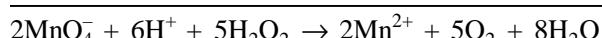
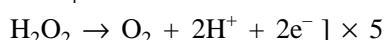
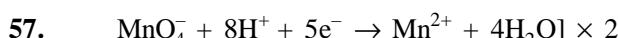
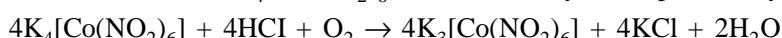


40.  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$   
 $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NaOH}$   
 $\text{NaOH} + \text{HNO}_2 \rightarrow \text{NaNO}_2 + \text{H}_2\text{O}$   
 $\text{NaHCO}_3 + \text{HNO}_2 \rightarrow \text{NaNO}_2 + \text{CO}_2 + \text{H}_2\text{O}$   
 $\text{Na}_2\text{CO}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{NaNO}_2 + \text{CO}_2$
41.  $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-] \times 2$   
 $2\text{NH}_3 + 6\text{OH}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} + 6\text{e}^-$   
 $2\text{MnO}_4^- + 2\text{NH}_3 \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + 2\text{H}_2\text{O} + \text{N}_2$   
or  $2\text{KMnO}_4 + 2\text{NH}_3 \rightarrow 2\text{MnO}_2 + 2\text{KOH} + 2\text{H}_2\text{O} + \text{N}_2$
42.  $\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}] \times 20$   
 $\text{P}_4 + 10\text{H}_2\text{O} \rightarrow 2\text{P}_2\text{O}_5 + 20\text{H}^+ + 20\text{e}^-$   
 $\text{P}_2\text{O}_5 + 3\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4] \times 2$   
 $20\text{NO}_3^- + 20\text{H}^+ + \text{P}_4 \rightarrow 20\text{NO}_2 + 4\text{H}_2\text{O} + 4\text{H}_3\text{PO}_4$
43.  $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-] \times 2$   
 $\text{C}_2\text{H}_4 + 2\text{OH}^- \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + 2\text{e}^-] \times 3$   
 $2\text{MnO}_4^- + 3\text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 2\text{OH}^- + 3\text{HOCH}_2\text{CH}_2\text{OH}$
44.  $2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2$   
 $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$   
 $2\text{NaHSO}_3 + 2\text{H}_2\text{S} \rightarrow \text{Na}_2\text{SO}_3 + 3\text{H}_2\text{O} + 3\text{S}$
45.  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2$
46.  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-] \times 7$   
 $\text{HNO}_3 + \text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}] \times 2$   
 $\text{HNO}_3 + 3\text{H}^+ + 3\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{NO}] \times 4$   
 $7\text{Cu} + 6\text{HNO}_3 + 14\text{H}^+ \rightarrow 7\text{Cu}^{2+} + 2\text{NO}_2 + 4\text{NO} + 10\text{H}_2\text{O}$   
or  $7\text{Cu} + 20\text{HNO}_3 \rightarrow 7\text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 4\text{NO} + 10\text{H}_2\text{O}$
47. On adding  $\text{Na}_2\text{CO}_3$  to copper sulphate solution, the solution becomes alkaline and thus  $\text{Cu}(\text{OH})_2$  is precipitated. The net reaction is  
 $\text{CuSO}_4 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2 + \text{Na}_2\text{SO}_4 + \text{CO}_2$
48.  $2\text{P} + 3\text{I}_2 + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_3 + 6\text{HI}$
49.  $2\text{KNO}_3(\text{s}) + 10\text{K}(\text{s}) \rightarrow 6\text{K}_2\text{O}(\text{s}) + \text{N}_2$
50.  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$   
 $2\text{HCl} \rightarrow \text{Cl}_2 + 2\text{H}^+ + 2\text{e}^-] \times 3$   
 $\text{Cr}_2\text{O}_7^{2-} + 6\text{HCl} + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{Cl}_2$   
or  $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \rightarrow 2\text{KCl} + 2\text{CrCl}_3 + 7\text{H}_2\text{O} + 3\text{Cl}_2$
51. Fluoroapatite on treating with phosphoric acid gives triple superphosphate.  
 $[\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2] + 6\text{H}_3\text{PO}_4 \rightarrow 4\text{Ca}(\text{H}_2\text{PO}_4)_2 + 2\text{HF}$   
fluroapatite triple superphosphate

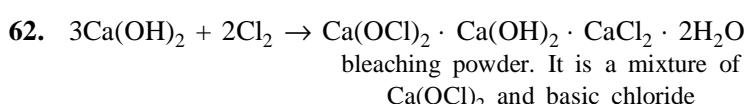
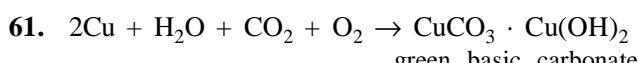
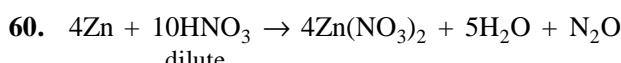
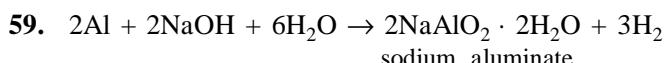
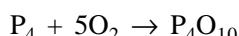
**18.28** IIT Chemistry: Topic-wise Solved Questions



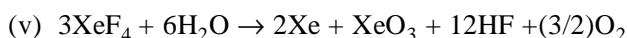
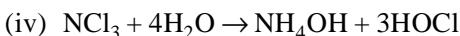
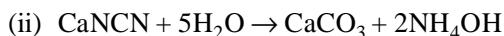
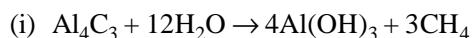
In acidic medium,  $\text{K}_4[\text{Co}(\text{NO}_2)_6]$  is oxidised by atmospheric oxygen



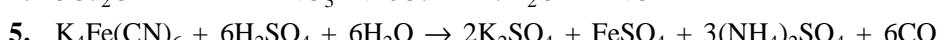
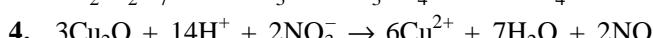
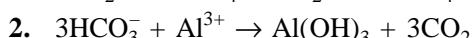
58. Manufacture of phosphoric acid from phosphorus is carried out by the ‘furnace process’. Molten phosphorus is burnt in a furnace with air and steam. First  $\text{P}_4\text{O}_{10}$  is formed by reaction between phosphorus and oxygen and then this is immediately hydrolysed.



63. The balanced chemical equations are as follows



#### Completing and Balancing Chemical Equations



6.  $\text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + 6\text{OH}^- \rightarrow \text{HCO}_2^- + 5\text{I}^- + 5\text{H}_2\text{O} + \text{CHI}_3$
7.  $4\text{Zn} + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Zn}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O}$
8.  $\text{Cr}_2\text{O}_7^{2-} + 3\text{C}_2\text{H}_4\text{O} + 8\text{H}^+ \rightarrow 3\text{C}_2\text{H}_4\text{O}_2 + 2\text{Cr}^{3+} + 4\text{H}_2\text{O}$
9.  $2\text{HNO}_3 + 6\text{HCl} \rightarrow 2\text{NO} + 3\text{Cl}_2 + 4\text{H}_2\text{O}$
10.  $2\text{Ce}^{3+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{Ce}^{4+} + 2\text{SO}_4^{2-}$
11.  $\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$
12.  $2\text{NH}_3 + \text{NaOCl} \rightarrow \text{H}_2\text{NNH}_2 + \text{NaCl} + \text{H}_2\text{O}$
13.  $\text{AgBr} + 2\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2] + \text{NaBr}$
14.  $(\text{NH}_4)_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O} + \text{MnSO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{MnO}_2 + 2\text{H}_2\text{SO}_4$
15.  $3[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO}_3^- + 4\text{H}^+ \rightarrow \text{NO} + 3[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 2\text{H}_2\text{O}$   
 $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO} \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+} + \text{H}_2\text{O}$
16.  $3\text{PbS} \xrightarrow[\text{air}]{\text{heat in}} 2\text{PbO} + \text{PbS} \xrightarrow{\text{heat}} 3\text{Pb} + \text{SO}_2$
17. (i)  $3\text{MnO}_4^- + 4\text{H}^+ \rightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 2\text{H}_2\text{O}$   
(ii)  $\text{Ca}_5(\text{PO}_4)_3\text{F} + 5\text{H}_2\text{SO}_4 + 10\text{H}_2\text{O} \xrightarrow{\text{heat}} 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{HF}$   
(iii)  $3\text{SO}_2(\text{aq}) + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{SC}_4^{2-} + \text{H}_2\text{O}$   
(iv)  $\text{Sn} + 2\text{KOH} + 4\text{H}_2\text{O} \rightarrow \text{K}_2\text{Sn}(\text{OH})_6 + 2\text{H}_2$
18. (i)  $\text{P}_4\text{O}_{10} + 6\text{PCl}_5 \rightarrow 10\text{POCl}_3$   
(ii)  $\text{SnCl}_4 + 2\text{C}_2\text{H}_5\text{Cl} + \text{Na} \rightarrow \text{C}_4\text{H}_{10} + \text{Na}_2[\text{SnCl}_6]$

### Subjective Type

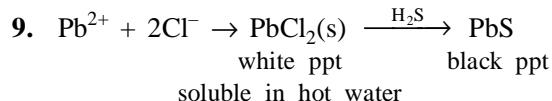
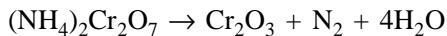
1. 20.04% FeO; 79.96%  $\text{Fe}_3\text{O}_4$
2. 59.33%
3. (A)  $\text{FeSO}_4$ ; (B)  $\text{BaSO}_4$ ; (C)  $\text{SO}_2$ ; (D)  $\text{SO}_3$ ;  
(E)  $\text{Fe}_2\text{O}_3$  (F)  $\text{FeCl}_3$ ; (G) S; (H)  $\text{FeCl}_2$
4. 0.565 g Al and 0.435 g Mg per gram of alloy.
5. 3.58%  $\text{Na}_2\text{O}$  and 10.62%  $\text{K}_2\text{O}$
6. (A)  $\text{ZnCO}_3$ ; (B)  $\text{CO}_2$ ; (C)  $\text{ZnO}$ ; (D)  $\text{ZnS}$   
(E)  $\text{Zn}(\text{OH})_2$
7. 5.3 g of  $\text{Na}_2\text{CO}_3$  and 4.2 g  $\text{NaHCO}_3$  per litre of the solution.
8. 0.00952 mol of hydrated ferric sulphate
9. (A)  $\text{FeSO}_4$ ; (B)  $\text{SO}_2$ ; (C)  $\text{SO}_3$ ;  
(D)  $\text{Fe}_2\text{O}_3$  (E)  $\text{BaSO}_4$ .
10.  $53.52 \text{ g mol}^{-1}$
11. 1.954 ppm
12. 1 meq
13. 1.338 g
14.  $n(\text{CO}_2): n(\text{CO}) :: 3:2$
15. 24 g  $\text{mol}^{-1}$
16. (A)  $\text{Pb}(\text{NO}_3)_2$ ; (B)  $\text{PbCl}_2$ ; (C)  $\text{PbS}$ ; (D)  $\text{PbI}_2$
17.  $\text{ZnSO}_4$  and  $\text{NaOH}$
18. (X)  $\text{NaHCO}_3$ ; (A)  $\text{CO}_2$ ; (B)  $\text{H}_2\text{O}$   
(Y)  $\text{Na}_2\text{CO}_3$
19.  $\text{NH}_4\text{Cl}$  and  $\text{FeCl}_2$
20. (A)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; (B)  $\text{FeSO}_4$ ;  
(C)  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$  (D)  $\text{Fe}_2\text{O}_3$ ;  
(E) and (F)  $\text{SO}_2$  and  $\text{SO}_3$ .
21. (A)  $\text{CO}_2$ ; (B)  $\text{H}_2\text{O}$ ; (X)  $\text{KHCO}_3$ ;  
(Y)  $\text{K}_2\text{CO}_3$
22.  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
23. (A)  $\text{NH}_4\text{Cr}_2\text{O}_7$ ; (B)  $\text{Cr}_2\text{O}_3$ ; (C)  $\text{N}_2$ ;
24. (A)  $\text{KO}_2$ ; (B)  $\text{K}_2\text{SO}_4$ ;

- (D)  $Mg_3N_2$  (E)  $NH_3$
25. (A)  $O_3$ ; (B)  $KO_3$ ; (C)  $O_2$
27. 4.48
29. 15.05
31. (A)  $NH_4NO_3$ ; (B)  $N_2O$ ; (C)  $H_2O$
33. 1.345
35. (M) As; (N)  $AsH_3$
37. (A)  $ZnS$ ; (B)  $H_2S$ ; (C)  $ZnSO_4$ ; (D) S;  
(E)  $SO_2$ .
39. (A)  $HgI_2$ ; (B) KI; (C)  $HgS$ ; (D) Hg.
- (C)  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
26. (A)  $Pb_3O_4$ ; (B)  $PbO_2$ ; (C)  $PbI_2$ ;  
(D)  $Pb(MnO_4)_2$
28. 16.7 mL
30. (A)  $NH_3$ ; (B)  $CaCO_3$
32. (A)  $Br_2(l)$ ; (B)  $NaBr$ ; (C)  $NaBrO_3$
34. (A) Ba; (B)  $Ba_3N_2$ ; (C)  $Ba(OH)_2$ ;  
(D)  $BaCO_3$ .
36. (X)  $BF_3$ ; (B)  $B_2H_6$ .
38. (X)  $NH_4Cl$ ; (B)  $CrO_2Cl_2$ ; (C)  $Na_2CrO_4$   
(C)  $PbCrO_4$ ; (D)  $H_2N-Hg-O-Hg-I$ .
40. (M) Cu; (A<sub>1</sub>)  $CuCO_3 \cdot Cu(OH)_2$ ;  
(A<sub>2</sub>)  $Cu_2S$ ; (S)  $CuO$ ; (P)  $Cu_2I_2$ ; (G)  $SO_2$ .

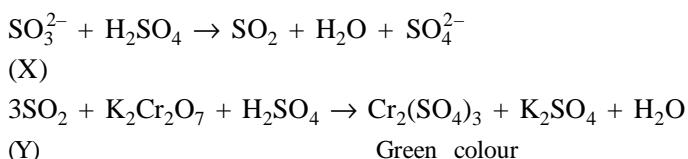
## HINTS AND SOLUTIONS

### Straight Objective Type

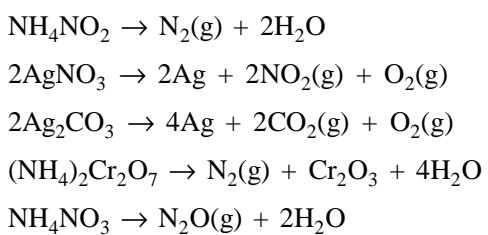
6. The Acid strength increases with increase in the electronegativity of the halogen atom.
8. Heating ammonium dichromate produces green coloured  $Cr_2O_3$  powder, which is blown in air by large volume of accompanying nitrogen gas and water vapour:



10. The pair contains  $SO_3^{2-}$  and  $SO_2$ .



11. The heating of given compounds produces gases as shown in the following:



Thus,  $(NH_4)_2Cr_2O_7$  produces the same gas as produced by  $NH_4NO_2$ .

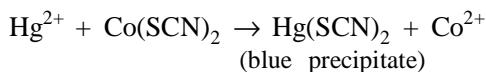
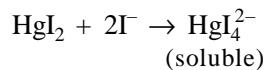
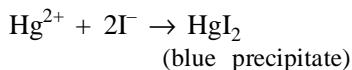
12. Bismuth ions give black precipitates with KI solution which dissolve in excess of KI to give orange-coloured solution. The reactions are



13. The hydroxide formed in aqueous solution is  $\text{Al}(\text{OH})_3$ .

14. The precipitation is of  $\text{Mg}(\text{NH}_4)\text{PO}_4$ .

15. The involved reactions are as follows

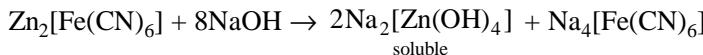
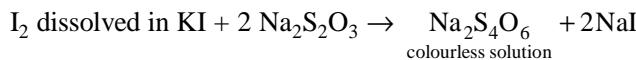
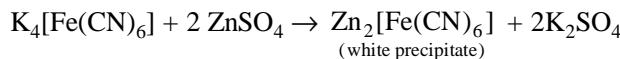
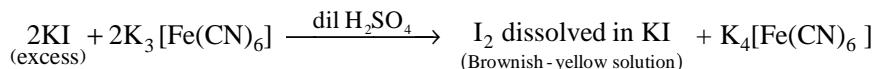


16. In acidic medium, when  $\text{H}_2\text{S}$  is passed, only the cations of Group II precipitate which include  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  ions. The ions  $\text{Mn}^{2+}$  and  $\text{Ni}^{2+}$  are precipitated in Group IV in which  $\text{H}_2\text{S}$  is passed in the presence of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ .

17. Zn(II) precipitates as ZnS when  $\text{H}_2\text{S}$  is passed through the ammoniacal solution of Zn(II) salt.

### Multiple Correct-Choice Type

1. The given reactions are as follows.



The first reaction is a redox reaction. Filtrate contains free iodine, so it gives blue colouration with starch solution.

2.  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  (Choice c) and also  $\text{Hg}^{2+}$  and  $\text{Bi}^{3+}$  belong to the same group of salt analysis. These are precipitated as sulphides when  $\text{H}_2\text{S}$  is passed in acidic medium.

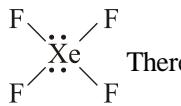
### Integer Answer Type

1. The black-coloured sulphides are :  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{HgS}$ ,  $\text{Ag}_2\text{S}$ ,  $\text{NiS}$ ,  $\text{CoS}$  and  $\text{Bi}_2\text{S}_3$ .

The yellow-coloured sulphide is  $\text{SnS}_2$ .

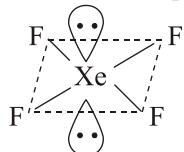
There are **seven** black-coloured sulphides.

2.  $\text{XeF}_4$ ; valence electrons =  $8 + 4 \times 7 = 36$ . Electronic distribution around  $\text{XeF}_4$  is



There are six pairs of electrons around Xe. The hybridization is  $\text{sp}^3\text{d}^2$  of Xe orbitals

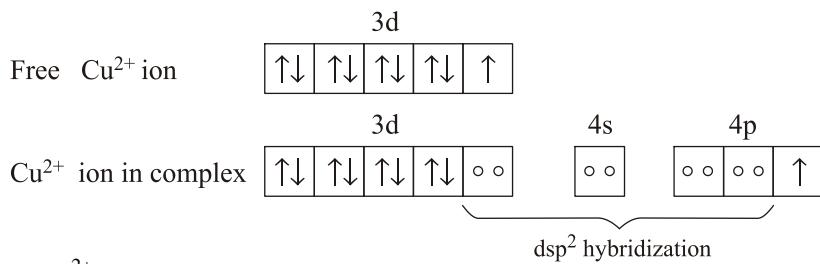
The actual shape is



The shape of  $\text{XeF}_4$  is square planar.

Working similarly, we find that  $\text{BrF}_4^-$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{PtCl}_4]^{2-}$  are also square planar. The explanations of the later two complexes are given in the following.

In  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , we have



The shape of  $\text{Cu}(\text{NH}_3)_4^{2+}$  is square planar.

In  $[\text{PtCl}_4]^{2-}$ , the electronic configuration of free  $\text{Pt}^{2+}$  ion is  $5\text{d}^8$ . The orbitals of Pt will undergo  $\text{dsp}^2$  hybridization to accommodate four  $\text{Cl}^-$  ligands and thus the shape of  $[\text{PtCl}_4]^{2-}$  is also square planar.

$[\text{FeCl}_4]^{2-}$  and  $[\text{CoCl}_4]^{2-}$  involve  $\text{sp}^3$  hybridization as there is no empty d orbital in the electronic configurations of free  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  ions and the ligand  $\text{Cl}^-$ , being a weak ligand, is not able to pair the 3d electrons.

$\text{SiF}_4$  and  $\text{BF}_4^-$  (no d orbitals available in B) involve  $\text{sp}^3$  hybridization.

$\text{SF}_4$  has five pairs of electrons around sulphur and thus involve  $\text{dsp}^3$  hybridization.

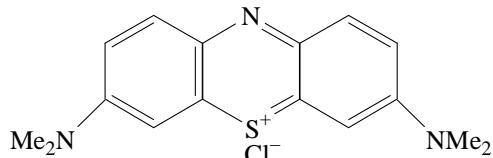
## **Reasoning Type**

1. Alkali metals dissolve in liquid ammonia to give ammoniated cations and ammoniated electrons. The blue colour of the solution is due to solvated electrons. Hence, the assertion (statement 1) is correct but the reason (statement 2) though correct, is not the true explanation.

## **Linked-Comprehension Type**

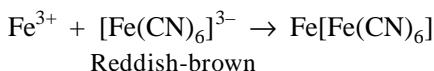
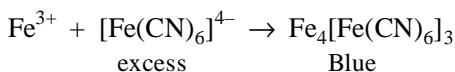
## **Passage-1**

1. The structure of methylene blue is



It follows that X must be  $\text{Na}_2\text{S}$ .

2. The involved reactions are as follows.

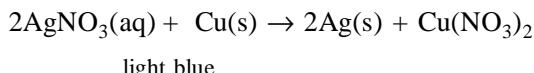


From the reactions of Y with  $K_4Fe(CN)_6$  and  $K_3Fe(CN)_6$ , it follows that Y is  $FeCl_3$ .

3. From the reactions shown in Eq. (17), it follows that Z is  $\text{Fe}[\text{Fe}(\text{CN})_6]$ .

## **Passage-2**

The metal M will be that of Cu, which reacts with the colourless compound N, which must be  $\text{AgNO}_3$ . The reaction is

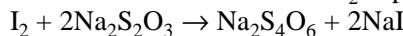
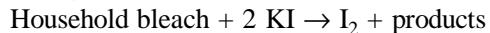


The addition of aqueous NaCl will cause the white precipitation of AgCl with the unreacted AgNO<sub>3</sub> in the solution.

The addition of aqueous ammonia forms the complex with  $\text{Ag}^+$  (from  $\text{AgNO}_3$  or/and from the dissolution of  $\text{AgCl}$  precipitates) and  $\text{Cu}^{2+}$  ions. The complexes are  $[\text{Ag}(\text{NH}_3)_2]^+$  and  $[\text{Cu}(\text{NH}_3)_4]^{2-}$ . The latter imparts intense blue colour in the solution. Hence, the **choice (b)** of Q. 1, **choice (a)** of Q. 2 and **choice (c)** of Q. 3 are correct.

**Passage-3**

For Q.1, we may write



$$\text{Amount of Na}_2\text{S}_2\text{O}_3 \text{ used} = VM = (48 \times 10^{-3} \text{ L}) (0.25 \text{ mol L}^{-1}) = 12 \times 10^{-3} \text{ mol}$$

$$\text{Amount of I}_2 \text{ generated} = \frac{1}{2} (12 \times 10^{-3} \text{ mol}) = 6 \times 10^{-3} \text{ mol}$$

Assuming 1 mol of household bleach produces 1 mol I<sub>2</sub>, we will have

$$\text{Amount of household bleach in 25 mL solution} = 6 \times 10^{-3} \text{ mol}$$

$$\text{Molarity of household bleach} = \frac{n}{V} = \frac{6 \times 10^{-3} \text{ mol}}{25 \times 10^{-3} \text{ L}} = 0.24 \text{ M}$$

For Q 2, we have

Bleaching powder contains Ca(OCl)Cl.

The oxoacid of this salt is HOCl. The formation of this acid through its anhydride is  $\text{Cl}_2\text{O} \xrightarrow{\text{anhydride}} \text{H}_2\text{O} \rightarrow 2\text{HOCl}$   $\xrightarrow{\text{oxoacid}}$

Hence, we have

1. The **choice (c)** is correct
2. The **choice (a)** is correct.

**Passage-4**

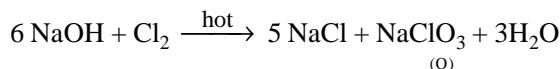
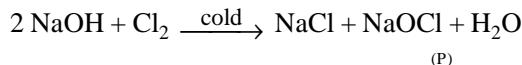
The precipitate P contains Pb<sup>2+</sup> ions as it gives white precipitate with dilute HCl which is soluble in hot water and reappears when the solution is cooled.

The coloured solution S is of Na<sub>2</sub>Cr O<sub>4</sub>. The filtrate Q contains Cr<sup>3+</sup> ions which get precipitated in an ammoniacal H<sub>2</sub>S medium and is oxidised to CrO<sub>4</sub><sup>2-</sup> when treated with H<sub>2</sub>O<sub>2</sub> in alkaline medium.

Therefore, the **choice (a) for Q. 1** and **choice (d) for Q. 2** are correct.

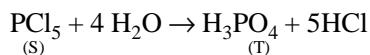
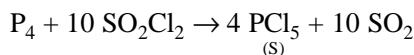
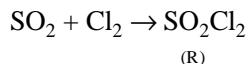
**Passage-5**

1. The reaction are :



Therefore, the **choice (a)** is correct.

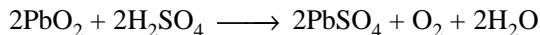
2. The reaction are :



Therefore, the **choice (a)** is correct.

## Matching Type

10. For the choice P in List I, we write the complete reaction as

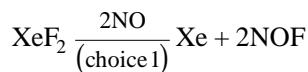
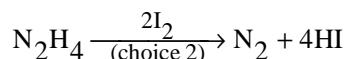


The reaction will proceed on warming the solution. This is given by the choice 3 in the List II.

For the choice Q in List I, we need a suitable oxidizing agent. This is accomplished by using  $\text{Cl}_2$  which is the choice 4 in List II. The complete reaction is



With the two cases considered above, it seems that the choice (d) of the given codes is the correct answer. We can complete the choices R and S in List I as follows.



Therefore, the **choice (d)** of the given codes is correct

## Matrix Match Type

- 1.(a)  $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$  is (i) a redox reaction (choice p), and (ii) a disproportionation reaction (choice s).
- (b)  $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow \dots$  has a product  $\text{Cr}_2\text{O}_7^{2-}$  which is dimeric bridged tetrahedral metal ion (choice r).
- (c)  $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow \dots$  (i) is a redox reaction (choice p) and (ii) one of the products ( $\text{NO}_3^-$ ) has trigonal planar structure (choice q).
- (d)  $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow \dots$  is a redox reaction in which  $\text{NO}_3^-$  in acidic medium oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  (choice p).

## Subjective Type

1. The involved reactions are



$$\text{Molar mass of FeO} = (55.8 + 16) \text{ g mol}^{-1} = 71.8 \text{ g mol}^{-1}$$

$$\text{Molar mass of Fe}_3\text{O}_4 = (3 \times 55.8 + 4 \times 16) \text{ g mol}^{-1} = 231.4 \text{ g mol}^{-1}$$

$$\text{Molar mass of Fe}_2\text{O}_3 = (2 \times 55.8 + 3 \times 16) \text{ g mol}^{-1} = 159.6 \text{ g mol}^{-1}$$

Let the percentage of FeO be  $y$ . From the chemical equations, we can write

$$\text{Mass of Fe}_2\text{O}_3 \text{ from FeO} = \left( \frac{159.6}{2 \times 71.8} \right) y$$

$$\text{Mass of Fe}_2\text{O}_3 \text{ from Fe}_3\text{O}_4 = \left( \frac{3 \times 159.6}{2 \times 231.4} \right) (100 - y)$$

Since the gain in mass is 5%, the total mass of  $\text{Fe}_2\text{O}_3$  obtained from FeO and  $\text{Fe}_3\text{O}_4$  will be 105 g.  
Hence

$$\left( \frac{159.6}{2 \times 71.8} \right) y + \left( \frac{3 \times 159.6}{2 \times 231.4} \right) (100 - y) = 105 \text{ g}$$

Solving for  $y$ , we get  $y = 20.04$  g

Hence, Percentage of FeO = 20.04 and Percentage of Fe<sub>3</sub>O<sub>4</sub> = 79.96

2. In 100 g of the original pyrolusite sample, we have

Mass of MnO<sub>2</sub> = 80 g

Mass of SiO<sub>2</sub> and other inert constituents = 15 g

Mass of water = 5 g

On igniting MnO<sub>2</sub> is converted into Mn<sub>3</sub>O<sub>4</sub>.

Molar mass of MnO<sub>2</sub> = (54.9 + 2 × 16) g mol<sup>-1</sup> = 86.9 g mol<sup>-1</sup>

Molar mass of Mn<sub>3</sub>O<sub>4</sub> = (3 × 54.9 + 4 × 16) g mol<sup>-1</sup> = 228.7 g mol<sup>-1</sup>

From the reaction 3MnO<sub>2</sub> → Mn<sub>3</sub>O<sub>4</sub> + O<sub>2</sub>, we find

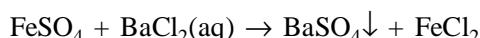
Mass of Mn<sub>3</sub>O<sub>4</sub> corresponding to 80 g of MnO<sub>2</sub> =  $\frac{228.7}{3 \times 86.9} \times 80$  g = 70.18 g

Total mass of ignited sample = 70.18 g + 15 g = 85.18 g

Mass per cent of Mn in this sample is

$$\left( \frac{3 \times 54.9}{228.7} \times 70.18 \right) \left( \frac{100}{85.18} \right) = 59.33$$

3. The given informations are as follows.



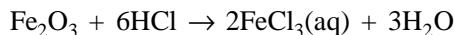
(A) (B)

(Green) (Insoluble in  
dil HCl)

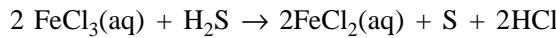


(E) (C) (D)

(red-brown)



(E) (Conc.) (F)



(F) (H) (G)

Hence, the compounds A to H are as follows.

A — FeSO<sub>4</sub> · 7H<sub>2</sub>O

B — BaSO<sub>4</sub>

C — SO<sub>2</sub>

D — SO<sub>3</sub>

E — Fe<sub>2</sub>O<sub>3</sub>

F — FeCl<sub>3</sub>

G — S

H — FeCl<sub>2</sub>

4. Al and Mg react with HCl according to the following equations.



The amount of H<sub>2</sub> evolved is

$$n = \frac{pV}{RT} = \frac{(0.92 \text{ atm})(1.20 \text{ L})}{(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(273.15 \text{ K})} = 0.0493 \text{ mol}$$

Let the mass of Al be  $x$  in 1 g of alloy. We will have

$$\text{Amount of H}_2 \text{ released from Al} = \left( \frac{3}{2} \right) \left( \frac{x}{27 \text{ g mol}^{-1}} \right)$$

$$\text{Amount of H}_2 \text{ released from Mg} = \frac{1 \text{ g} - x}{24.3 \text{ g mol}^{-1}}$$

Hence, we have

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$$\frac{3}{2} \frac{x}{27 \text{ g mol}^{-1}} + \frac{1g - x}{24.3 \text{ g mol}^{-1}} = 0.0493 \text{ mol}$$

Solving for  $x$ , we get  $x = 0.565 \text{ g}$

Hence, 0.565 g of Al and 0.435 g of Mg are present in 1 g alloy.

5. Let  $x$  be the mass of NaCl in 0.118 g of total chlorides. The masses of AgCl from NaCl and KCl are as follows.

$$\text{Mass of AgCl from NaCl} = \left( \frac{M_{\text{AgCl}}}{M_{\text{NaCl}}} \right) x = \left( \frac{143.5}{58.5} \right) x$$

$$\text{Mass of AgCl from KCl} = \left( \frac{M_{\text{AgCl}}}{M_{\text{KCl}}} \right) (0.118 \text{ g} - x) = \left( \frac{143.5}{74.5} \right) (0.118 \text{ g} - x)$$

The given mass of AgCl is 0.2451 g. Hence,

$$\left( \frac{143.5}{58.5} \right) x + \frac{143.5}{74.5} (0.118 \text{ g} - x) = 0.2451 \text{ g}$$

$$\text{i.e. } 2.453x + 1.926(0.118 \text{ g} - x) = 0.2451 \text{ g}$$

$$x = \frac{(0.2451 - 1.926 \times 0.118) \text{ g}}{2.453 - 1.926} = 0.0338 \text{ g}$$

From the identity,  $2 \text{ NaCl} \equiv \text{Na}_2\text{O}$  and  $2\text{KCl} \equiv \text{K}_2\text{O}$ , the masses of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  corresponding to the obtained masses of NaCl and KCl, are as follows.

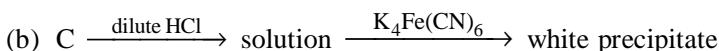
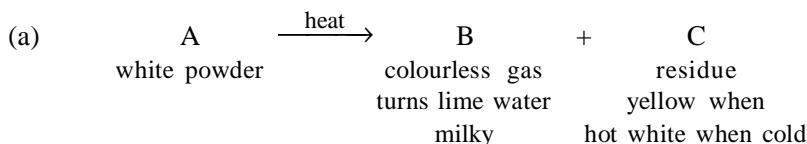
$$\text{Mass of Na}_2\text{O} = \left( \frac{M_{\text{Na}_2\text{O}}}{2M_{\text{NaCl}}} \right) (m_{\text{NaCl}}) = \left( \frac{62}{2 \times 58.5} \right) (0.0338 \text{ g}) = 0.0179 \text{ g}$$

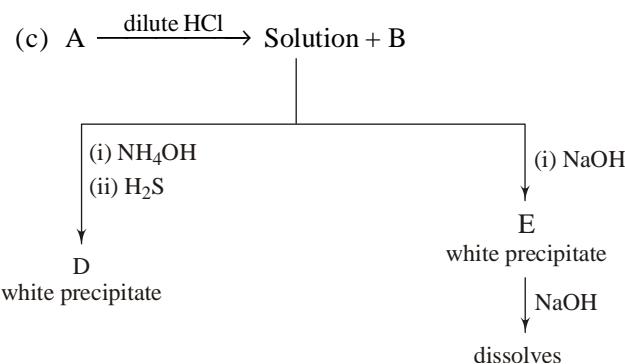
$$\text{Mass of K}_2\text{O} = \left( \frac{M_{\text{K}_2\text{O}}}{2M_{\text{KCl}}} \right) (m_{\text{KCl}}) = \left( \frac{94}{149} \right) (0.118 \text{ g} - 0.0338 \text{ g}) = 0.053 \text{ g.}$$

$$\text{Mass percentage of Na}_2\text{O} = \left( \frac{0.0179 \text{ g}}{0.5 \text{ g}} \right) (100) = 3.58$$

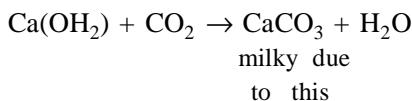
$$\text{Mass percentage of K}_2\text{O} = \left( \frac{0.0531 \text{ g}}{0.5 \text{ g}} \right) (100) = 10.62$$

6. The given information is as follows





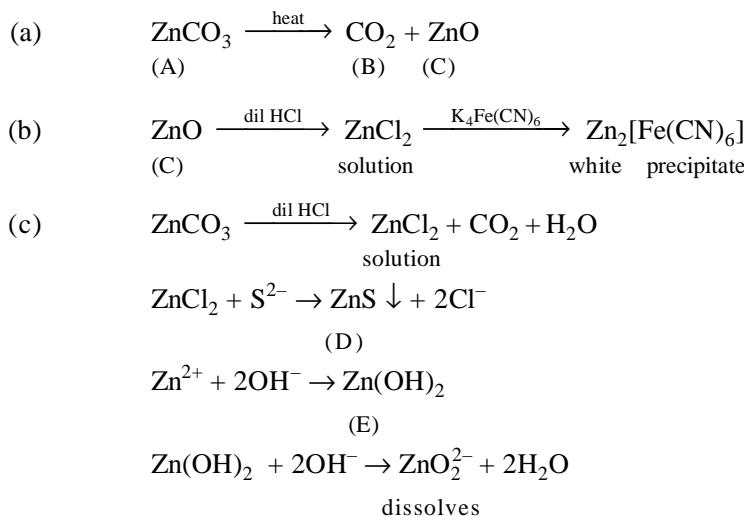
From part (a), we conclude that B is  $\text{CO}_2$  as it turns lime water milky:



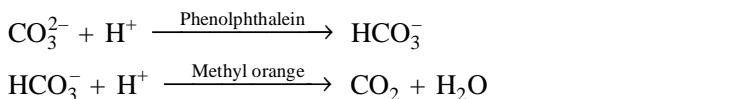
and C is  $\text{ZnO}$  as it becomes yellow on heating and is white in cold. Hence, the salt A must be  $\text{ZnCO}_3$ .

From part (b), it is confirmed that C is a salt of zinc(II) which dissolves in dilute HCl and white precipitate obtained after adding  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is due to  $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ .

From part (c), it is again confirmed that A is  $\text{ZnCO}_3$  as on adding dilute HCl, we get  $\text{CO}_2$  and zinc(II) goes into solution. White precipitate is of  $\text{ZnS}$  which is precipitated in ammoniacal medium as its solubility product is not very low. White precipitate E is of  $\text{Zn(OH)}_2$  which dissolves as zincate, in excess of NaOH. Hence, the given information is explained as follows.



7. The reaction occurring are as follows.



Let  $n_1$  and  $n_2$  be the respective amounts of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in 10 mL of the solution. We will have

$$\begin{aligned} n_1 &= \text{Amount of H}^+ \text{ in 2.5 mL of 0.1 M H}_2\text{SO}_4 \\ &= (2.5 \times 10^{-3} \text{ L}) (2 \times 0.1 \text{ mol L}^{-1}) = 5 \times 10^{-4} \text{ mol} \end{aligned}$$

$$\begin{aligned} n_1 + n_2 &= \text{Amount of H}^+ \text{ in 2.5 mL of 0.2 M H}_2\text{SO}_4 \\ &= (2.5 \times 10^{-3} \text{ L}) (2 \times 0.2 \text{ mol L}^{-1}) = 1 \times 10^{-3} \text{ mol} \end{aligned}$$

which gives  $n_1 = 5 \times 10^{-4} \text{ mol}$  and  $n_2 = 5 \times 10^{-4} \text{ mol}$

The above amounts are present in 10 mL of the solution.

Mass of  $\text{Na}_2\text{CO}_3$  per litre of the solution is

$$m_1 = (n_1 M_1) \left( \frac{1000 \text{ mL}}{10 \text{ mL}} \right) = (5 \times 10^{-4} \text{ mol}) (106 \text{ g mol}^{-1}) (100) \\ = 5.3 \text{ g}$$

Mass of  $\text{NaHCO}_3$  per litre of the solution is

$$m_2 = (5 \times 10^{-4} \text{ mol}) (84 \text{ g mol}^{-1}) (100) \\ = 4.2 \text{ g}$$

8. We have

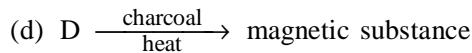
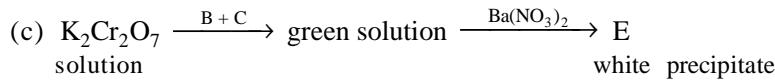
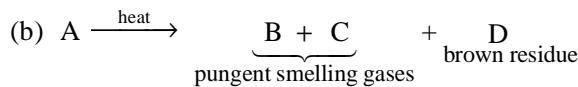
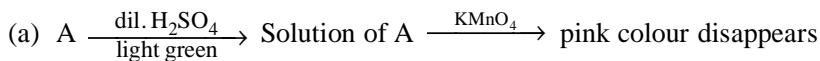
$$\begin{aligned} \text{Amount of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} &= \text{Amount in equivalent in } 5.4 \text{ mL of } 0.1\text{N } \text{KMnO}_4 \\ &= (5.4 \times 10^{-3} \text{ L}) (0.1 \text{ eq L}^{-1}) \\ &= 5.4 \times 10^{-4} \text{ eq.} \end{aligned}$$

$$\begin{aligned} \text{Mass of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = nM &= (5.4 \times 10^{-4} \text{ mol}) (278 \text{ g mol}^{-1}) \\ &= 0.150 \text{ g} \end{aligned}$$

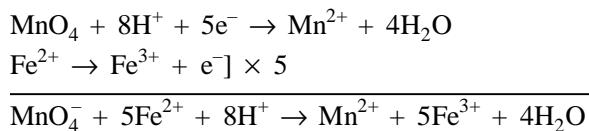
Mass of hydrated ferric sulphate =  $5.5 \text{ g} - 0.15 \text{ g} = 5.35 \text{ g}$

$$\text{Amount of hydrated ferric sulphate} = \frac{m}{M} = \frac{5.35 \text{ g}}{526 \text{ g mol}^{-1}} = 0.00952 \text{ mol}$$

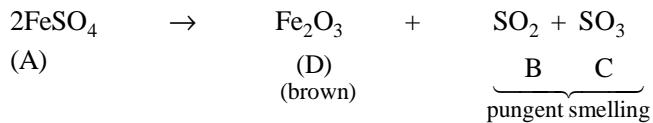
9. The given information is as follows.



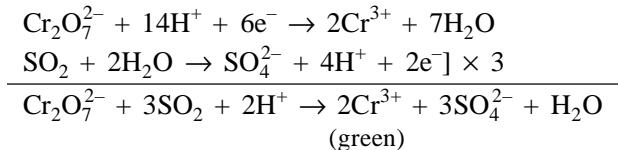
From (d), we conclude that D (hence also A) must be a salt of iron. Since A decolourises  $\text{KMnO}_4$  solution, it may be a salt of iron(II). the reactions involved are



From (b) and (c), we conclude that A must be  $\text{FeSO}_4$  as on heating it gives



$\text{SO}_2$  gas turns dichromate solution green due to the formation of chromium(III).



White precipitate E is of  $\text{BaSO}_4$ .

Hence, A is  $\text{FeSO}_4$ . B and C are  $\text{SO}_2$  and  $\text{SO}_3$ . D is  $\text{Fe}_2\text{O}_3$ . E is  $\text{BaSO}_4$ .

10. Since  $\text{NaCl}$  does not decompose on heating, the precipitation of  $\text{AgCl}$  when vapours are absorbed in  $\text{AgNO}_3$  solution must be due to unknown chloride (MCl). Thus, Mass of  $\text{AgCl}$  formed due to  $\text{NaCl}$  is given by

$$m = 2.567 \text{ g} - 1.341 \text{ g} = 1.226 \text{ g}$$

Mass of NaCl in the mixture is given by

$$m_1 = \left( \frac{M_{\text{NaCl}}}{M_{\text{AgCl}}} \right) m = \left( \frac{58.5 \text{ g mol}^{-1}}{143.5 \text{ g mol}^{-1}} \right) (1.226 \text{ g}) = 0.4998 \text{ g}$$

Mass of unknown chloride in the mixture is

$$m_2 = 1 \text{ g} - m_1 = 1 \text{ g} - 0.4998 \text{ g} = 0.5002 \text{ g}$$

The molar mass of unknown chloride is

$$\begin{aligned} M &= \left( \frac{m_2}{1.341 \text{ g}} \right) M_{\text{AgCl}} = \left( \frac{0.5002 \text{ g}}{1.341 \text{ g}} \right) (143.5 \text{ g mol}^{-1}) \\ &= 53.52 \text{ g mol}^{-1} \end{aligned}$$

- 11.** Molar mass of  $\text{CaCl}_2 = 111 \text{ g mol}^{-1}$

Molar mass of  $\text{MgCl}_2 = 95 \text{ g mol}^{-1}$

Molar mass of  $\text{CaCO}_3 = 100 \text{ g mol}^{-1}$

Mass of  $\text{CaCO}_3$  which is equivalent to 1 mg  $\text{CaCl}_2$ .

$$= \left( \frac{M_{\text{CaCO}_3}}{M_{\text{CaCl}_2}} \right) m_{\text{CaCl}_2} = \left( \frac{100}{111} \right) (1 \text{ mg}) = 0.901 \text{ mg}$$

Mass of  $\text{CaCO}_3$  which is equivalent to 1 mg  $\text{MgCl}_2$

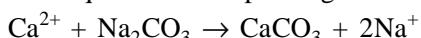
$$= \left( \frac{M_{\text{CaCO}_3}}{M_{\text{MgCl}_2}} \right) m_{\text{MgCl}_2} = \left( \frac{100}{95} \right) (1 \text{ mg}) = 1.053 \text{ mg}$$

Mass of 1 L of water =  $10^3 \text{ g} = 10^6 \text{ mg}$

Total hardness in  $10^6 \text{ mg}$  of water =  $0.901 \text{ mg} + 1.053 \text{ mg} = 1.954 \text{ mg}$

That is, 1.954 parts of  $\text{CaCO}_3$  is present in  $10^6$  parts of water.

- 12.** The chemical equation corresponding to the softening of water is



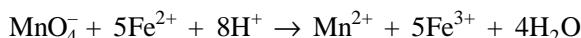
For softening 1 equivalent of  $\text{Ca}^{2+}$  ions, 1 equivalent of  $\text{Na}_2\text{CO}_3$  is required.

Amount in equivalent of  $\text{Ca}^{2+}$  ions

$$n = \frac{m}{M_{\text{eq}}(\text{Ca}^{2+})} = \frac{20 \text{ mg}}{20 \text{ g eq}^{-1}} = \frac{20 \times 10^{-3} \text{ g}}{20 \text{ g eq}^{-1}} = 10^{-3} \text{ eq}$$

Hence, amount in equivalent of  $\text{Na}_2\text{CO}_3$  required for softening 1 L water =  $10^{-3}$  eq = 1 mev

- 13.** The amount of  $\text{Fe}^{2+}$  ions remaining in step (ii) is equivalent to 50 mL of  $\text{KMnO}_4$  (Step iii) which is, in turn, equivalent to (50/25) (30mL of 0.1 M) ferrous sulphate (step iv). The reaction between  $\text{MnO}_4^-$  and  $\text{Fe}^{2+}$  ions is



Thus, amount of  $\text{Fe}^{2+}$  ions remaining in Step (ii) is

$$n_1 = \left( \frac{50}{25} \right) (30 \times 10^{-3} \text{ L}) (0.1 \text{ mol L}^{-1}) = 60 \times 10^{-4} \text{ mol}$$

The amount of  $\text{Fe}^{2+}$  ions consumed in step (ii) is

$$\begin{aligned} n_2 &= (\text{amount of } \text{Fe}^{2+} \text{ in } 100 \text{ mL of } 0.1 \text{ M } \text{FeSO}_4) - n_1 \\ &= (100 \times 10^{-3} \text{ L}) (0.1 \text{ mol L}^{-1}) - 60 \times 10^{-4} \text{ mol} \\ &= 40 \times 10^{-4} \text{ mol} \end{aligned}$$

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From the reactions



It follows that  $2 \text{ mol FeSO}_4 \equiv 1 \text{ mol of Mn}_3\text{O}_4 = 3 \text{ mol MnSO}_4$ .

Amount of  $\text{MnSO}_4$  in the given sample is

$$n_3 = \left( \frac{3 \text{ mol MnSO}_4}{2 \text{ mol FeSO}_4} \right) n_2 = \left( \frac{3}{2} \right) (40 \times 10^{-4} \text{ mol}) = 60 \times 10^{-4} \text{ mol}$$

Molar mass of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O} = (55 + 32 + 4 \times 16 + 4 \times 18) \text{ g mol}^{-1} = 223 \text{ g mol}^{-1}$

Mass of  $60 \times 10^{-4} \text{ mol of MnSO}_4 \cdot 4\text{H}_2\text{O} = (223 \text{ g mol}^{-1}) (60 \times 10^{-4} \text{ mol}) = 1.338 \text{ g}$

14. Passing the mixture over red-hot charcoal causes the reaction



Let  $x$  be the partial volume of  $\text{CO}_2$  in the mixture. The total volume after the process is over will be

$$(1 \text{ L} - x) + 2x = 1 \text{ L} + x. \text{ This is given to be } 1.6 \text{ L.}$$

Hence,  $x = 0.6 \text{ L}$

Thus,  $V_{\text{CO}_2} = 0.6 \text{ L}$  and  $V_{\text{CO}} = 1 \text{ L} - 0.6 \text{ L} = 0.4 \text{ L}$

The composition of mixture is in the ratio

$$\frac{n_{\text{CO}_2}}{n_{\text{CO}}} = \frac{0.6}{0.4} = \frac{3}{2}$$

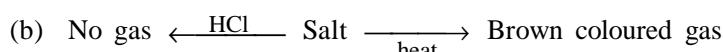
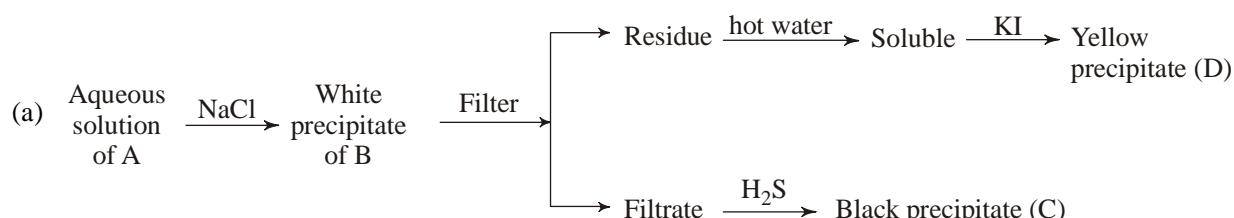
15. The chemical compound is  $\text{M}_3\text{N}_2$ . From the given percentages, we have

$$\frac{n(\text{N}_2)}{n(\text{M})} = \left( \frac{28 \text{ g } 14 \text{ g mol}^{-1}}{72 \text{ g } M} \right) = \frac{2M}{72 \text{ g mol}^{-1}}$$

This is given to be  $2 : 3$  (from the formula of the compound). Hence

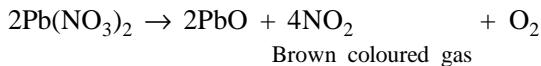
$$\frac{2M}{72 \text{ g mol}^{-1}} = \frac{2}{3} \Rightarrow M = \frac{72 \text{ g mol}^{-1}}{3} = 24 \text{ g mol}^{-1}$$

16. The given informations are as follows.



From the information given in part (a), it may be concluded that the compound A is a lead salt. B is lead chloride as it is soluble in hot water. Yellow precipitate D is due to  $\text{PbI}_2$ . Black precipitate C is due to  $\text{PbS}$ . Lead chloride being sparingly soluble in water, a little of it remains in the filtrate which is subsequently precipitated as  $\text{PbS}$ .

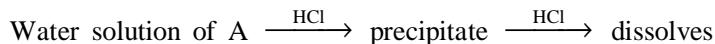
From the information given in part (b), it may be concluded that anion associated with lead(II) is nitrate because lead nitrate dissociates on heating as



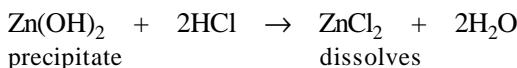
Hence, A is  $\text{Pb}(\text{NO}_3)_2$ , B is  $\text{PbCl}_2$ , C is  $\text{PbS}$  and D is  $\text{PbI}_2$ .

17. As the mixture is completely soluble in water,  $\text{CaCO}_3$  is excluded. As the water solution gives pink colour with phenolphthalein, the mixture contains  $\text{NaOH}$ .

It is given that

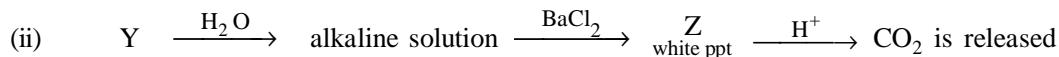
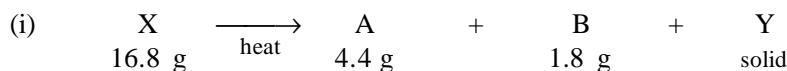


This fact excludes  $\text{BaCl}_2$  and  $\text{AgNO}_3$ . Barium chloride does not give precipitate with dilute HCl. Silver nitrate does give precipitate of  $\text{AgCl}$  but it is not soluble in dilute HCl. However, the mixture contains  $\text{ZnSO}_4$ . On dissolving  $\text{ZnSO}_4$  and  $\text{NaOH}$  in water, the former is present as zincate ( $\text{ZnO}_2^{2-}$ ) ions. On adding HCl,  $\text{NaOH}$  is neutralised and  $\text{ZnO}_2^{2-}$  is converted into  $\text{Zn(OH)}_2$  which being insoluble, precipitates out. This precipitate dissolves as more of HCl is added.

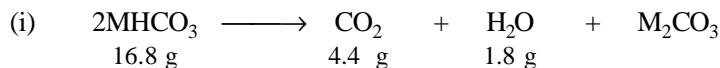


Hence, the mixture contains  $\text{ZnSO}_4$  and  $\text{NaOH}$ .

18. The given facts may be summarized as follows.



Since Z on treatment with an acid gives  $\text{CO}_2$  gas, Z must be a carbonate of barium, i.e.  $\text{BaCO}_3$ . Since  $\text{BaCO}_3$  is obtained by adding  $\text{BaCl}_2$  to an alkaline solution, Y must be a carbonate of an alkali metal. Let it be  $\text{M}_2\text{CO}_3$ . Now the gas A must be  $\text{CO}_2$  as it turns lime water milky. With this, we conclude that X must be a bicarbonate of M as on heating it will be converted to carbonate with the release of  $\text{CO}_2$  (i.e. A) and  $\text{H}_2\text{O}$  (i.e. B). Hence, we write



Let  $M$  be the molar mass of M. We will have

$$2 \left( \frac{M}{\text{mol}^{-1}} + 61 \text{ g} \right) \text{ of MHCO}_3 \text{ liberates } 44 \text{ g of CO}_2.$$

Hence, from the given data, we get

$$\frac{2 \left( \frac{M}{\text{mol}^{-1}} + 61 \text{ g} \right) \text{ of MHCO}_3}{44 \text{ g CO}_2} \times 4.4 \text{ g CO}_2 = 16.8 \text{ g of MHCO}_3$$

This gives,  $M = 23 \text{ g mol}^{-1}$

Thus,  $M$  must be sodium. The same conclusion is reached when  $M$  is determined from the given mass of  $\text{H}_2\text{O}$  formed. Hence, we have

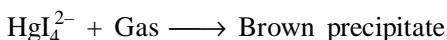
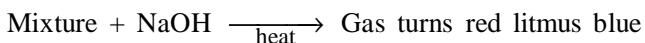


19. The reaction Mixture +  $\text{MnO}_2 + \text{H}_2\text{SO}_4 \rightarrow$  yellowish-green gas indicates that the mixture (conc.)

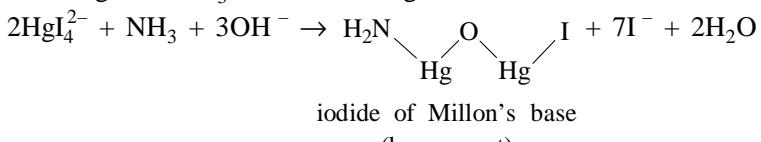
contains  $\text{Cl}^-$  ion as the gas is  $\text{Cl}_2$ , i.e.



### The reactions

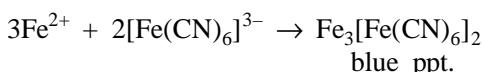


indicate that the gas is  $\text{NH}_3$ . It is a basic gas so it turns red litmus to blue. With  $\text{HgI}_4^{2-}$ , the reaction is

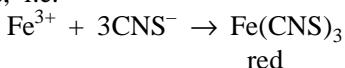


From these facts, we conclude that the mixture contains  $\text{NH}_4^+$  ions.

The reaction Mixture +  $K_3[Fe(CN)_6]$  → blue precipitate indicates that the mixture contains  $Fe^{2+}$  ions i.e.



The red coloration with  $\text{NH}_4\text{CNS}$  must be due to  $\text{Fe}^{3+}$  ions which is probably formed by aerial oxidation of  $\text{Fe}^{2+}$  ions, i.e.



Thus, the mixture contains  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$  and  $\text{Cl}^-$  ions or  $\text{NH}_4\text{Cl}$  and  $\text{FeCl}_2$  salts.

**20.** The given observations are as follows.

(i) Hydrated metallic salt  $\xrightarrow[\text{(A)}]{\text{heat}}$  white anhydrous residue  $\text{(B)}$

(ii) Aqueous solution of B  $\xrightarrow{\text{NO}}$  dark brown compound  
(C)

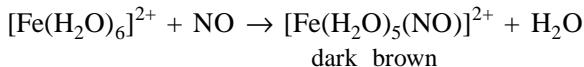
(iii) Salt B  $\xrightarrow[\text{heating}]{\text{strong}}$  Brown residue + Two gases  
(D) (E) + (F)

(iv) Gaseous mixture (E) + (F)

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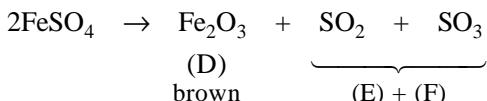
graph LR
    A["(iv) Gaseous mixture  
(E) + (F)"] --> B["acidified KMnO4"]
    A --> C["BaCl2 solution"]
    B --> D["Pink colour is  
discharged"]
    C --> E["White precipitate"]
  
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The observation (ii) shows that B must be ferrous sulphate since with NO, it gives dark brown compound according to the reaction

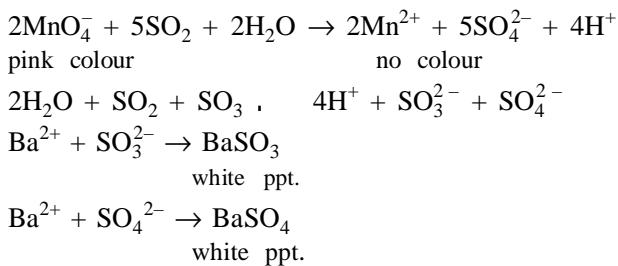


Hence, the salt A must be  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

The observation (iii) is



The gaseous mixture of  $\text{SO}_2$  and  $\text{SO}_3$  explains the observation (iv), namely,



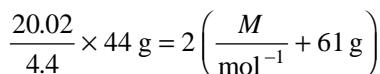
Hence, the various compounds are

- |   |   |         |                                 |   |   |
|---|---|---------|---------------------------------|---|---|
| A | $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | B       | $\text{FeSO}_4$                 | C | $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ |
| D | $\text{Fe}_2\text{O}_3$                   | E and F | $\text{SO}_2$ and $\text{SO}_3$ |   |   |

21. We are given that



It is given that 20.02 g of  $\text{MHCO}_3$  produces 4.4 g of  $\text{CO}_2$ . From this data, we can determine the value of  $M$ .



This gives  $M = 39 \text{ g mol}^{-1}$

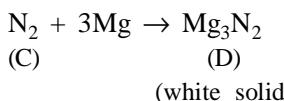
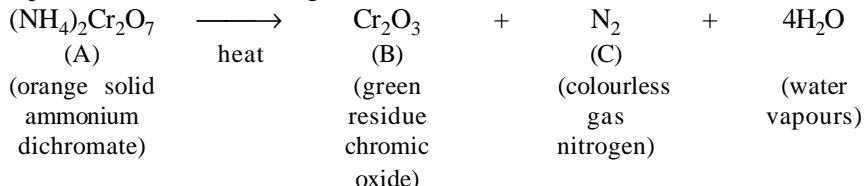
Thus, the element M is potassium. Hence

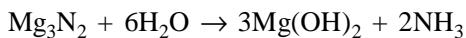


22. (i) Brown precipitate or colouration with alkaline  $K_2[HgI_4]$  suggests the presence of  $NH_4^+$  ions.  
(ii) Blue colouration with  $K_3Fe(CN)_6$  solution suggests the presence of  $Fe^{2+}$  ions.  
(iii) White precipitate with acidified  $BaCl_2$  solution suggests the presence of  $SO_4^{2-}$  ions.

The compound is Mohr's salt with molecular formula  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

- 23.** The compounds (A) to (E) along with the reactions involved are





(D) (E)

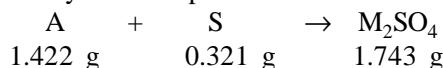


(E) (white fumes)

24. Since B forms a hydrated double salt with  $\text{Al}_2(\text{SO}_4)_3$  the structure of double salt may be



Hence, B may be a sulphate of univalent metal A. The reaction of A with sulphur may be written as



Hence, the compound A must be  $\text{M}_2\text{O}_4$ , i.e.  $2\text{MO}_2$ . The metal M may be identified from the given data of masses of  $\text{MO}_2$ , S and  $\text{M}_2\text{SO}_4$ . If M is the molar mass of the metal M, we have

$$\text{Molar mass of } \text{MO}_2 = M + 2 \times 16 \text{ g mol}^{-1}$$

Now 0.321 g of S reacts with 1.422 g of  $\text{MO}_2$ . The mass of  $\text{MO}_2$  that reacts with 32 g of S (= 1 molar mass of S) is

$$\frac{1.422 \text{ g}}{0.321 \text{ g}} \times 32 \text{ g} = 142.2 \text{ g}$$

This will be equal to the twice of molar mass of  $\text{MO}_2$ . Hence,

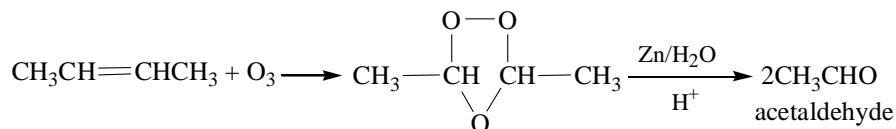
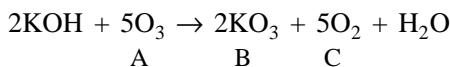
$$2(M + 2 \times 16 \text{ g mol}^{-1}) = 142.2 \text{ g mol}^{-1}$$

$$\text{or } M = \left( \frac{142.2}{2} - 2 \times 16 \right) \text{ g mol}^{-1} = 39.1 \text{ g mol}^{-1}$$

Thus, the metal M is potassium. Hence,

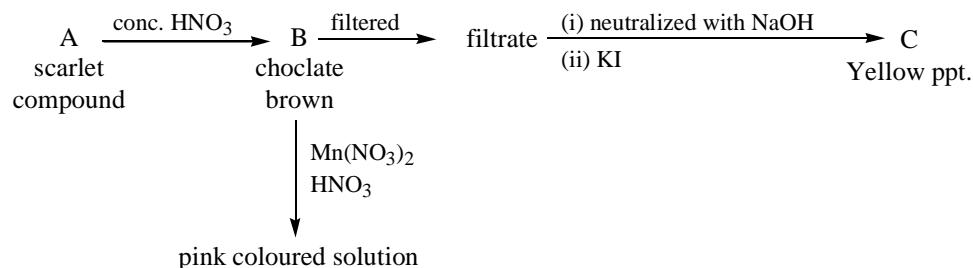
A is  $\text{KO}_2$ , potassium superoxide; B is  $\text{K}_2\text{SO}_4$ , potassium sulphate; and C is  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , potash alum.

25. The given reactions are



Hence, A is  $\text{O}_3$ , ozone; B is  $\text{KO}_3$ , potassium ozonide and C is  $\text{O}_2$ ; oxygen

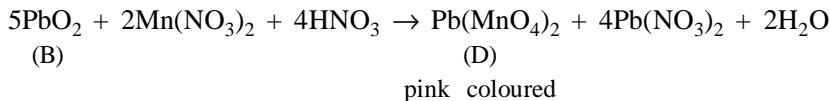
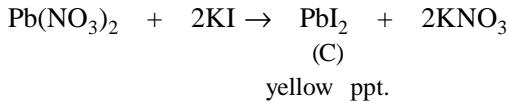
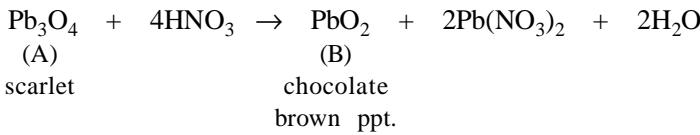
26. The given reactions may be summarized as follows.



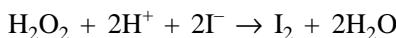
The compound B must be a powerful oxidizing agent which converts  $\text{Mn}^{2+}$  to the pink coloured  $\text{MnO}_4^-$  ion. Normally,  $\text{PbO}_2$  is used for this purpose.

The compound C may be  $\text{PbI}_2$  which is yellow in colour.

The given reactions may be explained as follows.



27. The involved reaction is



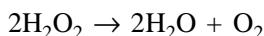
Hence, 1 mol  $\text{H}_2\text{O}_2 \equiv 1 \text{ mol I}_2$

$$\text{Amount of I}_2 \text{ liberated} = \frac{0.508 \text{ g}}{(2 \times 127) \text{ g mol}^{-1}} = 2 \times 10^{-3} \text{ mol}$$

Thus Amount of  $\text{H}_2\text{O}_2$  in  $5.0 \text{ cm}^3$  solution  $= 2 \times 10^{-3} \text{ mol}$

$$\text{Molar concentration of H}_2\text{O}_2 = \frac{2 \times 10^{-3} \text{ mol}}{5 \times 10^{-3} \text{ L}} = 0.4 \text{ mol L}^{-1}$$

The volume strength of  $\text{H}_2\text{O}_2$  is based on the reaction



2 mol  $\text{H}_2\text{O}_2 \equiv 1 \text{ mol O}_2 \equiv 22.4 \text{ O}_2$  at STP

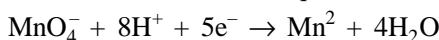
Now 2 molar solution of  $\text{H}_2\text{O}_2$  has volume strength of 22.4

Hence, 0.4 molar solution of  $\text{H}_2\text{O}_2$  has volume strength of  $\frac{22.4}{2 \text{ M}} \times 0.4 \text{ M} = 4.48$ .

28. Let  $N_1$ ,  $N_2$  and  $N_3$  be the normalities of the same 1 M  $\text{KMnO}_4$  solution in acidic, neutral and alkaline media, respectively. In a chemical reaction, the substances are consumed in equivalent amounts. Thus,

$$(20 \text{ mL})N_1 \equiv (33.4 \text{ mL})N_2 \equiv (100 \text{ mL})N_3 \quad (1)$$

In acidic medium, the chemical equation is



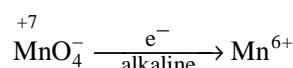
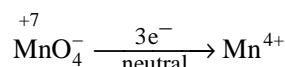
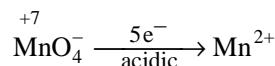
i.e., 1 M  $\text{KMnO}_4 \equiv 5 \text{ N KMnO}_4$

From Eq. (1), We can deduce

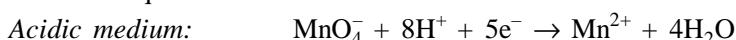
$$N_2 = \frac{20}{33.4} N_1 = \frac{20}{33.4} \times 5 \text{ N} = 3 \text{ N}$$

$$N_3 = \frac{20}{100} N_1 = \frac{20}{100} \times 5 \text{ N} = 1 \text{ N}$$

Thus, the oxidation states of manganese in the reduction products are as under:

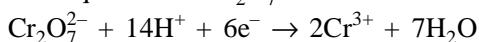


Balanced equations for the three half-reactions are:





The chemical equation of  $\text{Cr}_2\text{O}_7^{2-}$  in acidic medium is



i.e.,  $1 \text{ M Cr}_2\text{O}_7^{2-} \equiv 6 \text{ N Cr}_2\text{O}_7^{2-}$

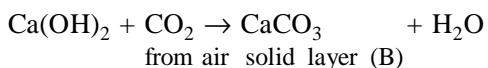
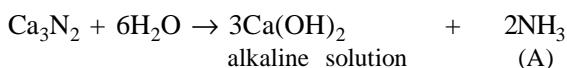
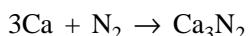
The volume of 1 M  $\text{Cr}_2\text{O}_7^{2-}$ , if the same volume of the reducing agent is titrated, will be

$$V = \frac{(20 \text{ mL})N_1}{6 \text{ N}} = \frac{(20 \text{ mL})(5 \text{ N})}{6 \text{ N}} = 16.7 \text{ mL}$$

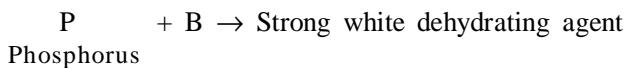
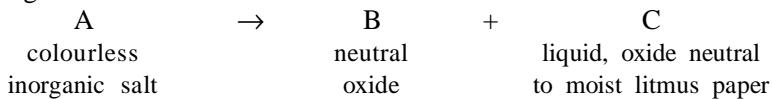
29. The compound  $\text{Fe}_{0.93} \text{ O}_{1.00}$  is a non-stoichiometric where electrical neutrality is achieved by converting appropriate  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions. There are 7  $\text{Fe}^{2+}$  ions missing out of the expected 100  $\text{Fe}^{2+}$  ions. The missing  $2 \times 7$  positive charge is compensated by the presence of  $\text{Fe}^{3+}$  ions. Replacement of one  $\text{Fe}^{2+}$  ion by  $\text{Fe}^{3+}$  ion increases one positive charge. Thus, 14 positive charge is compensated by the presence of 14  $\text{Fe}^{3+}$  ions out of a total of 93 iron ions. Hence, percent of  $\text{Fe}^{3+}$  ions present

$$= \frac{14}{93} \times 100 = 15.05$$

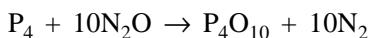
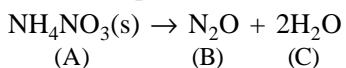
30. The reactions are as follows.



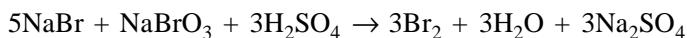
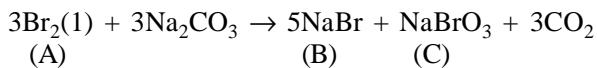
31. It is given that



The reactions are explainable if A is taken to be  $\text{NH}_4\text{NO}_3$ .

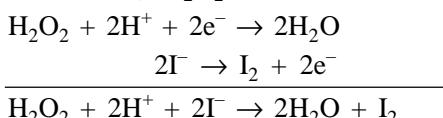


32. The liquid A is  $\text{Br}_2$  and the two salts B and C are  $\text{NaBr}$  and  $\text{NaBrO}_3$ , respectively. The equations involved are



33. The reactions involved are

- (i) Oxidation of  $\text{I}^-$  by  $\text{H}_2\text{O}_2$  in acidic medium



- (ii) Reaction of  $\text{I}_2$  with sodium thiosulphate



From Eq. (2), it follows that

$$\text{normality of } \text{S}_2\text{O}_3^{2-} = \text{molarity of } \text{S}_2\text{O}_3^{2-}$$

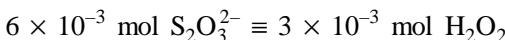
Also, from Eqs (1) and (2), it follows that



Now,

$$\text{Amount of } \text{S}_2\text{O}_3^{2-} \text{ consumed} = VM = (20 \times 10^{-3} \text{ L}) (0.3 \text{ mol L}^{-1}) \\ = 6 \times 10^{-3} \text{ mol}$$

From Eq. (3), it follows that



$$\text{Molarity of H}_2\text{O}_2 \text{ solution} = \frac{(3 \times 10^{-3} \text{ mol})}{25 \times 10^{-3} \text{ L}} = 0.12 \text{ mol L}^{-1}$$

From the reaction  $2\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ , it follows that 0.12 mol L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> will liberate 0.06 mol of O<sub>2</sub> or  $0.06 \times 22.414$  L of O<sub>2</sub> at 0 °C. Hence, the volume strength is  $0.06 \times 22.414 = 1.345$ .

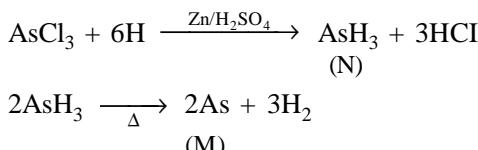
- 34.**  $3M + N_2 \rightarrow M_3N_2$   
 (A) (B)

$M_3N_2 + 6H_2O \rightarrow 3M(OH)_2 + 2NH_3$   
 (B) (C) (D)

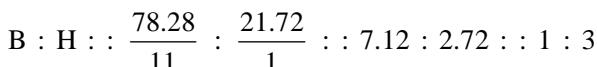
$M(OH)_2 + CO_2 \rightarrow MCO_3 + H_2O$   
 (C) (D)

M is either Ca or Ba. Magnesium may be excluded due to very low solubility of  $Mg(OH)_2$  in water.

35. The poisonous element M is arsenic. The given facts are as follows.



36. Since the hydride **Y** reacts with air forming boron trioxide, the compound **Y** must be an hydride of boron. From the given molecular composition of **Y**, we determine its empirical formula as shown in the following. Given mass ratio is B : H :: 78.28 : 21.72  
Its atomic ratio will be

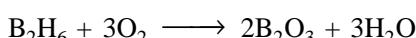
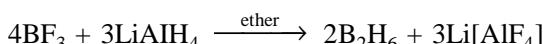


Hence, Empirical formula is  $\text{BH}_3$ .

Since boron forms two types of hydrides  $B_nH_{n+4}$  (nido-boranes) and  $B_nH_{n+6}$  (arachno-boranes), we conclude that

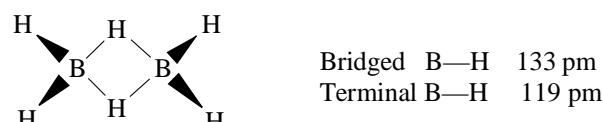
Molecular formula of **Y** is  $\text{B}_2\text{H}_6$ .

Its formation from **X** and its reaction with  $O_2$  are as follows.



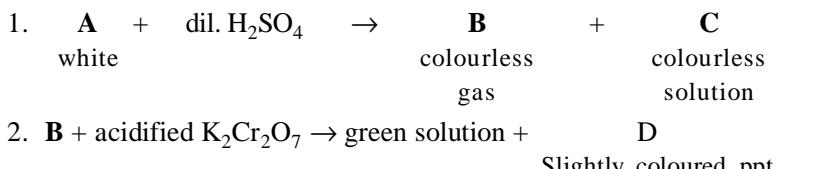
Hence, the compound **X** must be a boron halide ( $\text{BF}_3$  or  $\text{BCl}_3$ ).

The structure of borane is



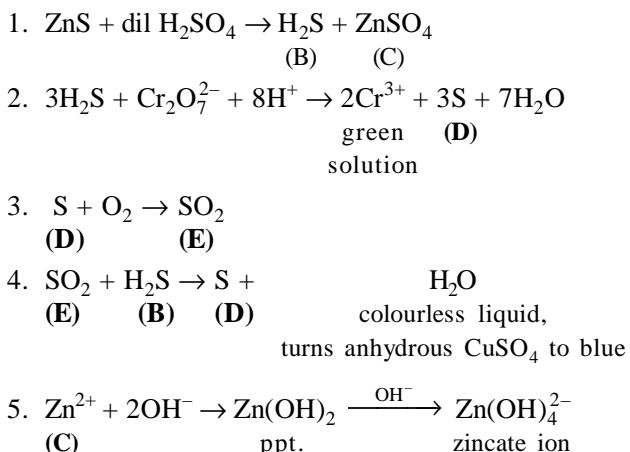
The two bridging H atoms are in a plane perpendicular to the rest of the molecule.

37. The given informations are as follows.

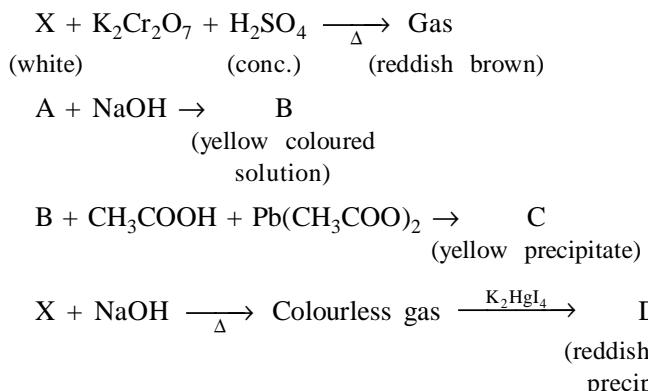


3.  $\text{D} + \text{air} \rightarrow \text{E}$   
gas
4.  $\text{E} + \text{B} \rightarrow \text{D} + \text{colourless liquid, turns anhydrous CuSO}_4 \text{ to blue}$
5.  $\text{C} + \text{NH}_3 \text{ or NaOH} \rightarrow \text{precipitates dissolved in excess of NH}_3 \text{ or NaOH}$

The above informations are explainable if we identify A with ZnS. We have

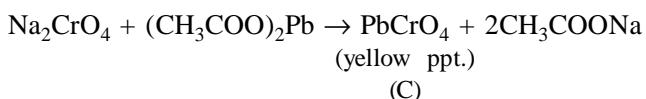
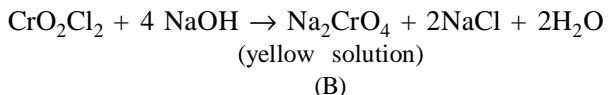
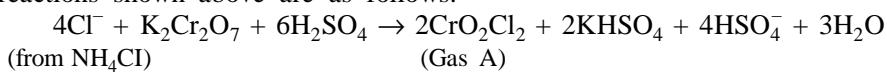


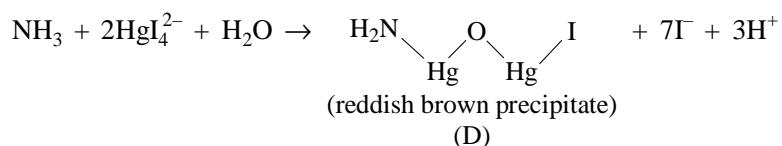
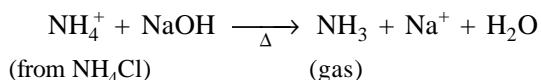
**38.** The given reactions are as follows.



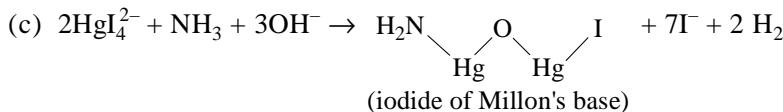
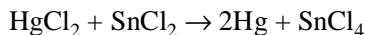
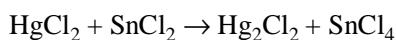
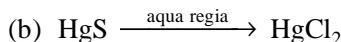
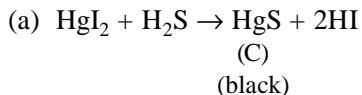
The above reactions indicate that the compound X contains  $\text{Cl}^-$  and  $\text{NH}_4^+$  Ions, hence the compound is  $\text{NH}_4\text{Cl}$ .

The reactions shown above are as follows.





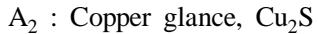
39. From the given information, it appears that A is  $\text{HgI}_2$ , and B is  $\text{KI}$ . The given reactions are as follows.



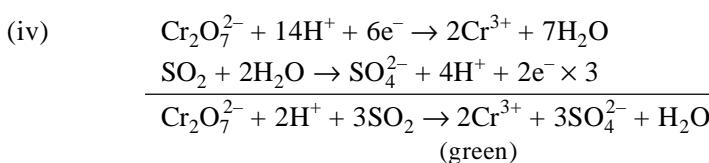
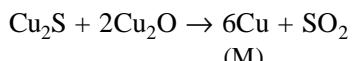
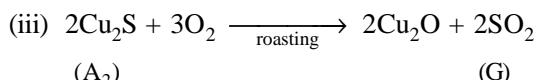
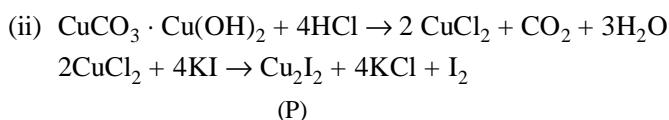
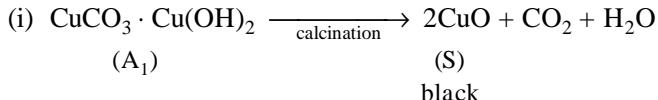
(d)  $I_2$  is absorbed in  $CCl_4$  giving violet colour.

(e)  $\Gamma^- + \text{Ag}^+ \rightarrow \text{AgI} \downarrow$  insoluble in  $\text{NH}_4\text{OH}$ .

- 40.** Metal M is copper and its two ores are



The given reactions are as follows.

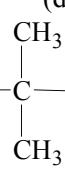


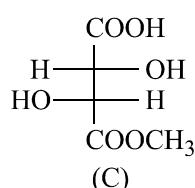
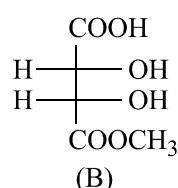
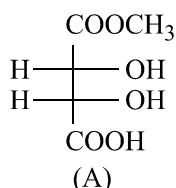


# HYBRIDIZATION, ISOMERISM & NOMENCLATURE

19

## Straight Objective Type

1. Molecule in which the distance between the two adjacent carbon atoms is largest is  
(a) ethane      (b) ethene      (c) ethyne      (d) benzene      (1981)
2. The compound which is not isomeric with diethyl ether is  
(a) *n*-propyl methyl ether      (b) 1-butanol  
(c) 2-methyl-2-propanol      (d) butanone      (1981)
3. The maximum number of isomers for an alkene with the molecular formula C<sub>4</sub>H<sub>8</sub> is  
(a) 2      (b) 3      (c) 4      (d) 5      (1982)
4. The compound with no dipole moment is  
(a) methyl chloride      (b) carbon tetrachloride  
(c) methylene chloride      (d) chloroform      (1982)
5. The compound 1, 2-butadiene has  
(a) only sp hybridised carbon atoms      (b) only sp<sup>2</sup> hybridised carbon atoms  
(c) both sp and sp<sup>2</sup> hybridised carbon atoms      (d) sp, sp<sup>2</sup> and sp<sup>3</sup> hybridised carbon atoms      (1983)
6. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?  
(a) 2-Butene      (b) 2-Butyne      (c) 2-Butanol      (d) Butanal      (1983)  

7. The IUPAC name of the compound having the formula H<sub>3</sub>C—C(CH<sub>3</sub>)<sub>2</sub>—CH=CH<sub>2</sub> is  
(a) 3, 3, 3-trimethyl-1-propene      (b) 1, 1, 1-trimethyl-2-propene  
(c) 3,3-dimethyl-1-butene      (d) 2,2-dimethyl-3-butene      (1984)
8. The bond between carbon atom (1) and carbon atom (2) in compound N≡C—<sub>1</sub>—CH=CH<sub>2</sub> involves respectively the hybrid orbitals  
(a) sp<sup>2</sup> and sp<sup>2</sup>      (b) sp<sup>3</sup> and sp      (c) sp and sp<sup>2</sup>      (d) sp and sp      (1987)
9. The IUPAC name of the compound CH<sub>2</sub>=CH—CH(CH<sub>3</sub>)<sub>2</sub> is  
(a) 1, 1-dimethyl-2-propene      (b) 2-vinylpropane  
(c) 3-methyl-1-butene      (d) 1-isopropylethene      (1987)
10. If two compounds have the same empirical formula but different molecular formulae they must have  
(a) different percentage composition      (b) different molar mass  
(c) same viscosity      (d) same vapour density      (1987)
11. The number of isomers of C<sub>6</sub>H<sub>14</sub> is  
(a) 4      (b) 5      (c) 6      (d) 7      (1987)

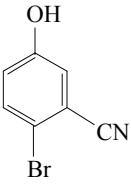


is



39. The number of structural isomers for  $C_6H_{14}$  is

- (a) 3      (b) 4      (c) 5      (d) 6      (2007)

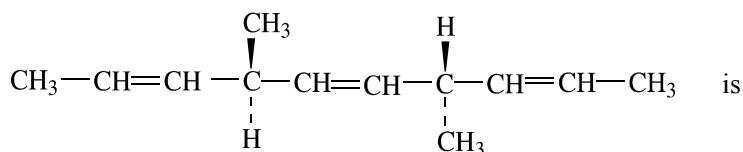
40. The IUPAC name of the compound  is

- (a) 4-Bromo-3-cyanophenol      (b) 2-Bromo-5-hydroxybenzonitrile  
 (c) 2-cyano-4-hydroxybromobenzene      (d) 6-Bromo-3-hydroxybenzonitrile      (2009)

41. In allene ( $C_3H_4$ ), the type(s) of hybridization of the carbon atom is (are)

- (a)  $sp$  and  $sp^3$       (b)  $sp$  and  $sp^2$       (c)  $sp^3$  only      (d)  $sp^2$  and  $sp^3$       (2012)

42. The number of optically active products obtained from the complete ozonolysis of the given compound



- (a) 0      (b) 1      (c) 2      (d) 4      (2012)

### Multiple Correct-Choice Type

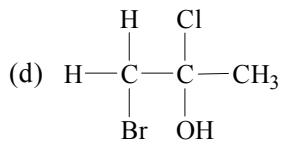
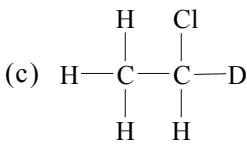
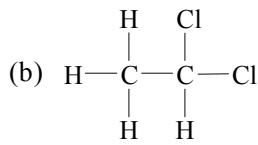
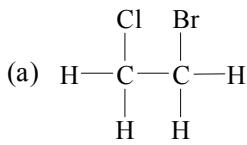
1. Resonating structures of a molecule should have

- (a) identical arrangement of atoms      (b) nearly the same energy content  
 (c) the same number of paired electrons      (d) identical bonding      (1984)

2. Only two isomeric monochloro derivatives are possible for

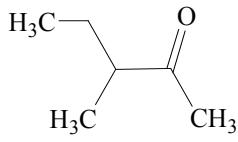
- (a) *n*-butane      (b) 2, 2-dimethylpentane  
 (c) benzene      (d) 2-methylpropane      (1986)

3. Which of the following have asymmetric carbon atom?

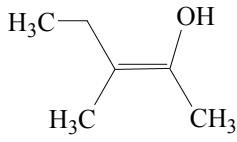


(1989)

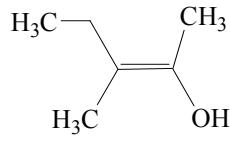
4. The correct statement(s) concerning the structures **E**, **F** and **G** is (are)



(E)



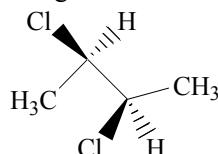
(F)



(G)

- (a) **E**, **F** and **G** are resonance structures      (b) **E**, **F** and **E**, **G** are tautomers  
 (c) **F** and **G** are geometrical isomers      (d) **F** and **G** are diastereomers      (2008)

5. The correct statement(s) about the compound given below is (are)



- (a) The compound is optically active
- (b) The compound possesses centre of symmetry
- (c) The compound possesses plane of symmetry
- (d) The compound possesses axis of symmetry

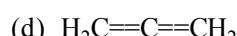
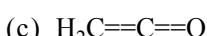
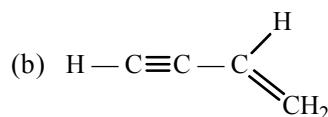
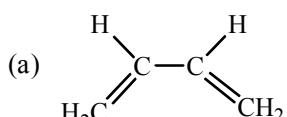
(2008)

6. The correct statement(s) about the compound X,  $\text{H}_3\text{C}(\text{HO})\text{HC}-\text{CH}=\text{CH}-\text{CH}(\text{OH})\text{CH}_3$  is (are)

- (a) The total number of stereoisomers possible for X is 6
- (b) The total number of diastereomers possible for X is 3
- (c) If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4
- (d) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2

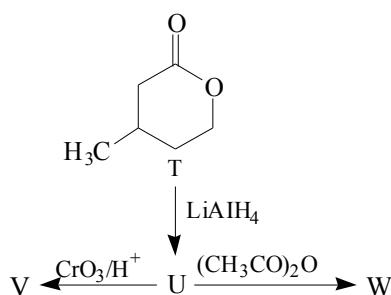
(2009)

7. Among the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any) is (are)



(2011)

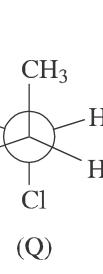
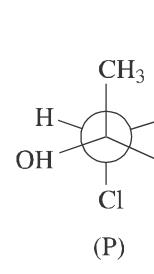
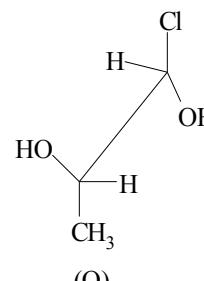
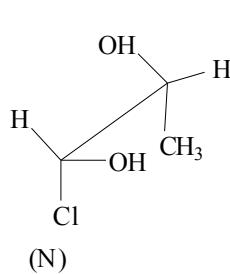
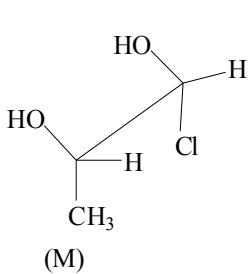
8. With reference to the scheme given, which of the given statement(s) about T, U, V and W is(are) correct?



- (a) T is soluble in hot aqueous NaOH.
- (b) U is an optically active compound.
- (c) Molecular formula of W is  $\text{C}_{10}\text{H}_{18}\text{O}_4$ .
- (d) V gives effervescence with aqueous  $\text{NaHCO}_3$ .

(2012)

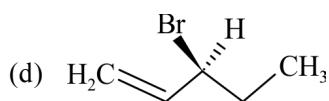
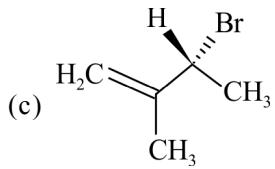
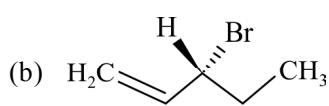
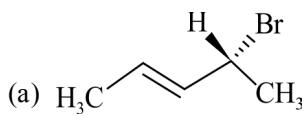
9. Which of the given statement(s) about N, O, P and Q with respect to M is(are) correct?



- (a) M and N are non-mirror image stereoisomers.
- (b) M and O are identical.
- (c) M and P are enantiomers.
- (d) M and Q are identical.

(2012)

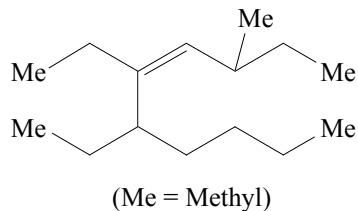
10. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are)



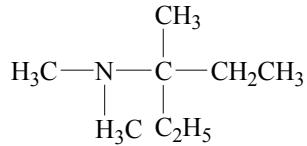
(2015)

### Fill-in-the-Blanks Type

- The terminal atom in butane is \_\_\_\_ hybridised. (1985)
- The IUPAC name of  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$  is \_\_\_\_\_. (1986)
- Isomers which are \_\_\_\_ mirror images are known as \_\_\_\_\_. (superimposable, non-superimposable, enantiomers, diastereomers, epimers) (1988)
- The IUPAC name of the compound



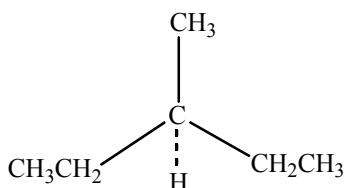
- is \_\_\_\_\_. (1990)
- The IUPAC name of the compound



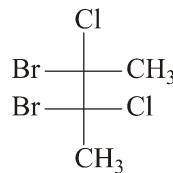
- is \_\_\_\_\_. (1991)
- The IUPAC name of succinic acid is \_\_\_\_\_. (1994)

### Integer Answer Type

- The total number of cyclic structure as well as stereoisomers possible for a compound  $\text{C}_5\text{H}_{10}$  is \_\_\_\_\_. (2009)
- The total number of cyclic isomers possible for a hydrocarbon with the molecular formula  $\text{C}_4\text{H}_6$  is \_\_\_\_\_. (2010)
- The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is \_\_\_\_\_. (2011)

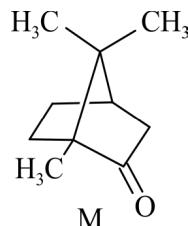


4. The total number(s) of **stable** conformers with non-zero dipole moment for the following compound is/are



(2014)

5. The total number of stereoisomers that can exist for **M** is \_\_\_\_\_.



(2015)

### True/False Type

1. 2,3,4-Trichloropentane has three asymmetric carbon atoms.

(1990)

### Reasoning Type

1. STATEMENT-1: Molecules that are not superimposable on their mirror images are chiral.

because

STATEMENT-2: All chiral molecules have chiral centres.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is correct explanation for Statement-1

(b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(c) Statement-1 is True, Statement-2 is False

(d) Statement-1 is False, Statement-2 is True

(2007)

### Short Answer Type

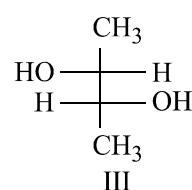
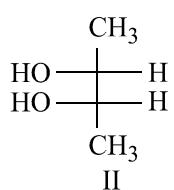
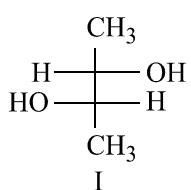
1. How many asymmetric carbon atoms are created during the complete reduction of benzil (PhC(=O)COPh) with LiAlH4? Also, write the number of possible stereoisomers in the product.

(1997)

2. Discuss the hybridisation of carbon atoms in allene (C3H4) and show the  $\pi$ -orbital overlaps.

(1999)

3. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III.



(2000)

4. A recemic mixture of  $(\pm)$  2-phenyl-propanoic acid on esterification with  $(+)$  2-butanol gives two esters. Mention the stereochemistry of the esters produced.

(2003)

5. (a)  $(-)$ -Lactic acid is racemised in aqueous sodium hydroxide. Explain

(b) Mandelic acid, C6H5CHOHCO2H, is readily racemised by warming with aqueous sodium hydroxide. On the other hand, atrolactic acid, C6H5C(CH3)(OH)CO2H, is not racemised. Explain.

(c) The addition of hydrogen cyanide to carbonyl compounds is accelerated by bases and retarded by acids. Explain.

(2003)

## **Straight Objective Type**

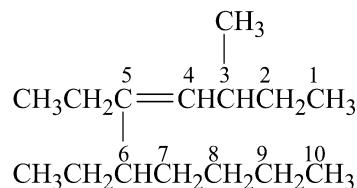
- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (d)  | 3. (c)  | 4. (b)  | 5. (d)  | 6. (a)  | 7. (c)  |
| 8. (c)  | 9. (c)  | 10. (b) | 11. (b) | 12. (a) | 13. (b) | 14. (d) |
| 15. (c) | 16. (d) | 17. (c) | 18. (b) | 19. (a) | 20. (c) | 21. (a) |
| 22. (b) | 23. (d) | 24. (a) | 25. (d) | 26. (b) | 27. (d) | 28. (c) |
| 29. (d) | 30. (a) | 31. (b) | 32. (d) | 33. (d) | 34. (a) | 35. (a) |
| 36. (c) | 37. (c) | 38. (a) | 39. (c) | 40. (b) | 41. (b) | 42. (a) |

## **Multiple Correct-Choice Type**

- 1.** (a), (b), (c)      **2.** (a), (d)      **3.** (c), (d)      **4.** (b), (c), (d)  
**5.** (a), (d)      **6.** (a), (d)      **7.** (a), (b), (c)      **8.** (a), (c), (d)  
**9.** (a), (b), (c)      **10.** (b), (d)

## **Fill-in-the-Blanks Type**

1.  $\text{sp}^3$
  2. Pent-2-ene-1-oic acid
  3. non-superimposable, enantiomers
  4. The given compound is



Its IUPAC name would be

### 5,6-Diethyl-3-methyldec-4-ene

- 5. 3-(*N,N*-dimethylamino)-3-methylpentane      6. butanedioic acid**

## **Integer Answer Type**

1. 7                  2. 5                  3. 8.                  4. 3  
5. 2

## **True/False Type**

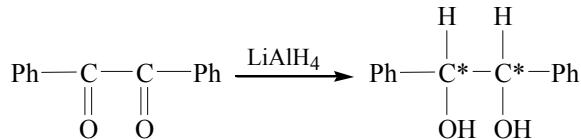
1. False

## **Reasoning Type**

1. (c)

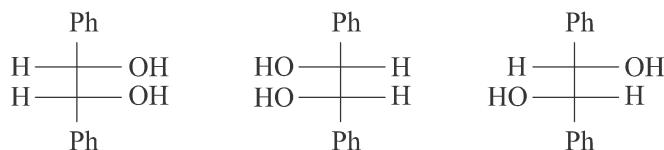
### Short Answer Type

1. The reaction is



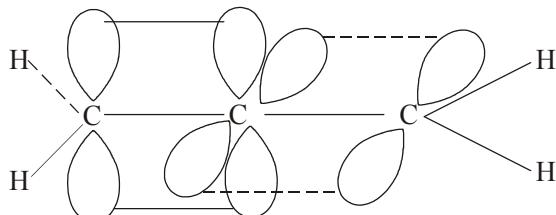
There are two asymmetric carbon atoms in the reduction product.

There are three stereoisomers of the reduction product.



2. The structure of allene is  $\text{H}_2\overset{1}{\text{C}}=\overset{2}{\text{C}}=\overset{3}{\text{CH}}_2$ . The carbons C1 and C3 are  $\text{sp}^2$  hybridised while C2 is  $\text{sp}$  hybridised.

The overlapping of  $\pi$ -orbitals in allene is as shown in Fig. C.1.



**Fig. C.1**

3. Enantiomers—Isomers are mirror images of each other.

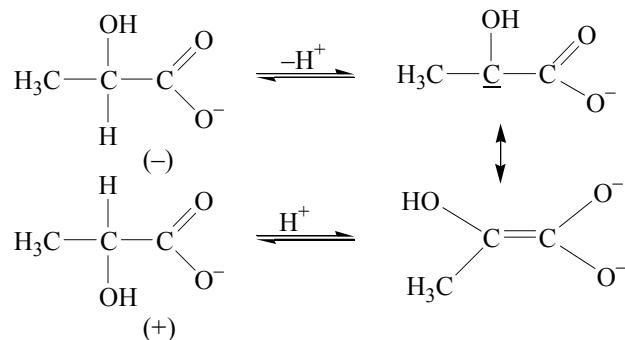
Diastereomers—Isomers are not mirror images of each other.

Hence, Structures I and III are enantiomers

Structures I and II, and II and III are diastereomers.

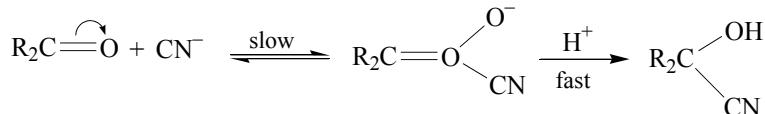
4. Since during esterification no bond is broken, the resultant esters will be ++ and +- isomers.

5. (a) The racemisation occurs via the enol form as shown in the following.



- (a) The methyl group in place of hydrogen atom in atrolactic acid prevents keto-enol tautomerism and hence racemisation.

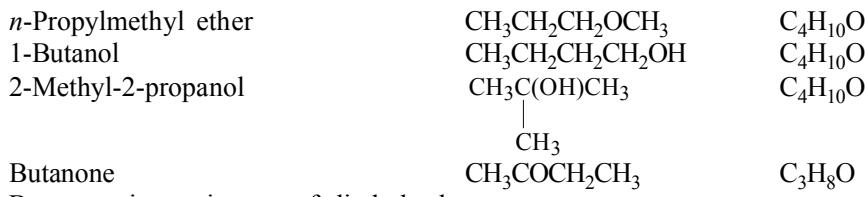
- (c) The addition of hydrogen cyanide proceeds as follows.



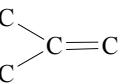
In bases,  $\text{CN}^-$  is formed from HCN while in acidic medium, the ionization of HCN to give  $\text{CN}^-$  is suppressed.

**HINTS AND SOLUTIONS****Straight Objective Type**

1. A single C—C bond has the largest bond distance.  
 2. Diethyl ether is  $C_2H_5OC_2H_5$  (molecular formula  $C_4H_{10}O$ ). The formulae of the given compounds are as follows.



Butanone is not isomer of diethyl ether.

3. The skeletons of  $C_4H_8$  are:  $C—C—C=C$ ;  $C—C=C—C$ ;   
*cis* and *trans*

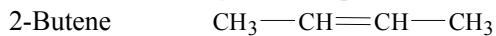
There are four isomers.

4. Carbon tetrachloride has no dipole moment.

5. 1, 2-Butadiene is  $\begin{matrix} CH_2 & = & C & = & CH & — & CH_3 \\ sp^2 & & sp & & sp^2 & & sp^3 \end{matrix}$

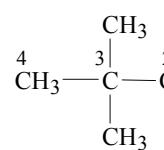
It has  $sp$ ,  $sp^2$  and  $sp^3$  carbon atoms.

6. The structure of given compounds are

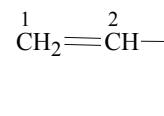


Only 2-Butene shows *cis-trans* isomerism.



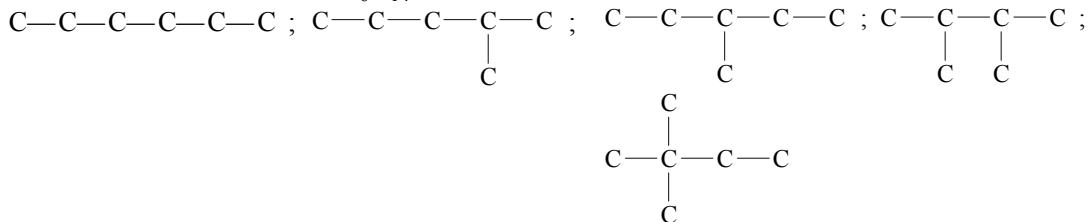
7. The IUPAC name of the compound  is 3, 3-dimethyl-1-butene.

8. C-1 is  $sp$  hybridised and C-2 is  $sp^2$  hybridised

9. The IUPAC name of the compound  is 3-methyl-1-butene.

10. Different formulae implies different molar masses.

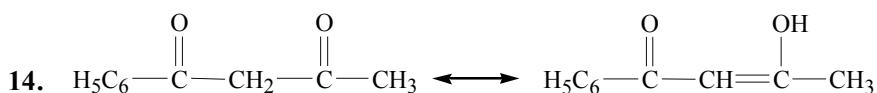
11. The skeletons of carbon in  $C_6H_{14}$  are as follows



12. C in 1,1,1,2-tetrachloroethene is  $sp^2$  hybridised. The angle Cl—C—Cl is expected to be  $120^\circ$ .  
 C in tetrachloromethane is  $sp^3$  hybridised. The angle Cl—C—Cl is expected to be  $109.5^\circ$ .

13.  $H_3C—CH_2—C\equiv C—CH_3 \xrightarrow{HBr} H_3CCH_2—\begin{matrix} | & | \\ H & Br \end{matrix}—C=C—CH_3 + H_3CCH_2—\begin{matrix} | & | \\ Br & H \end{matrix}—C=C—CH_3$

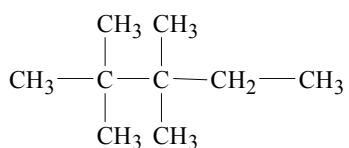
There will be 2 structural isomers and 4 configurational (*cis-trans*) isomers.



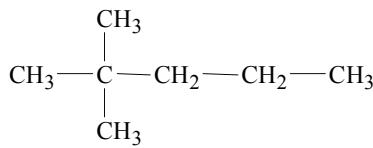
15.  $\text{HCOOH}$  involves  $\text{sp}^2$ ;  $(\text{H}_2\text{N})_2\dot{\text{C}}\text{O}$  involves  $\text{sp}^2$ ;  $(\text{CH}_3)_3\dot{\text{C}}\text{OH}$  involves  $\text{sp}^3$  and  $\text{CH}_3\dot{\text{C}}\text{HO}$  involves  $\text{sp}^2\dot{\text{C}}$  atom.

16. The structural formulae are

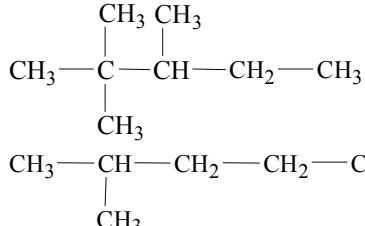
2, 2, 3, 3-tetramethylpentane



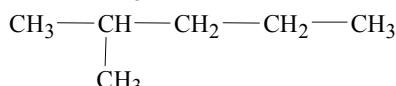
2, 2-dimethylpentane



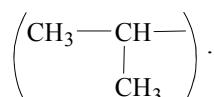
2, 2, 3-trimethylpentane



2-methylpentane



Only 2-methylpentane has one isopropyl group



17. The C—H bond length increases with decrease in the electronegativity of hybrid orbital of carbon atom. Hence, the bond length C—H will be largest in  $\text{C}_2\text{H}_6$ .

18. The structural formula in 1-butene-3-yne is  $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{CH}$

It has 7 sigma (4 C—H and 3 C—C) and 3 pi bonds (one in double and two in triple bond).



19. The enolic form of acetone is  $\text{H}_2\text{C}=\text{C}(\text{O})-\text{CH}_3$ . It contains 9 sigma bonds, 1 pi bond and two lone pairs of electrons on oxygen.

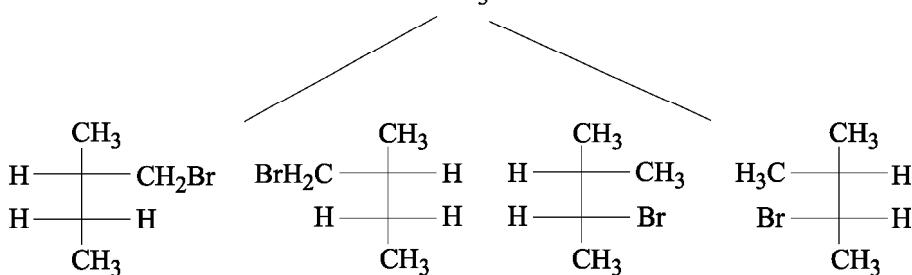
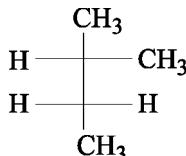
20. We have  $\text{HC}\equiv\text{C}-\underset{\text{sp}}{\text{CH}}=\underset{\text{sp}^2}{\text{CH}_2}$ .

21. Isomers which can be interconverted through rotation around a single bond are known as conformers.

22. The isomeric alcohols are

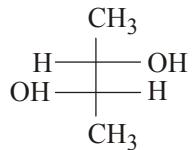


24.

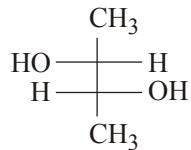


25. The rotation of (B) by  $180^\circ$  in the plane of paper produces the mirror image of (A). Hence, (A) and (B) are enantiomers.

26. The stereoisomers of butane-2,3-diol are



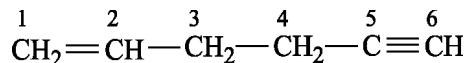
## Optically active enantiomers



$$\begin{array}{c}
 & \text{CH}_3 \\
 & | \\
 \text{H} & - & \text{OH} \\
 & | \\
 \text{H} & - & \text{OH} \\
 & | \\
 & \text{CH}_3
 \end{array}$$

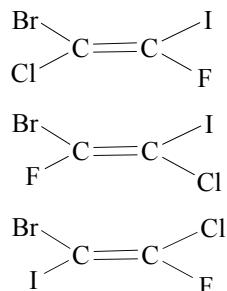
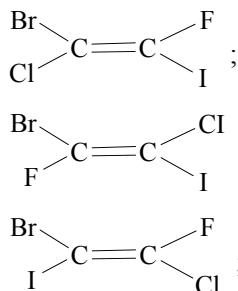
Meso- compound optically inactive

27. The compounds containing both double and triple bonds are called enynes. But, the numbering in the given compound goes as



The  $C_2 - C_3$  bond is  $sp^2 - sp^3$

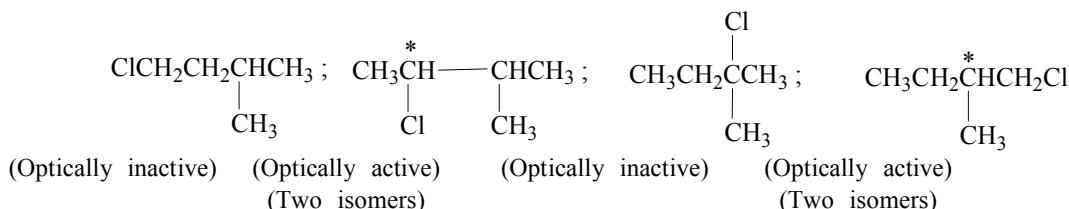
29. SbCl<sub>5</sub> extracts chloride leaving behind a carbocation.  
30. Only 1-phenyl-2-butene will exhibit *cis-trans* isomerism.  
32. The six compounds will be



33. 2-Methylbutanoic acid has one asymmetric carbon atom.

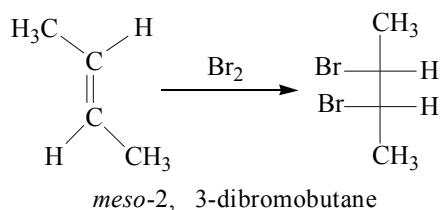
34. Choice a       $\text{sp}^2, \text{ sp}^2, \text{ sp}, \text{ sp}$   
                        $\text{sp}^3, \text{ sp}^2, \text{ sp}^2, \text{ sp}^3$       Choice b       $\text{sp}, \text{ sp}, \text{ sp}, \text{ sp}$   
                        $\text{sp}^2, \text{ sp}^2, \text{ sp}^2, \text{ sp}^2$       Choice d       $\text{sp}^2, \text{ sp}^2, \text{ sp}^2, \text{ sp}^2$

- ### 36. The possible products are



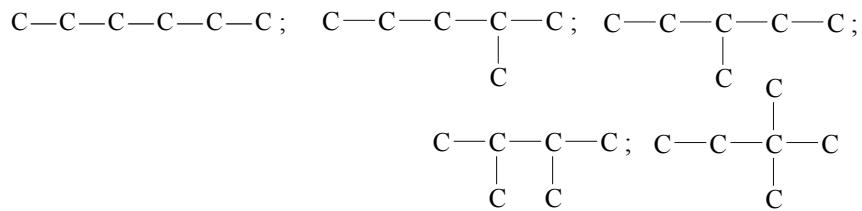
37. The IUPAC name of  $C_6H_5COCl$  is benzoyl chloride.

38. The addition of  $\text{Br}_2$  across a double bond involves the formation of a bromonium ion intermediate followed by the *anti* addition of  $\text{Br}^-$ . For *trans*-2-butene, the reaction proceeds so as to form *meso*-2, 3-dibromobutane.



Thus, only one stereoisomer is obtained.

39. The molecule  $C_6H_{14}$  is an alkane. It can have the following carbon skeletons.



Thus, the molecule  $C_6H_{14}$  can have 5 structure isomers.

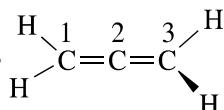
40. The order of preference of principal functional group is as follows.

Carboxylic acid, sulphonic acid, ester, acid halide, amide, nitrile, aldehyde, ketone, alcohol, amine, ether, alkene.

The given compound contains  $-OH$ ,  $-CN$  and  $-Br$  groups. Of these,  $-CN$  group gets the preference and thus the compound is named as nitrile. Hence, its name is

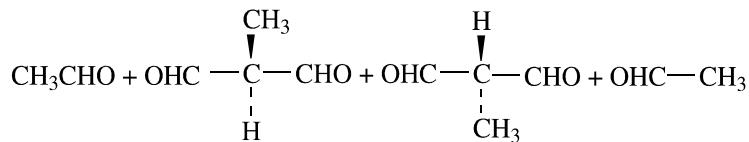
2-Bromo-5-hydroxybenzonitrile.

41. The structure of allene is



In this molecule, carbon atoms 1 and 3 are  $sp^2$  hybridized while the carbon atom 2 is  $sp$  hybridized.

42.  $CH_3-CH\ddot{C}(CH_3)-CH=C(CH_3)-CH=C(CH_3)-CH=C(CH_3)-CH_3 \xrightarrow{\text{Ozonolysis}}$

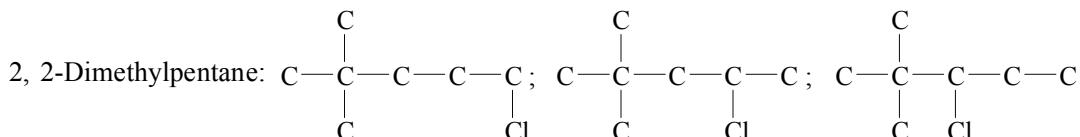


None of the products will be optically active.

### Multiple Correct-Choice Type

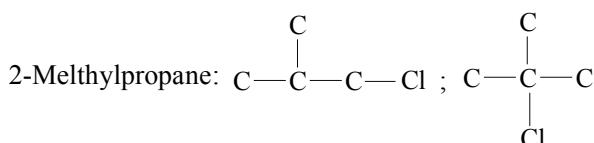
1. Resonance structures have identical arrangement of atoms, nearly the same energy content and the same number of unpaired electrons.

2. *n*-Butane:  $C-C-C-C-Cl$ ;  $C-C-C(Cl)-C$

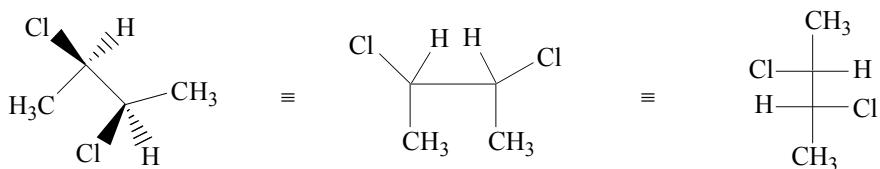


and so on.

Benzene :  $C_6H_5Cl$

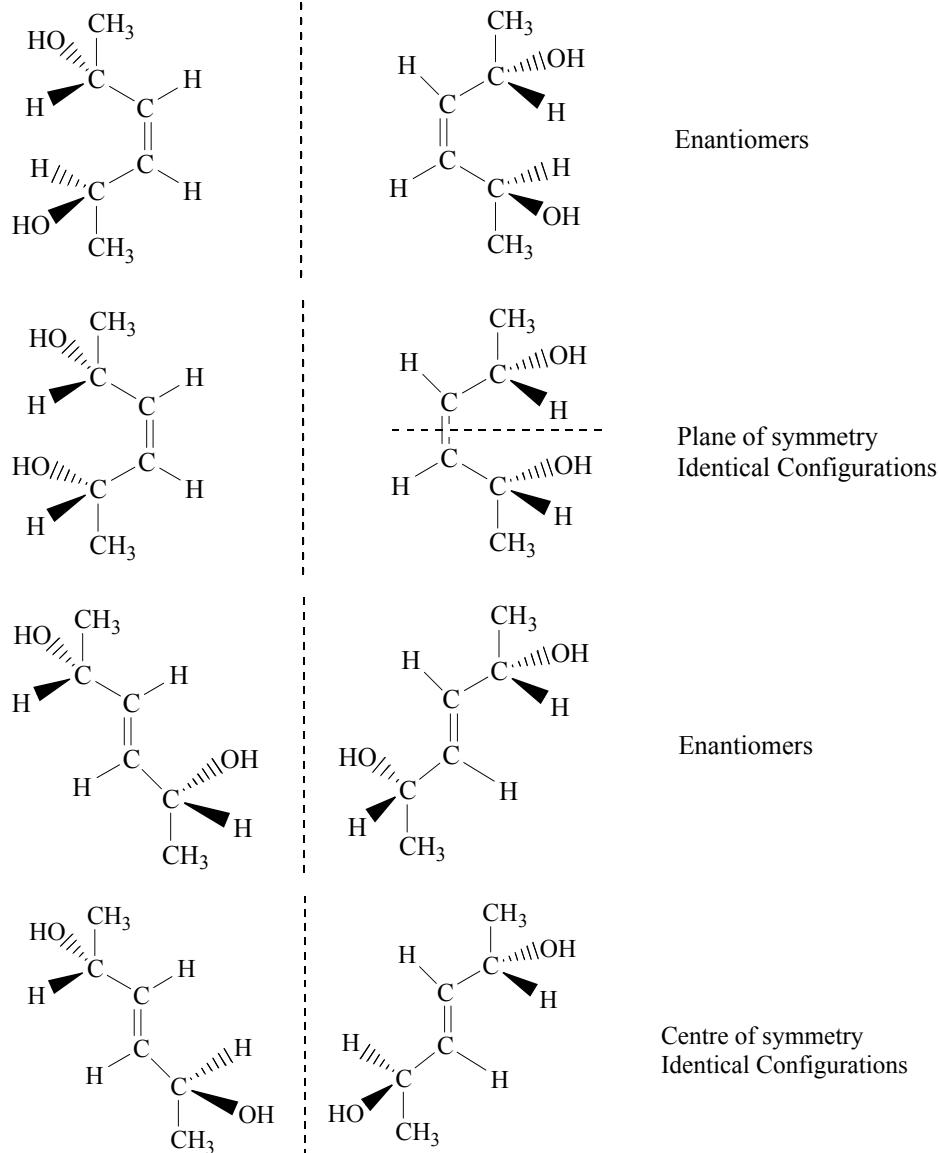


4. E and F, and G involve the migration of a proton from carbon atom to the adjacent atom. These are keto-enol tautomers (choice b).  
F and G are *cis*- and *trans*- isomers and thus constitute geometrical isomers (choice c)  
F and G are diastereomers. These are optical isomers that are not mirror images (choice d).
5. The given compound is



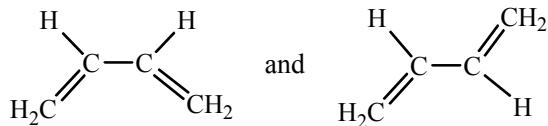
The compound is optically active and has diad axis of symmetry.

6. The configurations of the given compounds are as follows.



There are three isomers (RR), (SS) and (RS) in each of the two (*cis* and *trans*) configurations and hence six stereoisomers are possible. In these, (RR) and (SS) are enantiomers both in *cis* and *trans* configurations.

7. The choice (a) has two conformations.



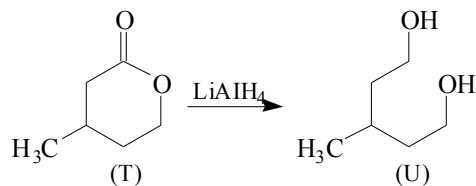
Because of extended conjugation, all atoms lie in the same plane.

The choice (b) has all the atoms in the same plane due to extended conjugation.

The choice (c) also has all the atoms in the same plane due to sp hybridization of the central carbon atom and the  $\pi$  bonds between C and C atoms. The two  $\pi$  bonds are perpendicular to each other.

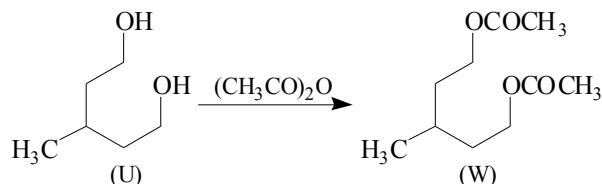
In choice (d), all the atoms are not in the same plane due to the fact that the two  $\pi$  bonds are perpendicular to each other. Hence, the **choices (a), (b) and (c)** are correct.

8. The compound T is a cyclic ester. It is soluble in hot aqueous NaOH  
The treatment of ester T with LiAlH<sub>4</sub> produces diol compound



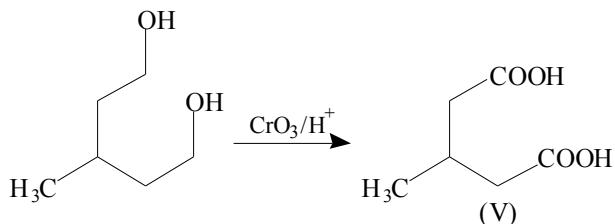
The compound U is not optically active as carbon bearing —CH<sub>3</sub> group contains two identical groups —CH<sub>2</sub>CH<sub>2</sub>OH.

The conversion of U to W is the acetylation of the two hydroxyl groups.



The molecular formula of W is C<sub>10</sub>H<sub>18</sub>O<sub>4</sub>.

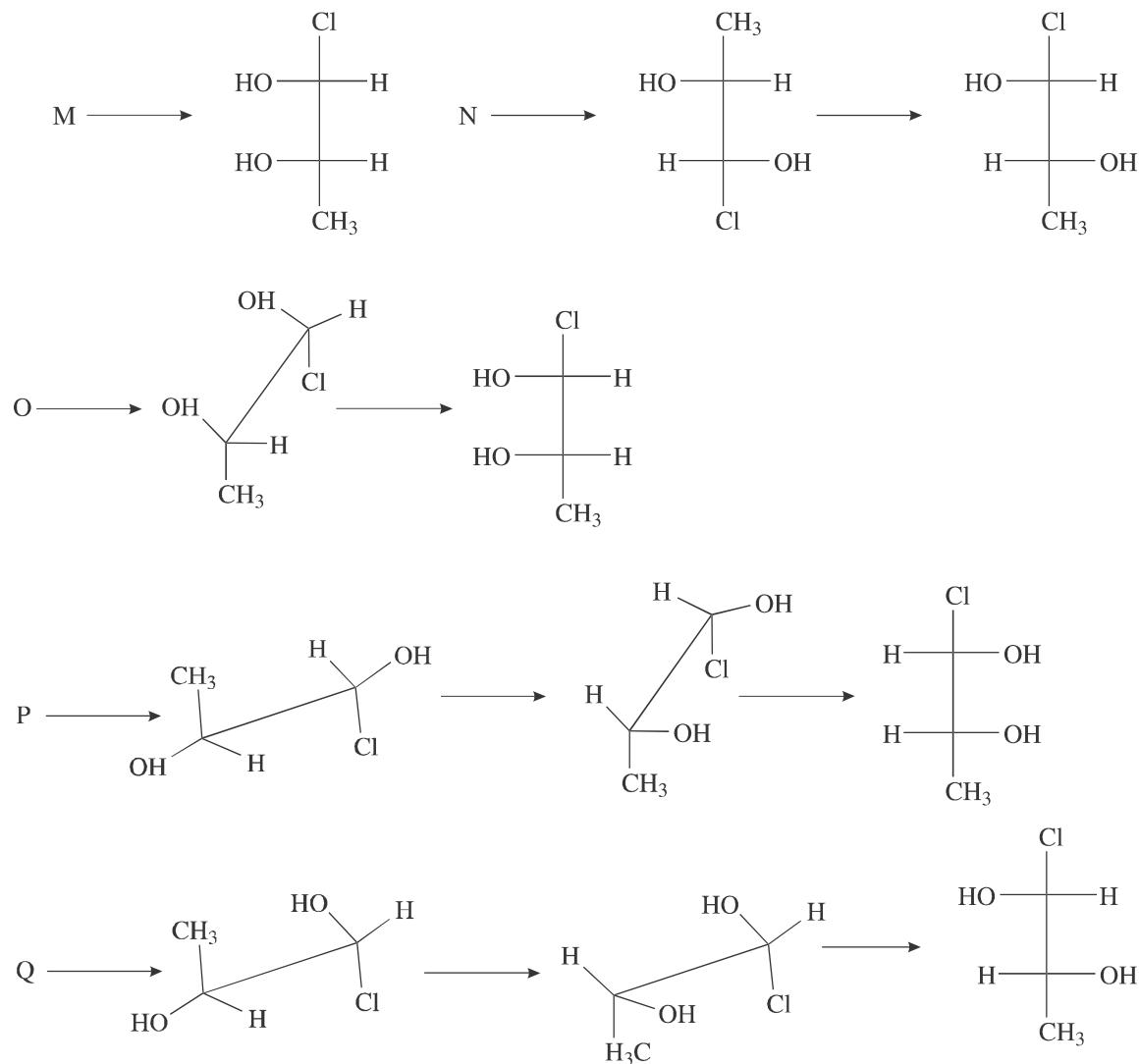
The conversion of U to V is the oxidation of the two —CH<sub>2</sub>OH groups to —COOH groups.



Being a dicarboxylic acid, it gives effervescence with NaHCO<sub>3</sub>(aq).

Therefore, the **choices (a), (c) and (d)** are correct.

9. First of all, we may draw Fischer projections of the given compounds



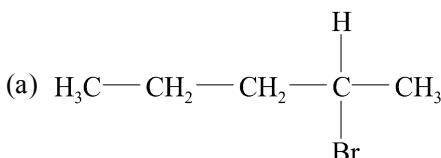
From the Fischer projections, it follows that

M and N are non-mirror images.

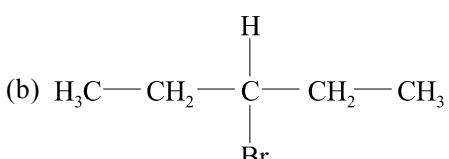
M and P are enantiomers.

Therefore the **choices (a), (b) and (c)** are correct.

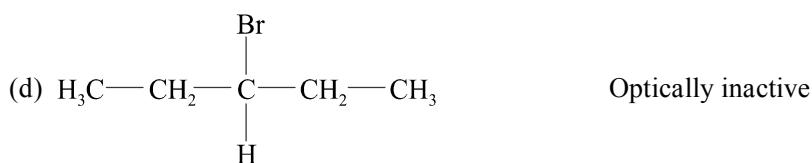
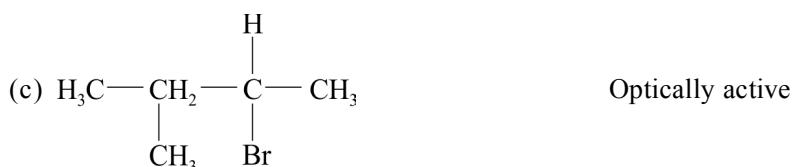
10. The hydrogenated products are:



Optically active



Optically inactive



Therefore the choice (b) and (d) are correct.

### **Fill-in-the-Blanks Type**

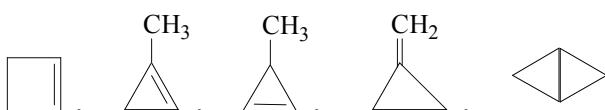
## **Integer Answer Type**

1. The following are the isomers of  $C_5H_{10}$

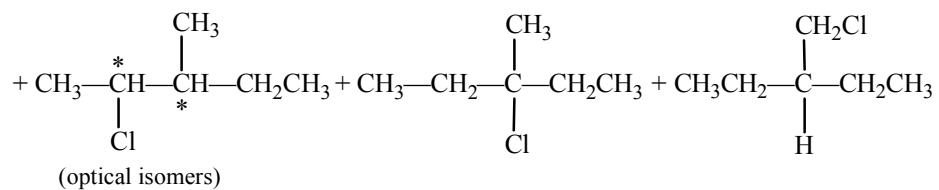
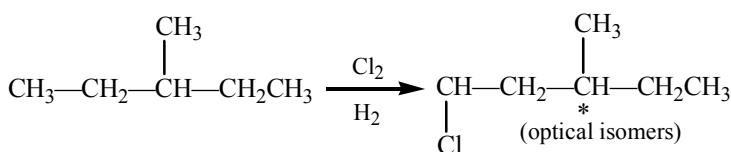
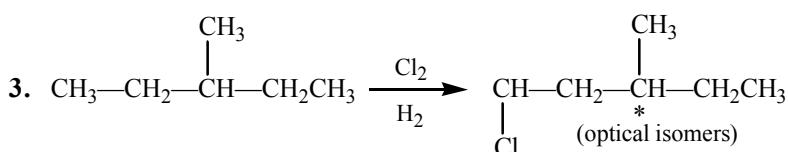


The structure  can exist as *cis-trans* isomers and one optical isomer are possible.

- Therefore, the total number of structures will be 7.



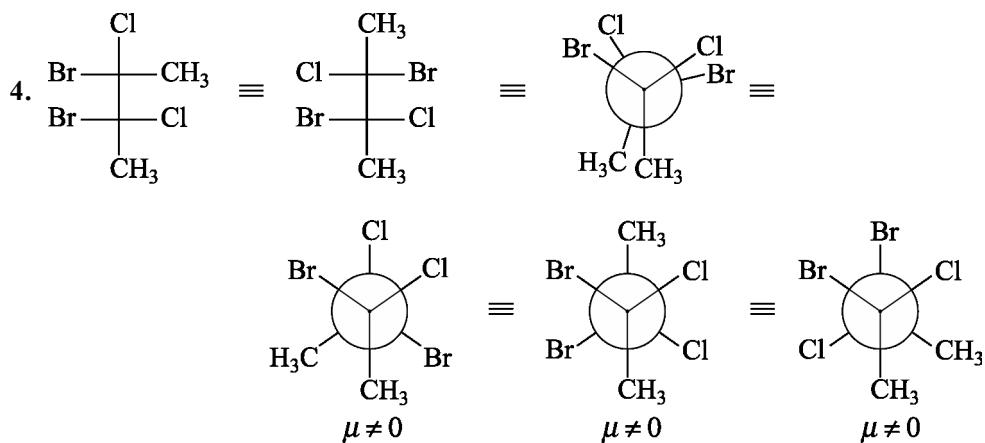
Hence there are five isomers



The number of isomers produced, respectively, from the above products is

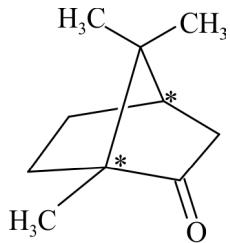
$$2^1 + 2^2 + 1 + 1 = 8$$

Hence, the correct answer is 8.



There are three stable conformers.

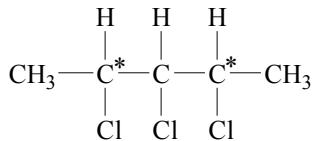
5. There are two asymmetric carbon atoms in the molecule.



Due to rigid bridged-bicyclic compound, the number of isomers observed is 2 instead of four.

### True/False Type

1. The structure of 2,3,4-trichloropentane is



It has two asymmetric carbon atoms shown as  $\text{C}^*$  in the above structure.

### Reasoning Type

1. Statement-1 is correct but statement-2 is not correct. For example, 2,3-pentadiene has no chiral C's, yet it is a chiral molecule (it has two enantiomers).

# INDUCTIVE AND RESONANCE EFFECTS

## Straight Objective Type

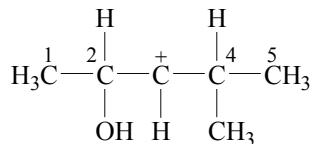
- Which of the following has the highest nucleophilicity?  
 (a)  $\text{F}^-$       (b)  $\text{OH}^-$       (c)  $\text{CH}_3^-$       (d)  $\text{NH}_2^-$       (2000)
- An  $\text{S}_{\text{N}}2$  reaction at an asymmetric carbon of a compound always gives  
 (a) an enantiomer of the substrate      (b) a product with opposite optical rotation  
 (c) a mixture of diastereomers      (d) a single stereoisomer      (2001)
- For 1-methoxy-1, 3-butadiene, which of the following resonating structures is the least stable?  
 (a)  $\text{H}_2\text{C}=\text{CH}-\overset{\oplus}{\text{CH}}-\overset{\ominus}{\text{CH}}-\text{O}-\text{CH}_3$       (b)  $\text{H}_2\text{C}=\text{CH}-\overset{\ominus}{\text{CH}}_2-\overset{\oplus}{\text{CH}}=\overset{\ominus}{\text{O}}-\text{CH}_3$   
 (c)  $\overset{\ominus}{\text{H}_3\text{C}}-\overset{\oplus}{\text{CH}}_2-\text{CH}=\text{CH}-\text{O}-\text{CH}_3$       (d)  $\text{H}_2\text{C}-\overset{\oplus}{\text{CH}}=\text{CH}-\overset{\ominus}{\text{CH}}=\overset{\oplus}{\text{O}}-\text{CH}_3$       (2005)
- The correct order of reactivity of the following types of H atom towards radical substitution is  
 (a) allylic > vinylic >  $1^\circ$  H      (b) allylic >  $1^\circ$  H > vinylic  
 (c)  $1^\circ$  H > allylic > vinylic      (d) vinylic > allylic >  $1^\circ$  H      (2005)
- Among the following, the least stable resonance structure is  
 (a)   
 (b)   
 (c)   
 (d)      (2007)
- Hyperconjugation involves overlap of the following orbitals  
 (a)  $\sigma - \sigma$       (b)  $\sigma - \text{p}$       (c)  $\text{p} - \text{p}$       (d)  $\pi - \pi$       (2008)
- The correct stability order for the following species is  
 (I)   
 (II)   
 (III)   
 (IV)

- (a) (II) > (IV) > (I) > (III)  
 (c) (II) > (I) > (IV) > (III)

- (b) (I) > (II) > (III) > (IV)  
 (d) (I) > (III) > (II) > (IV)

(2008)

8. In the carbocation

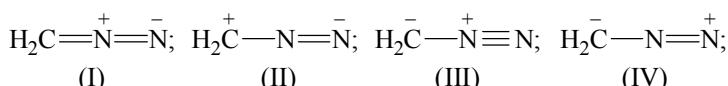


the species  $\text{H}/\text{CH}_3$  that is most likely to migrate the positively charged carbon is

- (a)  $\text{CH}_3$  at C—4    (b) H at C—4    (c)  $\text{CH}_3$  at C—2    (d) H at C—2

(2009)

9. The correct stability order of the resonance structures

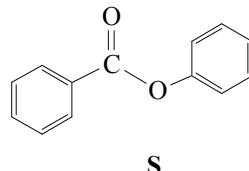
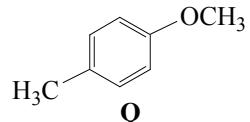
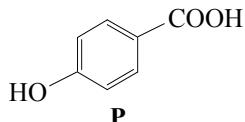


is

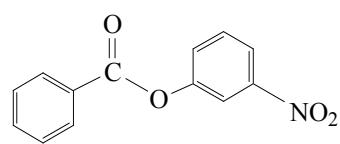
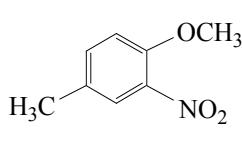
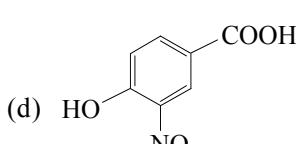
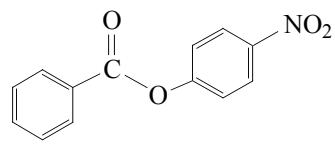
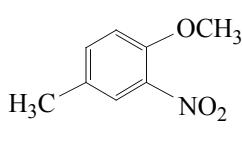
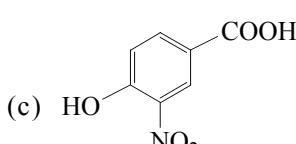
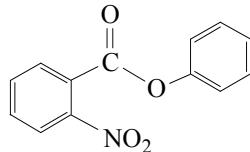
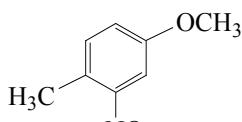
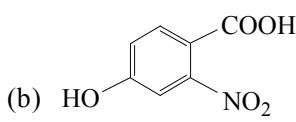
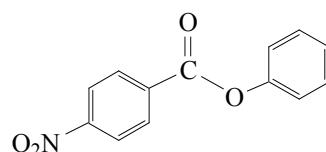
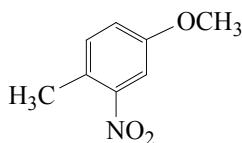
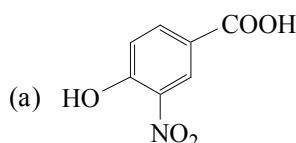
- (a) (I) > (II) > (IV) > (III)    (b) (I) > (III) > (II) > (IV)  
 (c) (II) > (I) > (III) > (IV)    (d) (III) > (I) > (IV) > (II)

(2009)

10. The compounds P, Q and S



were separately subjected to nitration using  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture. The major product formed in each case respectively, is



(2010)

11. The hyperconjugative of *tert*-butyl cation and 2-butene, respectively, are due to
- $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi^*$  electron delocalization
  - $\sigma \rightarrow \sigma^*$  and  $\sigma \rightarrow \pi$  electron delocalization
  - $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalization
  - p (filled)  $\sigma^*$  and  $\sigma \rightarrow \pi^*$  electron delocalization
- (2013)

### Mulitple Correct-Choice Type

1. Hydrogen bonding plays a central role in the following phenomena:
- Ice floats in water
  - Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions
  - Formic acid is more acidic than acetic acid
  - Dimerization of acetic acid in benzene.
- (2014)

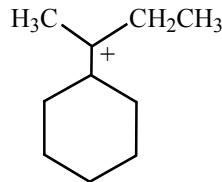
### Fill-in-the-Blanks Type

- Among the given cations, \_\_\_\_\_ is most stable (*sec*-butyl carbonium ion, *tert*-butyl carbonium ion, *n*-butyl carbonium ion) (1981)
- The kind of delocalization involving sigma bond orbitals is called \_\_\_\_\_. (1994)
- Draw the stereochemical structures of the products in the following reaction



### Integer Answer Type

1. The total number of contributing structures showing hyperconjugation (involving C—H bonds) for the following carbocation is \_\_\_\_\_. (2011)



### True/False Type

1. During S<sub>N</sub>1 reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule. (1990)

### Reasoning Type

1. **STATEMENT-1:** Bromobenzene upon reaction with Br<sub>2</sub>/Fe gives 1, 4-dibromobenzene as the major product. and  
**STATEMENT-2:** In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in direction of the incoming electrophile.

- (A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1  
 (B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is **NOT** a correct explanation for STATEMENT-1  
 (C) STATEMENT-1 is True, STATEMENT-2 is False  
 (D) STATEMENT-1 is False, STATEMENT-2 is True

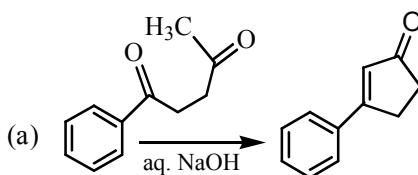
(2008)

### Matrix Match Type

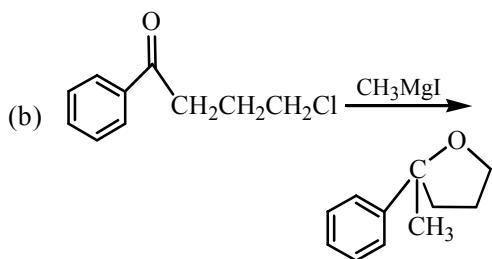
1. Match the reactions in **Column I** with appropriate type of steps/reactive intermediate involved in these reactions as given in **Column II**.

**Column I**

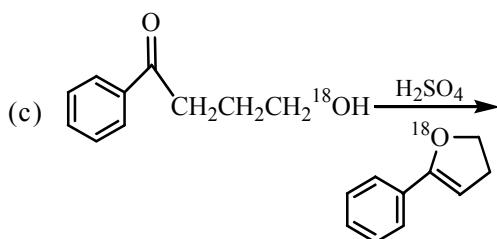
**Column II**



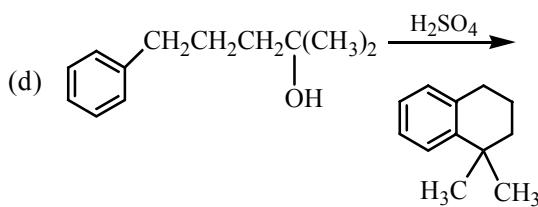
(p) Nucleophilic substitution



(q) Electrophilic substitution



(r) Dehydration



(s) Nucleophilic addition

(t) Carbanion

(2011)

### Short Answer Type

1. For nitromethane molecule, write structure(s) indicating (a) significant resonance stabilisation, and (b) tautomerism.

(1986)

2. Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ( $C_6H_5-C_6H_5$ ) is more reactive than benzene towards electrophilic substitution. (1992)
3. In acylium ion, the structure  $R-C\equiv\overset{+}{O}$  is more stable than  $R-\overset{+}{C}=O$ . (1994)
4. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995)
5. Predict the structure of the product in the following reaction.



6. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why? (1997)

## ANSWERS

### Straight Objective Type

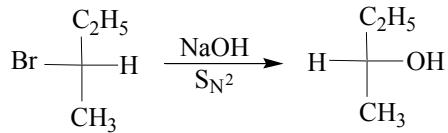
1. (c)      2. (d)      3. (a)      4. (d)      5. (a)      6. (b)  
 7. (d)      8. (d)      9. (b)      10. (c)      11. (a)

### Mulitple Correct-Choice Type

1. (a), (b), (d)

### Fill-in-the-Blanks Type

1. *tert*-butyl carbonium  
 2. hyperconjugation  
 3. In  $S_N2$  reactions, the substitution occurs with stereochemical inversion. Hence the reaction is



### Integer Answer Type

1. 6

### True/False Type

1. True

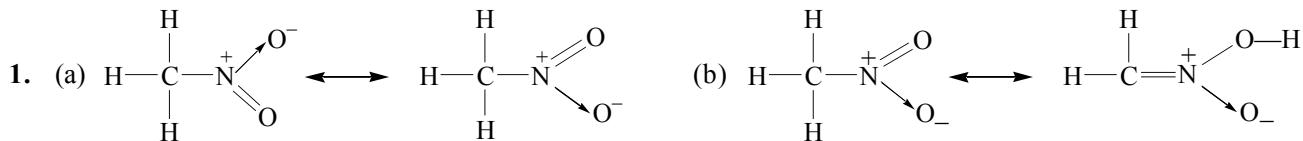
### Reasoning Type

1. (c)

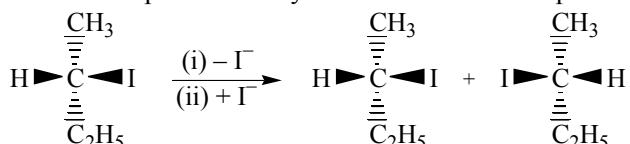
### Matrix Match Type

1. (a)  $\leftrightarrow$  (r), (s), (t)      (b)  $\leftrightarrow$  (p), (s)      (c)  $\leftrightarrow$  (r), (s)      (d)  $\leftrightarrow$  (q), (r)

### Short Answer Type

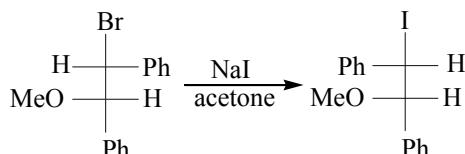


2. In biphenyl, one of the phenyl group acts as electron donor and the other electron acceptor. This makes the phenyl ring more reactive than benzene towards electrophilic substitution.
3. The acylium ion  $R-C\equiv\overset{+}{O}$  is more stable than  $R-\overset{+}{C}=O$ , the ordinary carbonium ion. In the former the octet of every atom is complete while in the latter it is not so, as in the case of the carbon atom which has only 6 electrons.
4. There occurs breaking and reforming of C—I bond. This results into two enantiomers which form racemic mixtures. The latter does not show optical activity due to external compensation.

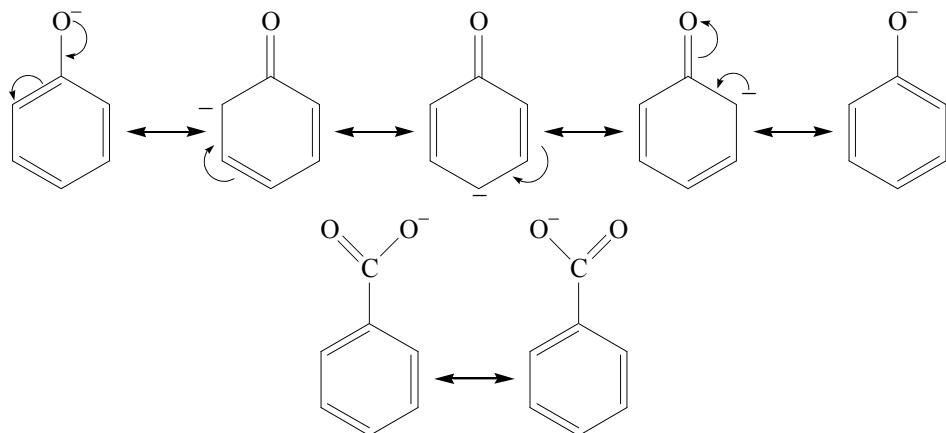


Racemic modification

5. Br is replaced by I following  $S_N2$  mechanism. There will be Walden inversion at the place of replacement.



6. The resonating structures are



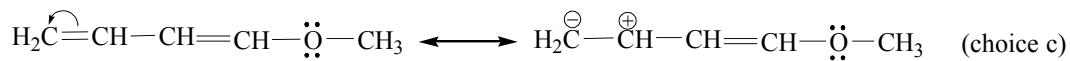
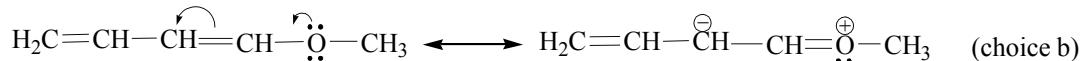
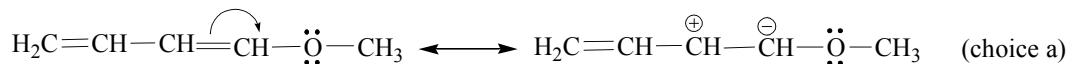
The benzoate ion is more stabilised because the negative charge is on the more electronegative oxygen atom, whereas in phenoxide ion, it is on the less electronegative carbon atoms. This causes benzoic acid to be a stronger acid than phenol.

## HINTS AND SOLUTIONS

### Straight Objective Type

3. 1 methoxy-1, 3-butadiene is  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\ddot{\text{O}}-\text{CH}_3$

Its resonating structures may be visualized as follows.

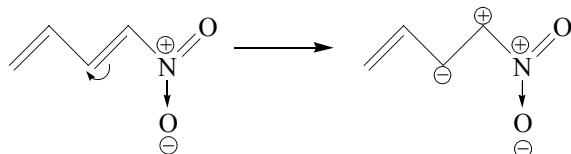


The structure  $\text{H}_2\text{C}=\text{CH}-\overset{+}{\text{CH}}-\overset{-}{\text{CH}}-\ddot{\text{O}}-\text{CH}_3$  (choice a) is expected to be least stable as the movement of electrons is in the opposite direction to that of electrons from oxygen of methoxy group.

4. The correct order is allylic >  $1^\circ$  alkyl > vinylic

The less positive  $\Delta H$  for the dissociation of C—H bond, the more reactive is H atom. The order of  $\Delta H$ 's is allylic <  $1^\circ$  alkyl < vinylic.

5. In the structure (a), the movement of  $\pi$ -electrons of —C=C— bond moves away from nitro group generating positively charged C near to the neighbouring positively charged N as shown in the following.



This leads to the least stability in the resonance structure.

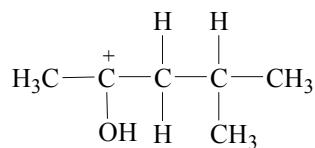
6. Hyperconjugation occurs in a molecular of the type —CH<sub>3</sub> where p orbitals of benzene overlap with  $\sigma$  orbitals of CH<sub>3</sub> group. Hence, hyperconjugation involves  $\sigma - p$  orbitals overlap.

7. Electron-donating species stabilises carbocation. Hence, (I) is more stable than (III).

$2^\circ$  carbocation is more stable than  $1^\circ$  carbocation. Hence, (II) is more stable than (IV).

Of the species (II) and (III), the species (III) will be more stable due to the lone-pair of electrons on oxygen atom. Hence, the order of stability is (I) > (III) > (II) > (IV).

8. It is H at C—2 that migrates to give



The positive charge on C—2 is resonance stabilised due to the neighbouring oxygen.

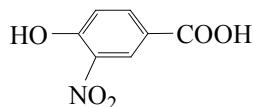
9. The structure (I) will be the most stable as it maintains conjugation.

The structure (IV) will be the least stable as it loses conjugation and lesser electronegative carbon acquires negative charge

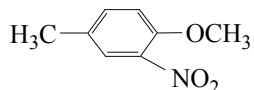
The structure (III) will be more stable than (II) as it maintains a triple bond between two nitrogens.

Hence, the correct order of stability is (I) > (III) > (II) > (IV)

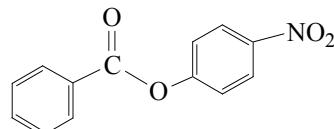
10. In the compound P,  $\text{---OH}$  is the controlling substituent. The compound obtained will be



In the compound Q,  $-\text{OCH}_3$  is the controlling substituent. The compound obtained will be



In the compound R, the benzene attached to O will be nitrated. The compound obtained will be



11.

$\sigma \rightarrow p$  (empty) electron delocalization

$\sigma \rightarrow \pi^*$

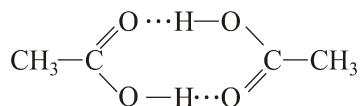
electron delocalization

## **Multiple Correct-Choice Type**

- Ice floats in water because it is less dense than the liquid water due to its open crystal structure because of hydrogen bondings.

Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attached to the nitrogen in the conjugate acid, the larger is its stability and thus larger is the basicity of the corresponding base. Thus, primary amines are more basic than tertiary amines in aqueous solution.

Acetic acid dimerise in benzene due to hydrogen bonding.



## **Integer Answer Type**

1. There are six  $\alpha$ -hydrogens present and thus there will be six contributing structures showing hyperconjugation (involving C—H bonds).

## **True/False Type**

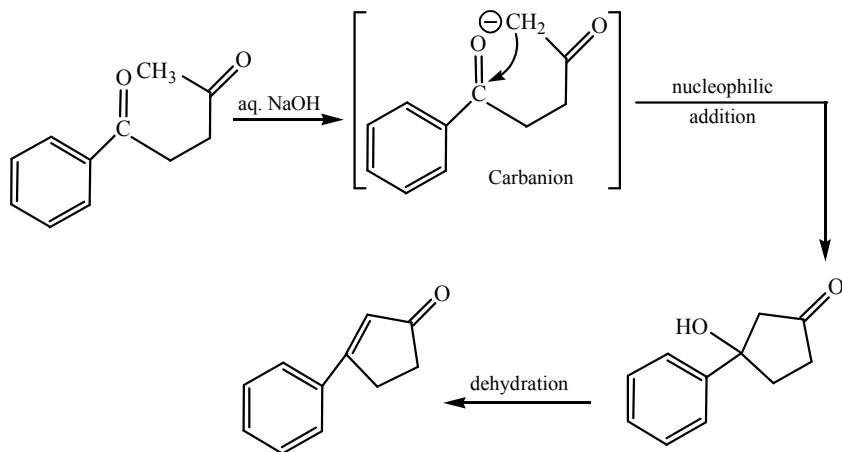
1.  $S_N1$  stands for nucleophilic substitution reaction of the first order. In this, the outgoing group breaks first to give carbocation followed by the addition of the incoming group.

**Reasoning Type**

1. Bromobenzene is *ortho*- and *para*-director due to the fact that in the electrophilic substitution reaction, mesomeric effect is more dominant than the inductive effect.

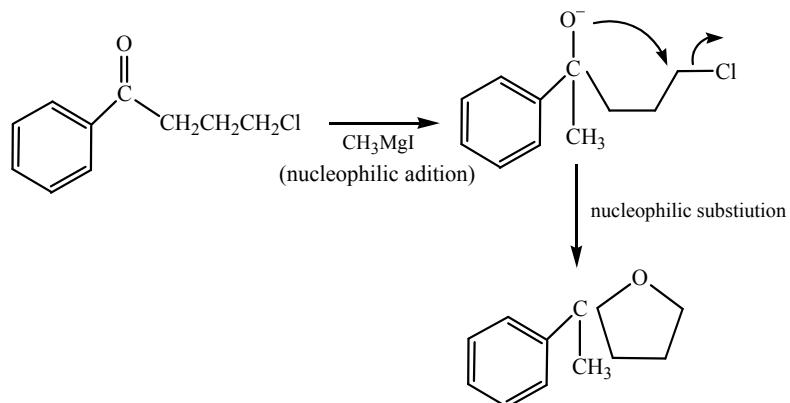
**Matrix Match Type**

1. (a) The intramolecular aldol reaction proceeds as follows.



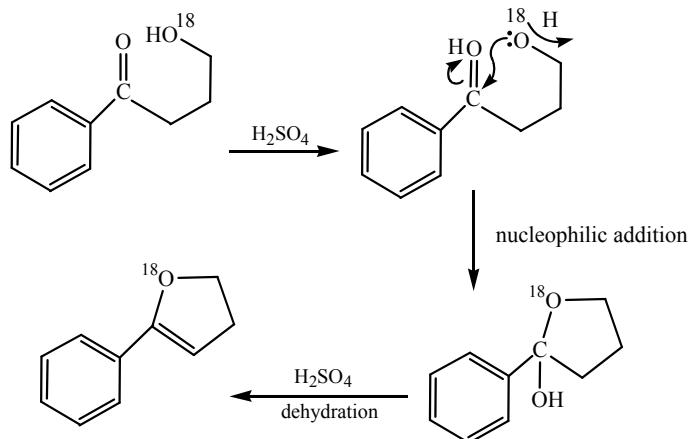
Hence, the correct matching is (a)  $\leftrightarrow$  (r), (s), (t)

- (b) The reaction proceeds as follows.



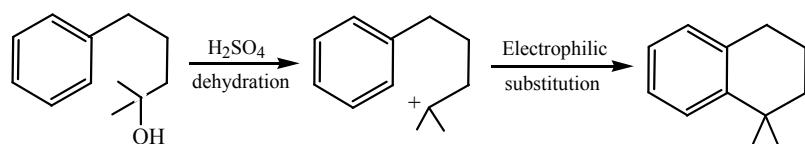
Hence, the correct matching is (b)  $\leftrightarrow$  (p), (s)

(c) The reaction proceeds as follows.



Hence, the correct matching is (c)  $\leftrightarrow$  (r), (s)

(d) The reaction proceeds as follows.



Hence, the correct matching is (d)  $\leftrightarrow$  (q), (r)



# ALKANES

21

## **Straight Objective Type**

1. Marsh gas mainly contains  
 (a)  $\text{C}_2\text{H}_2$       (b)  $\text{CH}_4$       (c)  $\text{H}_2\text{S}$       (d)  $\text{CO}$       (1980)

2. The compound with the highest boiling point is  
 (a) *n*-hexane      (b) *n*-pentane  
 (c) 2, 2-dimethylpropane      (d) 2-methylbutane      (1982)

3. The reaction conditions leading to the best yield of  $\text{C}_2\text{H}_5\text{Cl}$  are  
 (a)  $\text{C}_2\text{H}_6$ (excess) +  $\text{Cl}_2$   $\xrightarrow{\text{uv light}}$   
 (b)  $\text{C}_2\text{H}_6$  +  $\text{Cl}_2$   $\xrightarrow[\text{room temperature}]{\text{dark}}$   
 (c)  $\text{C}_2\text{H}_6$  +  $\text{Cl}_2$ (excess)  $\xrightarrow{\text{uv light}}$   
 (d)  $\text{C}_2\text{H}_6$  +  $\text{Cl}_2$   $\xrightarrow{\text{uv light}}$       (1986)

4. The highest boiling point is expected for  
 (a) isoctane      (b) *n*-octane  
 (c) 2,2,3,3-tetramethylbutane      (d) *n*-butane      (1986)

5. Which of the following will have least hindered rotation about carbon-carbon bond?  
 (a) Ethane      (b) Ethylene      (c) Acetylene      (d) hexachloroethane      (1987)

6. When cyclohexane is poured on water, it floats, because:  
 (a) cyclohexane is in ‘boat’ form      (b) cyclohexane is in ‘chair’ form  
 (c) cyclohexane is in ‘crown’ form      (d) cyclohexane is less dense than water.      (1987)

7. Benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) can be prepared from toluene by chlorination with  
 (a)  $\text{SO}_2\text{Cl}_2$       (b)  $\text{SOCl}_2$       (c)  $\text{Cl}_2$       (d)  $\text{NaOCl}$       (1998)

8. Consider the following reaction:  $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\underset{\text{CH}_2}{\text{CH}}-\text{CH}_3 + \dot{\text{Br}} \rightarrow \text{X} + \text{HBr}$

Identify the structure of the major product 'X'

- (a)  $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\dot{\text{CH}}_2$

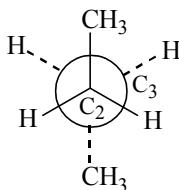
(b)  $\text{H}_3\text{C}-\underset{\text{D}}{\text{CH}}-\underset{\text{CH}_3}{\overset{\bullet}{\text{C}}}-\text{CH}_3$

(c)  $\text{H}_3\text{C}-\underset{\text{D}}{\overset{\bullet}{\text{C}}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

(d)  $\text{H}_3\text{C}-\dot{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$

(2002)

9. In the given conformation,



$C_2$  is rotated about  $C_2-C_3$  bond clockwise by an angle of  $120^\circ$ . The obtained conformation is

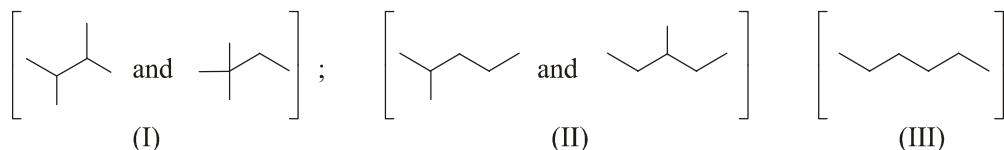


10. In the reaction

$(CH_3)_2CHCH_2CH_3 \xrightarrow[\text{hv}]{Cl_2} N$  isomers of  $C_5H_{11}Cl \xrightarrow{\text{Fractional distillation}} n$  distilled products. The values of  $N$  and  $n$  respectively are



- 11.** Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.



The correct order of their boiling points is

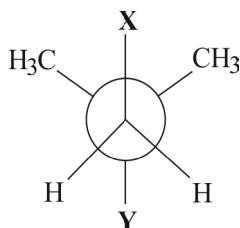
- (a) I > II > III      (b) III > II > I      (c) II > III > I      (d) III > I > II      (2014)

## **Multiple Correct-Choice Type**

1. A new carbon-carbon bond formation is possible in



2. In the Newman projection for 2,2-dimethylbutane



X and Y can respectively be



## **Fill-in-the-Blanks Type**

- The halogen which is most reactive in the halogenation of alkanes under sunlight is \_\_\_\_\_ (chlorine, bromine, iodine) (1981)
  - \_\_\_\_\_ ring is not strained (cyclopropane, cyclobutane, cyclopentane) (1981)
  - The shape of  $\text{CH}_3^+$  is \_\_\_\_\_. (1991)

**True/False Type**

1. Methane does not react with chlorine in the dark. (1983)
2. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio 9:1. (1993)

**Short Answer Type**

1. Nitrobenzene does not undergo Friedel–Crafts alkylation (1998)

**ANSWERS****Straight Objective Type**

- |        |        |        |         |         |        |
|--------|--------|--------|---------|---------|--------|
| 1. (b) | 2. (a) | 3. (a) | 4. (b)  | 5. (a)  | 6. (d) |
| 7. (c) | 8. (b) | 9. (b) | 10. (b) | 11. (b) |        |

**Multiple Correct-Choice Type**

1. (b), (d)
2. (b), (d)

**Fill-in-the-Blanks Type**

1. chlorine
2. cyclopentane
3. planar

**True/False Type**

1. True
2. False

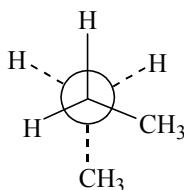
**Short Answer Type**

1. The nitro group in nitrobenzene strongly deactivates the benzene ring. This decreases the reactivity of benzene towards Friedel-Crafts alkylation.

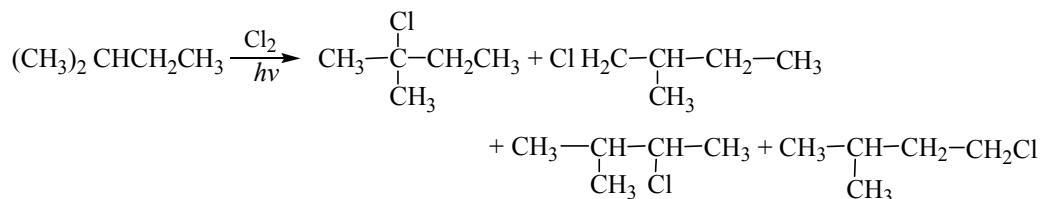
**HINTS AND SOLUTIONS****Straight Objective Type**

2. The boiling point decreases with increasing branching of carbon chain. It increases with increase in the number of carbon atoms. Hence, *n*-hexane is expected to have the highest boiling point.
3. Excess quantity of C<sub>2</sub>H<sub>6</sub> will yield mono chlorinated product (i.e. C<sub>2</sub>H<sub>5</sub>Cl).
4. Same as Q.2. *n*-Octane is expected to have the highest boiling point.
5. Ethane will have least hindered rotation about C—C bond.
8. The choice (b) involves 3° radical.

9. The resultant configuration is gauche.



10. Monochlorination of the given compound gives four products.



Of the four products, two are optically active each will produce two isomers. Hence, the number of isomers is 6 and the number of product is 4.

11. Greater the extent of branching, lesser the boiling point of hydrocarbon.

### Multiple Correct Choice Type

2. The given compound is  $\text{X---CH}_2\text{---}\underset{\text{CH}_3}{\text{C}}\text{---Y}$  and 2, 2-dimethylbutane is  $\text{CH}_3\text{---}\underset{\text{CH}_3}{\text{C}}\text{---CH}_3\text{---CH}_3$ .

Hence, either X should be H and Y should be  $\text{CH}_2\text{CH}_3$  or X should be  $\text{CH}_3$  and Y should also be  $\text{CH}_3$ .

### True/False Type

1. In the presence of light,  $\text{Cl}_2$  dissociates to give  $2\text{Cl}^-$  radicals which react with  $\text{CH}_4$  via free radical mechanism.
2.  $\text{Br}^-$  radical being less reactive is less influenced by the probability factor. The bromination primarily depends on the reactivity of H atom which is  $3^\circ > 2^\circ > 1^\circ$ .

# ALKENES

22

## Straight Objective Type

1. Baeyer's reagent is
  - (a) alkaline potassium permanganate solution
  - (b) acidified potassium permanganate solution
  - (c) neutral potassium permanganate solution
  - (d) aqueous bromine solution

(1984)
2. Anti-Markovnikov addition of HBr is not observed in
  - (a) propene
  - (b) butene
  - (c) 2-butene
  - (d) 2-pentene

(1985)
3. Of the following compounds, which will have a zero dipole moment?
  - (a) 1,1-dichloroethylene
  - (b) *cis*-1,2-dichloroethylene
  - (c) *trans*-1,2-dichloroethylene
  - (d) none of these compounds

(1987)
4. *n*-Propyl bromide on treating with ethanolic potassium hydroxide produces
  - (a) propane
  - (b) propene
  - (c) propyne
  - (d) propanol

(1987)
5. In CH<sub>3</sub>CH<sub>2</sub>OH, the bond that undergoes heterolytic cleavage most readily is
  - (a) C—C
  - (b) C—H
  - (c) C—O
  - (d) O—H

(1988)
6. 1-Chlorobutane on reaction with alcoholic potash gives
  - (a) 1-butene
  - (b) 1-butanol
  - (c) 2-butene
  - (d) 2-butanol

(1991)
7. Which one of the following has the smallest heat of hydrogenation per mole?
  - (a) 1-Butene
  - (b) *trans*-2-Butene
  - (c) *cis*-2-Butene
  - (d) 1,3-Butadiene

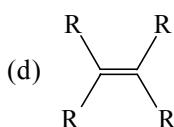
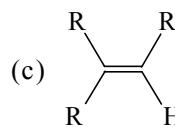
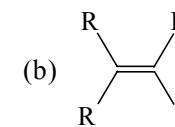
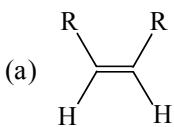
(1993)
8. During debromination of *meso*-dibromobutane, the major compound formed is
  - (a) *n*-butane
  - (b) 1-butene
  - (c) *cis*-2-butene
  - (d) *trans*-2-butene.

(1997)
9. The intermediate during the addition of HCl to propene in the presence of peroxide is
  - (a) CH<sub>3</sub>·CHCH<sub>2</sub>Cl
  - (b) CH<sub>3</sub>·<sup>+</sup>CHCH<sub>3</sub>
  - (c) CH<sub>3</sub>CH<sub>2</sub>·CH<sub>2</sub>
  - (d) CH<sub>3</sub>CH<sub>2</sub>·<sup>+</sup>CH<sub>2</sub>

(1997)
10. The reaction of CH<sub>3</sub>CH=CH——OH with HBr gives
  - (a) CH<sub>3</sub>CHBrCH<sub>2</sub>——OH
  - (b) CH<sub>3</sub>CH<sub>2</sub>CHBr——OH
  - (c) CH<sub>3</sub>CHBrCH<sub>2</sub>——Br
  - (d) CH<sub>3</sub>CH<sub>2</sub>CHBr——Br

(1998)

11. Which one of the following alkenes will react fastest with  $H_2$  under catalytic hydrogenation condition?



(2000)

12. The reaction of propene with  $HOCl$  proceeds via the addition of

(a)  $H^+$  in the first step

(b)  $Cl^+$  in the first step

(c)  $OH^-$  in the first step

(d)  $Cl^+$  and  $OH^-$  in a single step

(2001)

13. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because

(a) both are highly ionic

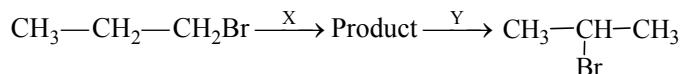
(b) one is oxidising and the other is reducing

(c) one of the steps is endothermic in both the cases

(d) all the steps are exothermic in both the cases

(2001)

14. Identify the set of reagents/reaction conditions 'X' and 'Y' in the following set of transformations:



(a) X = dilute aqueous  $NaOH$ , 20 °C; Y =  $HBr$ /acetic acid, 20 °C

(b) X = concentrated alcoholic  $NaOH$ , 80 °C; Y =  $HBr$ /acetic acid, 20 °C

(c) X = dilute aqueous  $NaOH$ , 20 °C; Y =  $HBr/CHCl_3$ , 0 °C

(d) X = concentrated alcoholic  $NaOH$ , 80 °C; Y =  $Br_2/CHCl_3$ , 0 °C

(2002)

15. The product of acid catalysed hydration of 2-phenylpropene is

(a) 1-phenyl-2-propanol

(b) 2-phenyl-2-propanol

(c) 1-phenyl-1-propanol

(d) 2-phenyl-1-propanol

(2004)

16. In the reaction  $CH_3—CH=CH_2 \xrightarrow{NOCl}$  A, the compound A is

(a)  $CH_3CH(NO)CH_2Cl$

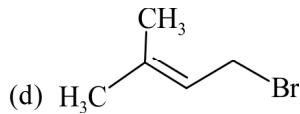
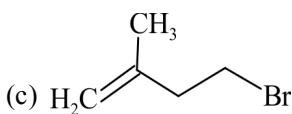
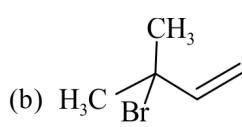
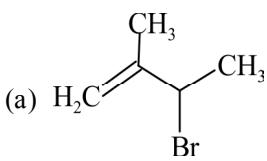
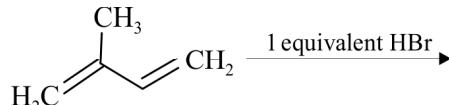
(b)  $CH_3CHClCH_2NO$

(c)  $CH_2(NO)CH_2CH_2Cl$

(d)  $CH_3CH(Cl)CH_2CH(Cl)CH_3$

(2006)

17. In the following reaction, the major product is



(2015)

### Multiple Correct-Choice Type

1. Dipole moment is shown by

(a) 1,4-dichlorobenzene

(b) *cis*-1,2-dichloroethene

(c) *trans*-1,2-dichloroethene

(d) 1,2-dichloro-2-pentene

(1986)

2. The molecules that will have dipole moment are

- |                          |                               |
|--------------------------|-------------------------------|
| (a) 2,2-dimethylpropane  | (b) <i>trans</i> -2-pentene   |
| (c) <i>cis</i> -3-hexene | (d) 2,2,3,3-tetramethylbutane |
- (1992)

3. Which of the following compounds will show geometrical isomerism?

- |                     |                       |
|---------------------|-----------------------|
| (a) 2-butene        | (b) propene           |
| (c) 1-phenylpropene | (d) 2-methyl-2-butene |
- (1998)

### Fill-in-the-Blanks Type

1. The main product obtained when ethene mixed with air is passed under pressure over a silver catalyst at 250°C is \_\_\_\_\_. (1981)

2. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with \_\_\_\_\_. (1983)

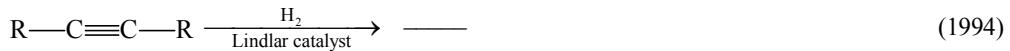
3. 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide provided \_\_\_\_ is present. (1984)

4. The structural formula of 4-chloro-2-pentene is \_\_\_\_\_. (1988)

5. The valence atomic orbitals on C in silver acetylidyde is \_\_\_\_ hybridised. (1990)

6. Kolbe electrolysis of potassium succinate gives CO<sub>2</sub> and \_\_\_\_\_. (1993)

7. Draw the stereochemical structures of the products in the following reaction.

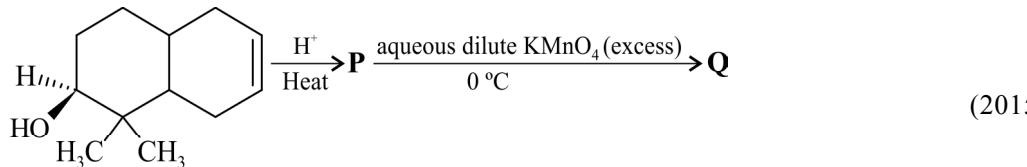


8. 1,3-Butadiene with bromine in molar ratio generates predominantly \_\_\_\_\_. (1997)

### Integer Answer Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is \_\_\_\_\_. (2011)

2. The number of hydroxyl group(s) in Q is



### True/False Type

1. Propene reacts with HBr to give *n*-propyl bromide. (1983)

2. Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1982)

3. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule. (1989)

### Reasoning Type

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subsection.

**Code**

- (a) If both assertion and statement are true and statement is an explanation of assertion.
- (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
- (c) If assertion is wrong and statement is correct, statement is an explanation of assertion
- (d) If both assertion and statement are wrong and statement is not explanation of assertion.

**Assertion (Column 1)****Reason (Column 2)**

1. Addition of $\text{Br}_2$ to 1-butene gives	The product contains one asymmetric carbon. two optical isomers.	(1998)
2. 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.	It involves the formation of a primary radical.	(2000)
3. Addition of bromine to <i>trans</i> -2-butene yields <i>meso</i> -2, 3-dibromobutane.	Bromine addition to an alkene is an electrophilic addition.	(2001)
4. Dimethylsulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compounds.	It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates.	(2001)

**Short Answer Type**

1. Write down the structures of the stereoisomers formed when *cis*-2-butene is reacted with bromine. (1995)
2. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions.
 

(a) HBr in the presence of peroxide	(b) $\text{Br}_2/\text{H}_2\text{O}$
(c) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}; \text{NaBH}_4$ .	

(1996)
3. Explain very briefly why alkynes are generally less reactive than alkenes towards electro-philic reagents such as  $\text{H}^+$ . (1997)
4. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When A is oxidised vigorously with  $\text{KMnO}_4$ , a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. (1997)
5. The central carbon-carbon bond in 1, 3-butadiene is shorter than that of *n*-butane. (1998)
6.  $\text{CH}_2 = \text{CH}^-$  is more basic than  $\text{HC} \equiv \text{C}^-$ . (2000)

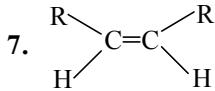
**ANSWERS****Straight Objective Type**

- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (c)  | 3. (c)  | 4. (b)  | 5. (d)  | 6. (a)  |
| 7. (d)  | 8. (d)  | 9. (b)  | 10. (b) | 11. (a) | 12. (b) |
| 13. (c) | 14. (b) | 15. (b) | 16. (b) | 17. (d) |         |

**Multiple Correct-Choice Type**

- |             |             |             |
|-------------|-------------|-------------|
| 1. (b), (d) | 2. (b), (c) | 3. (a), (c) |
|-------------|-------------|-------------|

**Fill-in-the-Blanks Type**

1. ethylene oxide
2. ethylene
3. peroxide
4.  $\text{CH}_3\overset{2}{\text{C}}=\overset{3}{\text{CH}}-\overset{4}{\text{CH}}-\overset{5}{\text{CH}_3}$
5. sp
6.  $\text{H}_2\text{C}=\text{CH}_2$
7. 
8. 3, 4-dibromo-1-butene (at low temperature) or 1, 4-dibromo-2-butene (at high temperature)

**Integer Answer Type**

1. 5
2. 4

**True/False Type**

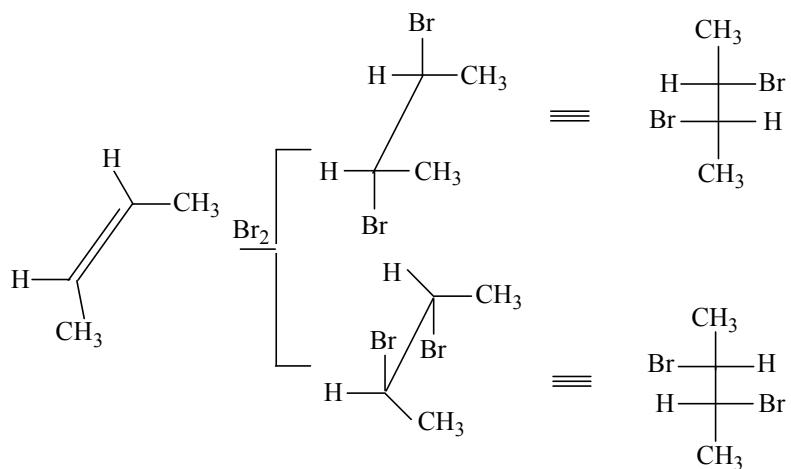
1. False
2. False
3. False

**Reasoning Type**

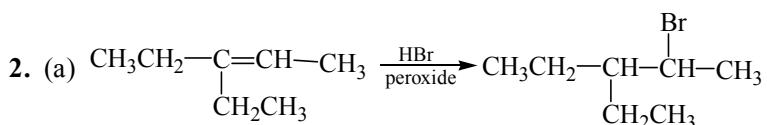
1. (a)
2. (c)
3. (b)
4. (a)

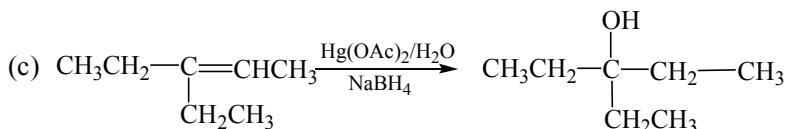
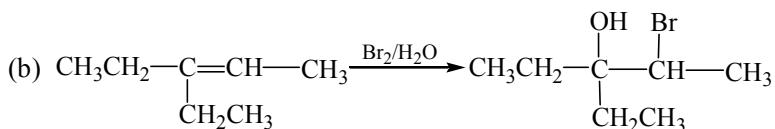
**Short Answer Type**

1. The addition of bromine to the 2-butene involves *anti*-addition, i.e. bromines are attached to opposite faces of the double bond. This addition can be done in two different ways.

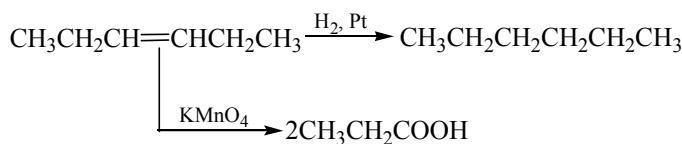


These two different ways are equally likely and thus *rac*-2, 3-dibromobutane is formed.

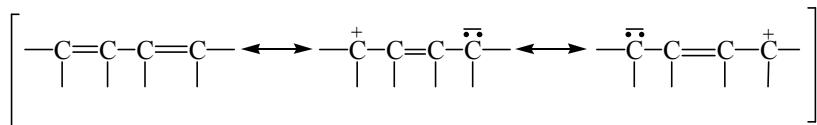




3. The reaction of alkyne or alkene with the electrophilic reagent proceeds through the formation of carbocation. Since, the alkyl carbocation from the alkene group is more stable than the vinyl carbocation from the alkyne group, the  $\Delta H^\ddagger$  for its formation is less in case of alkene and hence alkene reacts faster than alkynes.
4. The hydrocarbon A is  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ . The given reactions are

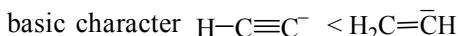
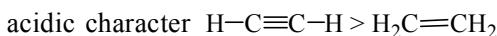


5. 1, 3-Butadiene is a conjugated diene and is a resonance hybrid.



The uncharged structure involves a larger contribution than the charged structures. The latter induces some double bond character in the central C—C bond leading to the shortening of this bond. Besides this, the central C—C bond involves  $\text{sp}^2 - \text{sp}^2$  carbon atoms which also shortens the bond as compared to the ‘C—C bond in *n*-butane which involves  $\text{sp}^3 - \text{sp}^3$  hybrid orbitals.

6. The hydrogen atoms in acetylene are more acidic than those in ethylene. This is due to the fact that carbons in acetylene are more electronegative (due to sp hybrid orbitals) than those in ethylene (which involves sp<sup>2</sup> hybrid orbitals). The conjugate base of acetylene and ethylene follow the reverse order. Thus



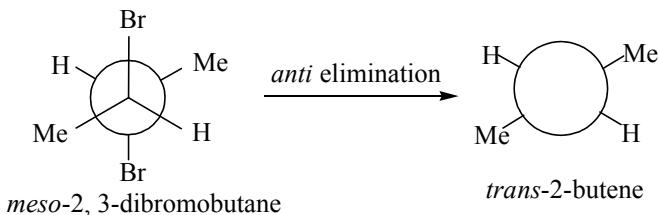
## HINTS AND SOLUTIONS

### Straight Objective Type

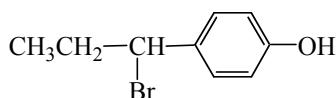
1. Baeyer's reagent is an alkaline potassium permanganate solution.
2. 2-Butene is  $\text{CH}_3\text{CH}=\text{CHCH}_3$ . The addition of HBr gives the same product whether it occurs via Markovnikov or anti-Markovnikov rule.
3. *trans*-1, 2-dichloroethene will have zero dipole moment.
4.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[\text{KOH}]{\text{ethanolic}} \text{CH}_3\text{CH}=\text{CH}_2$ .
5. O—H will show heterolytic cleavage.
6.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow[\text{KOH}]{\text{ethanolic}} \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$

7. The more stable the compound, the smallest the heat of hydrogenation per mole. 1, 3-Butadiene has the most stable double bonds due to conjugation.

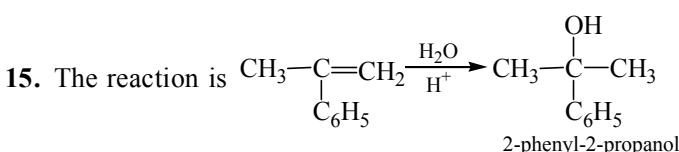
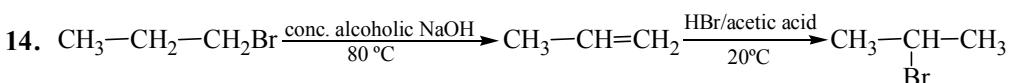
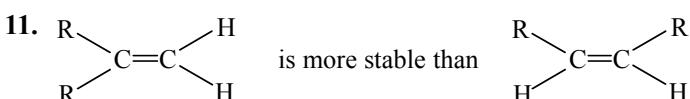
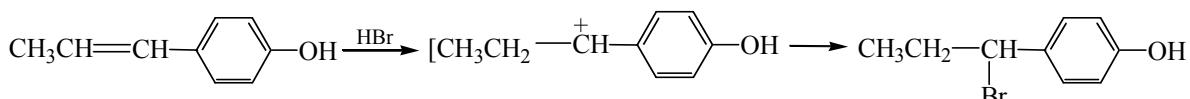
8.



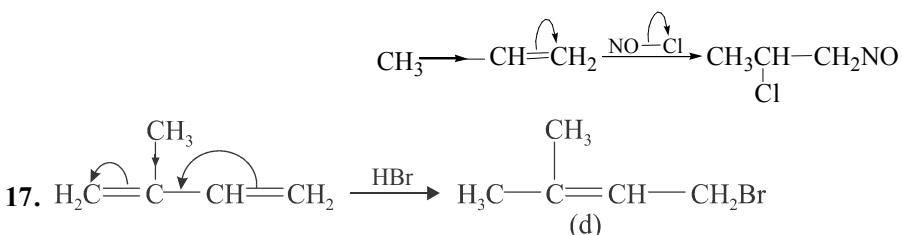
9. The addition of HCl proceeds through ionic mechanism. It is not affected by the presence or absence of peroxide.
10. The addition of HBr across a double bond proceeds via the formation of carbocation or free radical. The final product is governed by the stability of the intermediate carbocation or free radical. Since the benzyl cation or radical is more stable than the other possibilities, the final product is



The reaction is



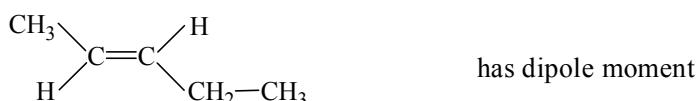
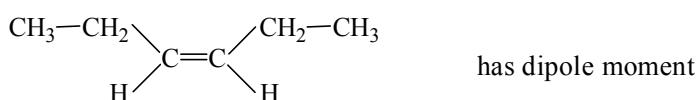
14. Due to the electron-releasing methyl group, the reaction proceeds as follows.



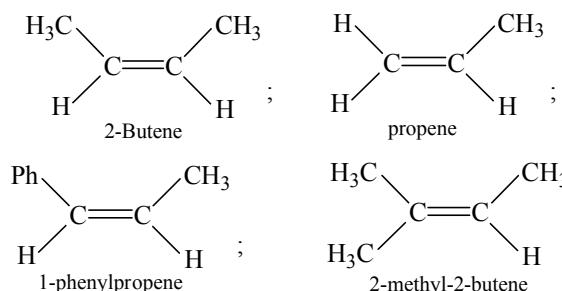
### Multiple Correct-Choice Type

1. *cis*-1, 2-dichloroethene ( $\text{ClHC}=\text{CHCl}$ ) and 1,2-dichloro-2-pentene ( $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{Cl}$ ) will have dipole moment.

2. *trans*-2-pentene and *cis*-3-hexene will have nonzero dipole moment.



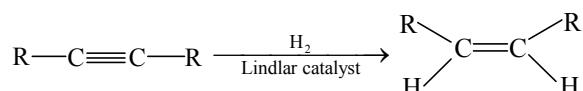
3. The structures of the given compounds are



Only 2-butene and 1-phenylpropene can show geometrical isomerism (*cis*-and *trans*-isomers).

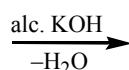
## **Fill-in-the-Blanks Type**

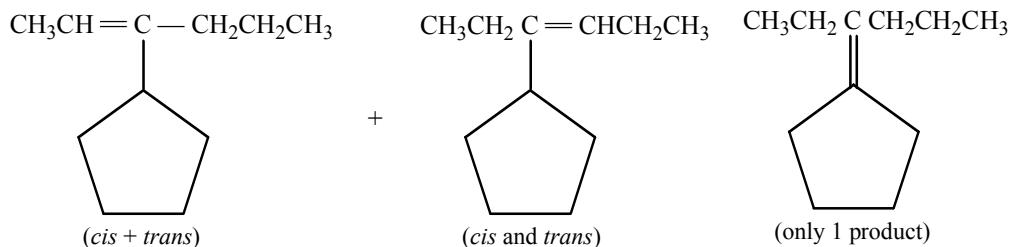
7. On using Lindlar catalyst ( $\text{Pd/C}$ ), *cis*-addition of hydrogen occurs and the product is *cis*-alkene. This is because both the hydrogen atoms are originally present on the surface of the catalyst. Hence, they attach on the same side of the triple bond and give *cis*-product.



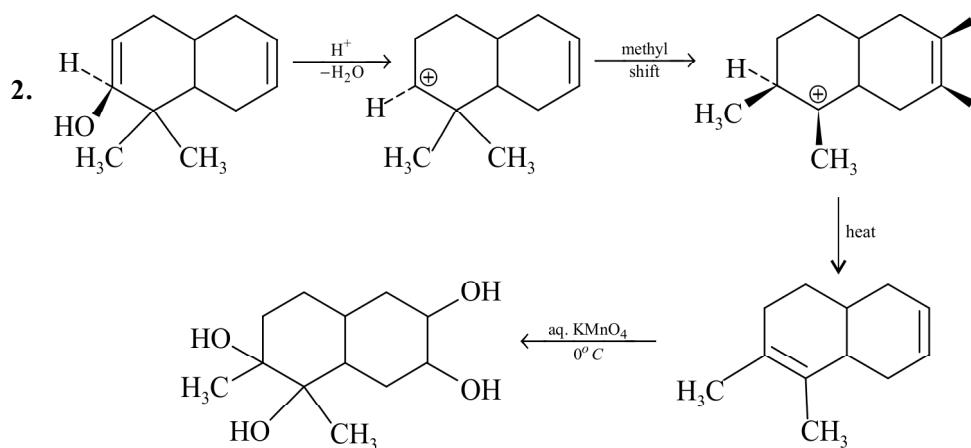
## **Integer Answer Type**

1.  $\text{CH}_3-\text{CH}_2-\overset{\text{Br}}{\underset{|}{\text{C}}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$





Thus, there are five compounds. Hence, the correct answer is 5.



There are 4 hydroxyl groups.

## **True/False Type**

1. In the presence of peroxide, HBr reacts with propene to give *n*-propyl bromide (anti-Markovnikov's rule). In the absence of peroxide, normal addition takes place. It gives isopropyl bromide as secondary carbocation is more stable than primary one.
  2. With  $\text{H}_2\text{SO}_4$ , ethylene will give additional product.
  3. Anti-Markovnikov's rule is applicable to the addition of HBr in the presence of peroxide.

## **Reasoning Type**

2. There is a formation of secondary radicals.

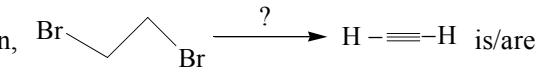


# ALKYNES

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## Straight Objective Type

1. When propyne is treated with aqueous  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$ , the major product is
  - (a) propanol
  - (b) propyl hydrogen sulphate
  - (c) acetone
  - (d) propanal(1983)
2. Acidic hydrogen is present in
  - (a) ethyne
  - (b) ethene
  - (c) benzene
  - (d) ethane(1985)
3. What is the decreasing order of strength of the bases  $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{HC}\equiv\bar{\text{C}}$  and  $\text{CH}_3\text{CH}_2^-$ ?
  - (a)  $\text{CH}_3-\text{CH}_2^- > \text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^-$
  - (b)  $\text{H}-\text{C}\equiv\text{C}^- > \text{CH}_3-\text{CH}_2^- > \text{NH}_2^- > \text{OH}^-$
  - (c)  $\text{OH}^- > \text{NH}_2^- > \text{HC}\equiv\text{C}^- > \text{CH}_3-\text{CH}_2^-$
  - (d)  $\text{NH}_2^- > \text{H}-\text{C}\equiv\text{C}^- > \text{OH}^- > \text{CH}_3-\text{CH}_2^-$(1993)
4. The product(s) obtained via oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-butyne would be
  - (a)  $\text{CH}_3\text{CH}_2\text{COCH}_3$
  - (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
  - (c)  $\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO}$
  - (d)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$(1999)
5. Propyne and propene can be distinguished by
  - (a) conc.  $\text{H}_2\text{SO}_4$
  - (b)  $\text{Br}_2$  in  $\text{CCl}_4$
  - (c) dil.  $\text{KMnO}_4$
  - (d)  $\text{AgNO}_3$  in ammonia(2001)
6. Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne:
  - (a) bromine,  $\text{CCl}_4$
  - (b)  $\text{H}_2$ , Lindlar catalyst
  - (c) dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HgSO}_4$
  - (d) ammoniacal  $\text{Cu}_2\text{Cl}_2$  solution(2002)
7. Which of the following hydrocarbons has the lowest dipole moment?
  - (a)  $\begin{array}{c} \text{H}_3\text{C} & & \text{CH}_3 \\ & \diagdown & \diagup \\ & \text{C} & -\text{C} \\ & \diagup & \diagdown \\ & \text{H} & & \text{H} \end{array}$
  - (b)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$
  - (c)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
  - (d)  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$(2002)
8. In the reaction
$$\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hg}^{2+}/\text{H}^+} \text{A}$$
the product A is
  - (a)  $\text{PhCOCH}_2\text{CH}_3$
  - (b)  $\text{PhCH}_2\text{COCH}_3$
  - (c)  $\text{PhC(OH)}=\text{CH}-\text{CH}_3$
  - (d)  $\text{PhC}=\text{C(OH)}\text{CH}_3$(2003)

9. Which of the following reagents is used for the conversion of 2-hexyne into *cis*-2-hexene?  
 (a)  $\text{H}_2/\text{Pd-BaSO}_4$     (b)  $\text{H}_2$ , Pt    (c)  $\text{Zn}/\text{HCl}$     (d)  $\text{Li-NH}_3/\text{C}_2\text{H}_5\text{OH}$     (2004)
10. The reagent(s) for the following conversion,  is/are  
 (a) alcoholic KOH    (b) alcoholic KOH followed by  $\text{NaNH}_2$   
 (c) aqueous KOH followed by  $\text{NaNH}_2$     (d)  $\text{Zn}/\text{CH}_3\text{OH}$     (2007)
11. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are  
 (a)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$   
 (b)  $\text{BrCH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$   
 (c)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{C}\equiv\text{CH}$   
 (d)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$     (2010)

### Fill-in-the-Blanks Type

- \_\_\_\_\_ is most acidic (ethane, ethene, ethyne)    (1981)
- The treatment of the compound obtained by the hydration of ethyne with dilute alkali gives \_\_\_\_\_.    (1981)
- Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess of methyl iodide. The final product is \_\_\_\_\_.    (1983)
- Addition of water to acetylenic compounds is catalysed by \_\_\_\_\_ and \_\_\_\_\_.    (1993)

### True/False Type

- Ethyne and its derivatives give white precipitate with ammoniacal silver nitrate solution.    (1984)

## ANSWERS

### Straight Objective Type

- |        |        |        |         |         |        |
|--------|--------|--------|---------|---------|--------|
| 1. (c) | 2. (a) | 3. (a) | 4. (a)  | 5. (d)  | 6. (d) |
| 7. (b) | 8. (a) | 9. (a) | 10. (b) | 11. (d) |        |

### Fill-in-the-Blanks Type

- |                                    |  |
|------------------------------------|--|
| 1. Ethyne                          | 2. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ |
| 3. $\text{CH}_3\equiv\text{CCH}_3$ | 4. $\text{H}_2\text{SO}_4$ , $\text{HgSO}_4$               |

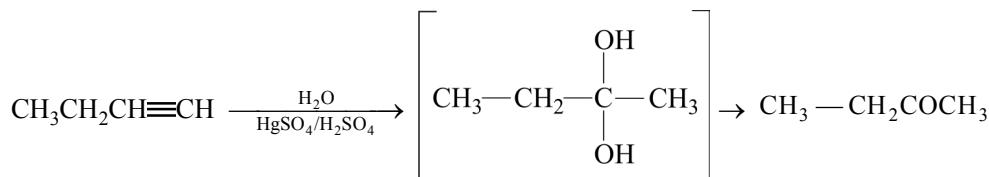
### True/False Type

- False

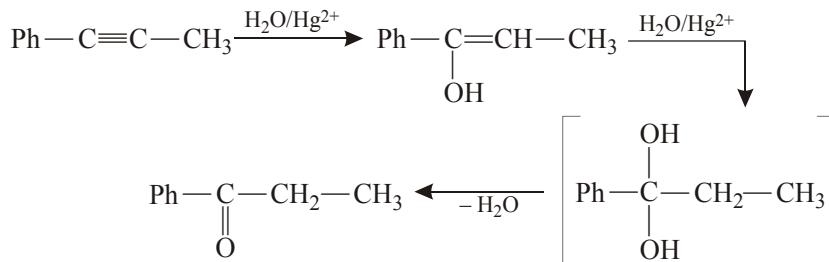
## HINTS AND SOLUTIONS

### Straight Objective Type

- $\text{CH}_3\text{C}\equiv\text{CH} \xrightarrow{\text{H}_2\text{SO}_4/\text{HgSO}_4} \text{CH}_3\text{COCH}_3$
- Ethyne ( $\text{HC}\equiv\text{CH}$ ) contains acidic hydrogen.
- The strength of conjugate acids follows the order  $\text{CH}_3\text{CH}_3 < \text{NH}_3 < \text{HC}\equiv\text{CH} < \text{H}_2\text{O}$   
The strength of given bases follows the order  $\text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{HC}\equiv\text{C}^- > \text{OH}^-$
- In oxymercuration, addition of water follows Markovnikov's rule.



- Propyne forms insoluble acetylides with ammoniacal silver nitrate solution.  
Propene does not form acetylides.
- 1-Butyne contains acetylinic hydrogen atom. It will form insoluble acetylides.
- The dipole moment of  $\text{CH}_3\text{C}\equiv\text{CCH}_3$  is zero. It is a linear molecule and has symmetrical arrangements of methyl substituents.
- The carbocation  $\text{Ph}-\overset{+}{\text{C}}=\overset{-}{\text{C}}-\text{CH}_3$  is more stable than  $\text{Ph}-\overset{-}{\text{C}}=\overset{+}{\text{C}}-\text{CH}_3$ . Hence, OH group is added to the former molecule.



- The use of Lindlar catalyst ( $\text{Pb-BaSO}_4$ ) produces *cis* product.
- Alcoholic KOH can be used to remove one molecule of HBr to generate a double bond. The removal of second HBr requires more stronger base, that is,  $\text{NaNH}_2$ .
- Only the constituents given by the choice (d) will produce 3-octyne.



### Fill-in-the-Blanks Type

- $\text{CH}\equiv\text{CH} \xrightarrow[\text{H}_2\text{SO}_4/\text{HgSO}_4]{\text{H}_2\text{O}} \text{CH}_3\text{CHO} \xrightarrow[\text{NaOH}]{\text{CH}_3\text{CHO}} \text{CH}_3\overset{\text{OH}}{\underset{\text{O}}{\text{C}}}\text{CHCH}_2\text{CH}_3$
- $\text{CH}\equiv\text{CH} \xrightarrow{\text{Na}} \text{NaC}\equiv\text{CNa} \xrightarrow{\text{CH}_3\text{I}} \text{CH}_3\equiv\text{CCH}_3$

### True/False Type

- White precipitate is obtained only when  $-\text{C}\equiv\text{C}-$  functional group is present at the terminal(s) of the molecule, since only then it will have acidic hydrogen atom.



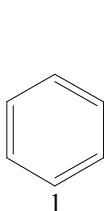
# BENZENE

24

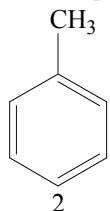
## Straight Objective Type

1. Among the following, the compound that can be most readily sulphonated is  
(a) benzene      (b) nitrobenzene      (c) toluene      (d) chlorobenzene      (1982)
2. The compound that is most reactive towards electrophilic nitration is  
(a) toluene      (b) benzene      (c) benzoic acid      (d) nitrobenzene      (1985)
3. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly  
(a) benzoyl chloride      (b) *m*-chlorotoluene  
(c) benzyl chloride      (d) *o*- and *p*-chlorotoluene      (1986)
4. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives  
(a) *o*-cresol      (b) *p*-cresol  
(c) 2,4-dihydroxytoluene      (d) benzoic acid      (1990)
5. Nitrobenzene can be prepared from benzene by using a mixture of concentrated  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$ . In the nitrating mixture,  $\text{HNO}_3$  acts as  
(a) base      (b) acid      (c) reducing agent      (d) catalyst      (1997)
6. Among the following statements on the nitration of aromatic compounds, the false one is  
(a) the rate of nitration of benzene is almost the same as that of hexadeuterobenzene  
(b) the rate of nitration of toluene is greater than that of benzene  
(c) the rate of nitration of benzene is greater than that of hexadeuterobenzene  
(d) nitration is an electrophilic substitution reaction      (1997)
7. Benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) can be prepared from toluene by chlorination with  
(a)  $\text{SO}_2\text{Cl}_2$       (b)  $\text{SOCl}_2$       (c)  $\text{Cl}_2$       (d)  $\text{NaOCl}$       (1998)
8. Arrange the following compounds in order of increasing dipole moment.  
Toluene (I)      *m*-dichlorobenzene (II)  
*o*-dichlorobenzene (III)      *p*-dichlorobenzene (IV)  
(a) I < IV < II < III (b) IV < I < II < III (c) IV < I < III < II (d) IV < II < I < III      (1997)
9. In the reaction *p*-chlorotoluene with  $\text{KNH}_2$  in liq.  $\text{NH}_3$ , the major product is:  
(a) *o*-toluidine      (b) *m*-toluidine      (c) *p*-toluidine      (d) *p*-chloroaniline      (1997)

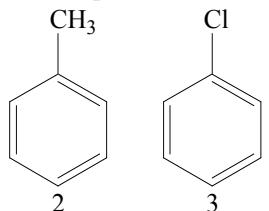
**10.** Identify the correct order of reactivity in electrophilic substitution reaction of the following compounds:



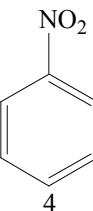
(a) 1>2>3>4



(b) 4>3>2>1



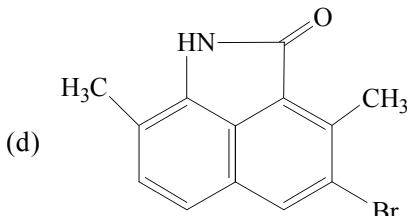
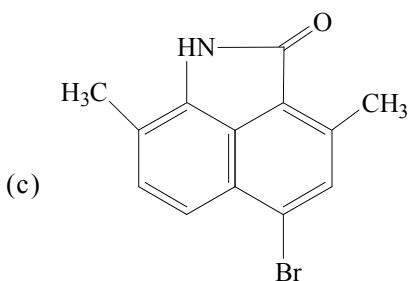
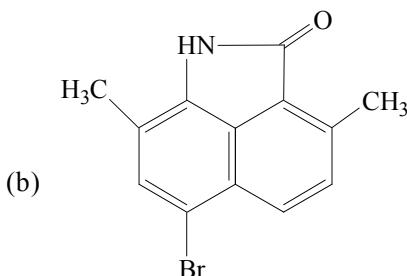
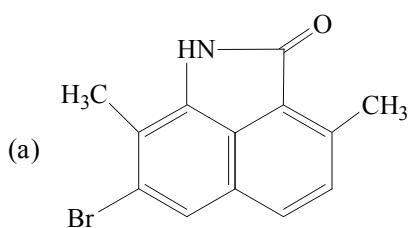
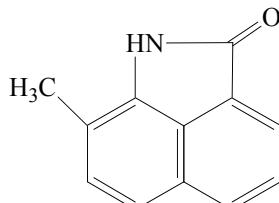
(c) 2>1>3>4



(d) 2>3>1>4

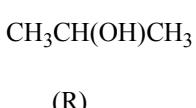
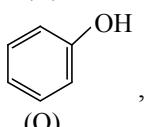
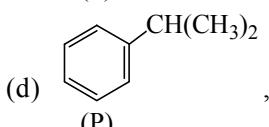
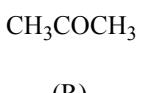
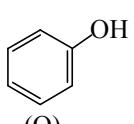
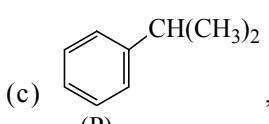
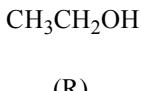
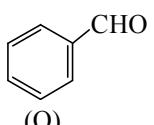
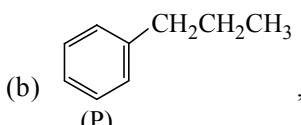
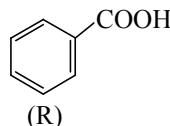
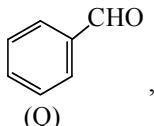
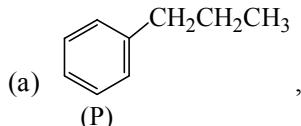
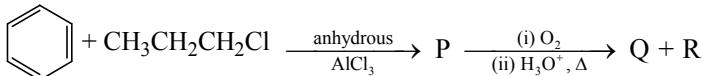
(2002)

**11.** The major product obtained when  $\text{Br}_2/\text{Fe}$  is treated with



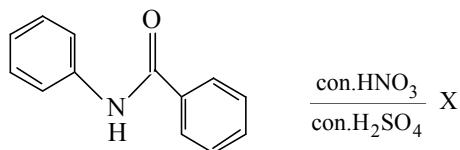
(2004)

**12.** Identify the major products P, Q and R in the following reaction.

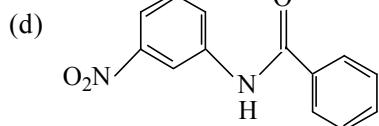
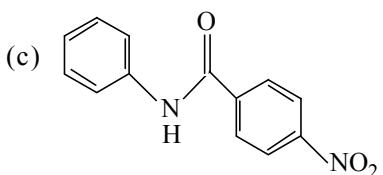
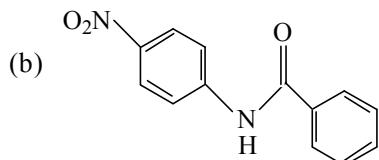
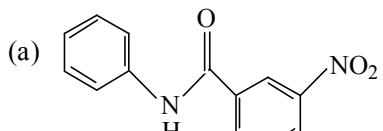


(2006)

13. In the following reaction,

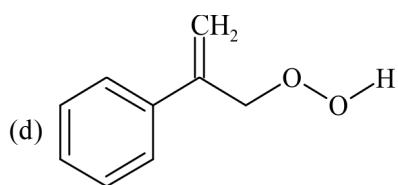
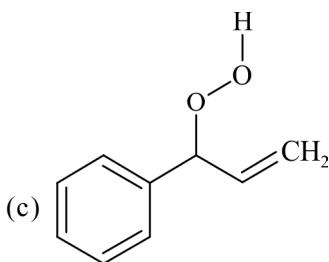
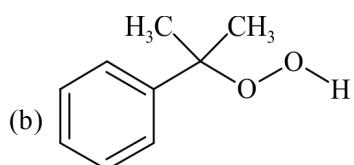
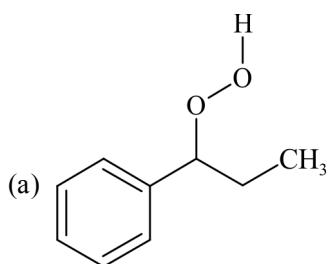
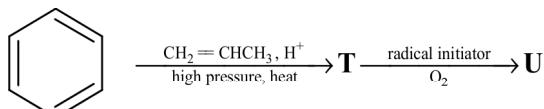


the structure of the major product 'X' is



(2007)

14. The major product **U** in the following reactions is



(2015)

### Multiple Correct-Choice Type

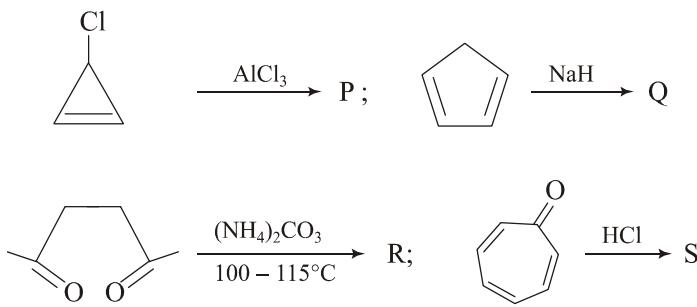
- Toluene, when treated with  $\text{Br}_2/\text{Fe}$ , gives *p*-bromotoluene as the major product because the  $\text{CH}_3$  group
  - (a) is para directing
  - (b) is meta directing
  - (c) activates the ring by hyperconjugation
  - (d) deactivates the ring
- When nitrobenzene is treated with  $\text{Br}_2$  in presence of  $\text{FeBr}_3$ , the major product formed is *m*-bromonitrobenzene. Statement which are related to obtain the *m*-isomer are
  - (a) The electron density on **meta** carbon is more than that on **ortho** and **para** positions
  - (b) The intermediate carbonium ion formed after initial attack of  $\text{Br}^+$  at the **meta** position is least destabilised.

- (c) Loss of aromaticity when  $\text{Br}^+$  attacks at the **ortho** and **para** positions and not at **meta** position.  
 (d) Easier loss of  $\text{H}^+$  to regain aromaticity from the **meta** position than from **ortho** and **para** positions.

**3.** An aromatic molecule will



4. Among P, Q, R and S, the aromatic compound(s) is/are



### **Fill-in-the-Blanks Type**

1. The structure of the intermediate product, formed by the oxidation of toluene with  $\text{CrO}_3$  and acetic anhydride, whose hydrolysis gives benzaldehyde, is \_\_\_\_\_. (1992)
  2. The bond dissociation energy needed to form the benzyl radical from toluene is \_\_\_\_\_ than the formation of the methyl radical from methane. (1994)

## **True/False Type**

1. Although benzene contains three double bonds, normally it does not undergo addition reaction. (1983)
  2. *m*-chlorobromobenzene is an isomer of *m*-bromochlorobenzene. (1985)
  3. In benzene, carbon uses all the three p orbitals for hybridisation. (1987)
  4. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta* position (1987)

## **Short Answer Type**

1. Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of  $\text{FeBr}_3$  it gives *p*-bromotoluene. Give explanation for the above observations. (1996)
  2. Give reasons for the following:  
*tert*-Butylbenzene does not give benzoic acid on treatment with acidic  $\text{KMnO}_4$ . (2000)
  3. Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. (2000)
  4. 7-bromo-1,3,5-cycloheptatriene exists as an ion whereas 5-bromo-1, 3-cyclopentadiene does not form an ion even in the presence of  $\text{Ag}^+$ . Explain. (2004)
  5. State with balanced equations, what happens when *p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH. (1984)

**ANSWERS****Straight Objective Type**

1. (c)      2. (a)      3. (d)      4. (d)      5. (a)      6. (c)      7. (c)  
 8. (b)      9. (b)      10. (d)     11. (b)     12. (c)     13. (b)     14. (b)

**Multiple Correct-Choice Type**

1. (a), (c)      2. (a), (d)      3. (b), (c), (d)  
 4. (a), (b), (c), (d)

**Fill-in-the-Blanks Type**

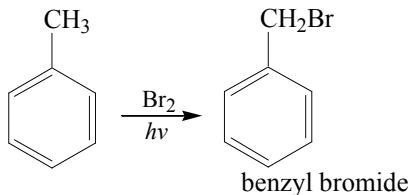
1.  $C_6H_5CH(OCOCH_3)_2$ , benzylidene acetate.    2. Less

**True/False Type**

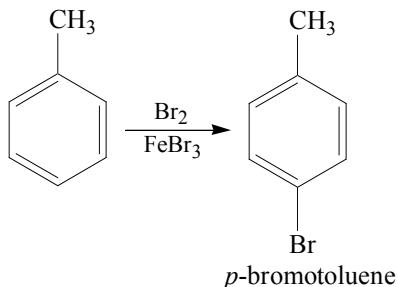
1. True      2. False      3. False      4. False

**Short Answer Type**

1. Side chain bromination is favoured under photochemical irradiation and involves a free radical mechanism.

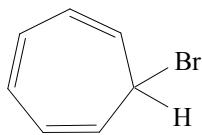


In the presence of  $FeBr_3$ , electrophilic substitution in the benzene ring occurs.

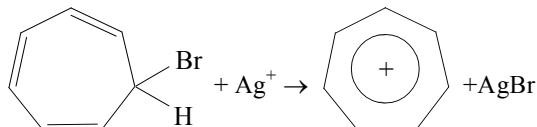


2. The first step in the oxidation of side alkyl chain is to abstract a benzylic hydrogen. Since no such hydrogen atom is present in *tert*-butylbenzene, it is resistant to side-chain oxidation.
3. The typical reactions of the benzene ring are those in which the  $\pi$ -electrons serve as a source of electrophilic reagents. Because of delocalization of  $\pi$ -electrons benzene does not show additional reactions as in the case of alkenes but undergoes substitution reactions in which hydrogen atom attached to carbon atom is replaced by another atom or group of atoms.

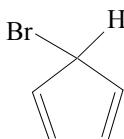
4. The structure of 7-bromo-1,3,5-cycloheptatriene is



In the presence of  $\text{Ag}^+$  in solution, bromine gets precipitated as  $\text{AgBr}$  giving a stable cycloheptatrienyl carbocation due to its aromatic character (six  $\pi$  electrons delocalized in seven overlapping p orbitals).

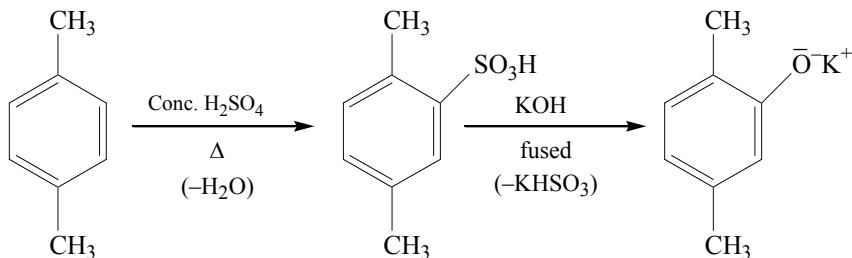


The structure of 5-bromo-1,3-cyclopentadiene is



The bromine in this case is not precipitated in the presence of  $\text{Ag}^+$  ions because the cyclopentadiene carbocation will not be stable as it is not aromatic ( $4\pi$  electrons distributed over 5p orbitals). It is for this reason, the carbocation is not formed.

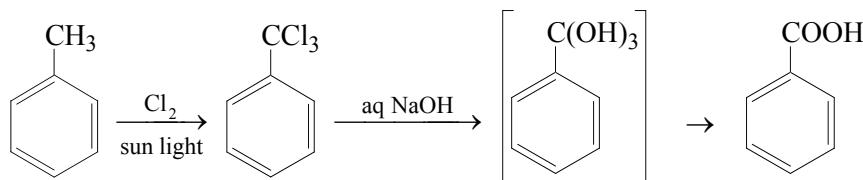
5. The reactions are:



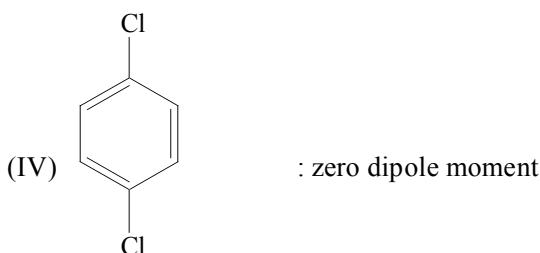
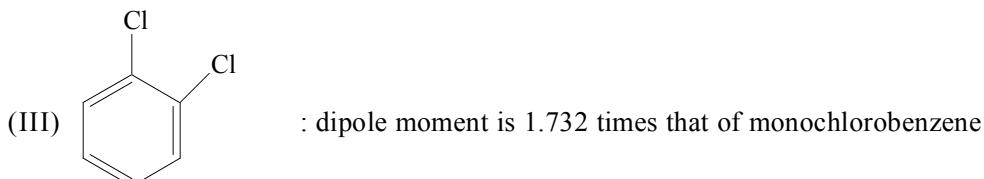
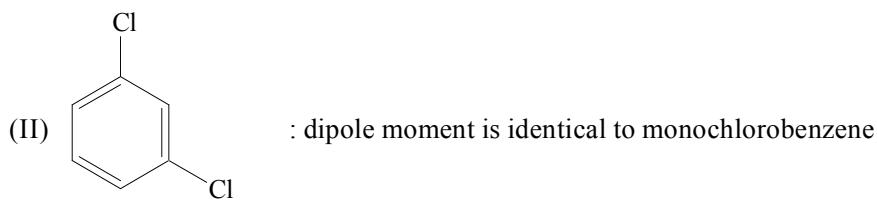
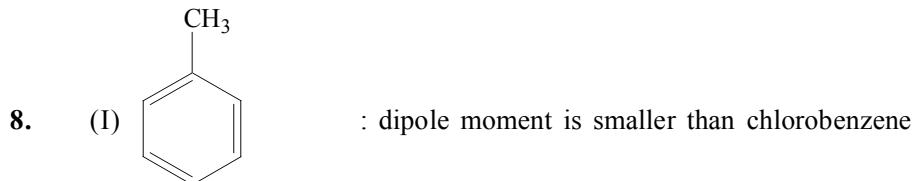
### HINTS AND SOLUTIONS

#### Straight Objective Type

- Methyl group is electron-releasing group. It makes benzene ring more active towards electrophilic substitution reaction.
- Same as Q.1.
- Methyl group is *ortho* and *para* directing.
- In the presence of sun light, side chain is chlorinated.

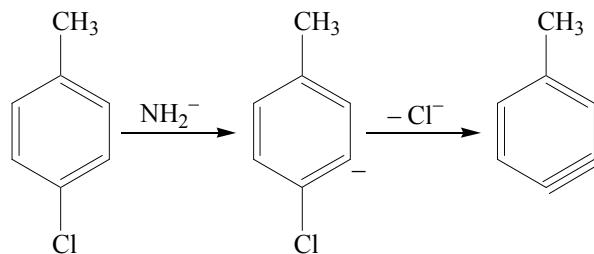


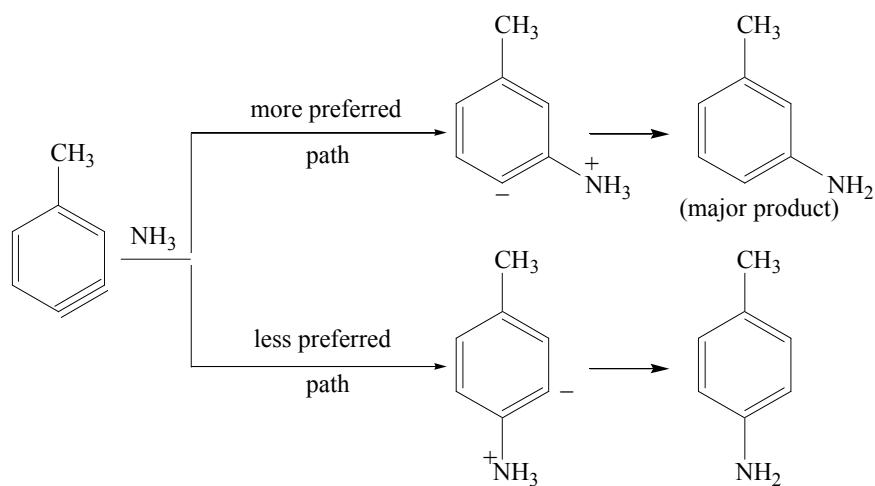
5.  $\text{HNO}_3$  acts as a base in the nitrating mixture.
6. The statement that the rate of nitration of benzene is greater than that of hexadeuterobenzene is incorrect because the rate determining step does not involve breaking of the C—H or C—D bond.
7.  $\text{Cl}_2$  in the presence of sun light is used to carry out the side chain halogenation.



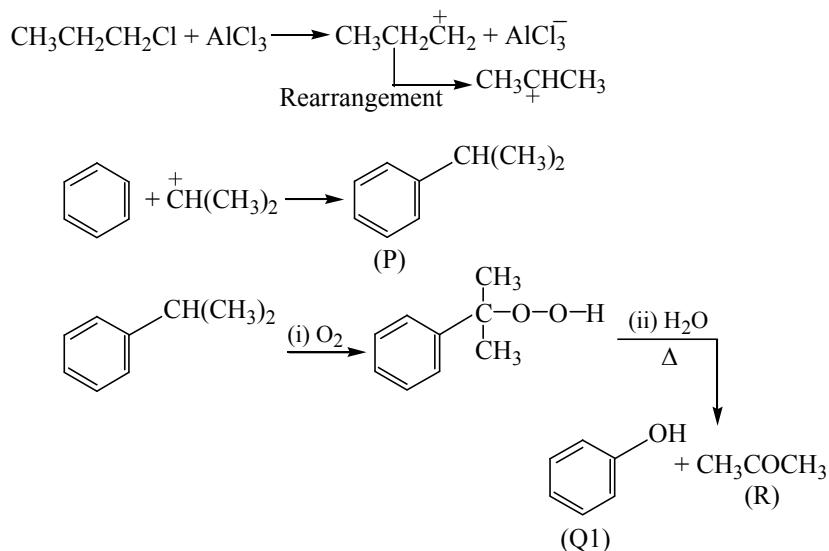
Hence, the increasing order is IV < I < II < III.

9. The reaction proceeds via elimination-addition mechanism

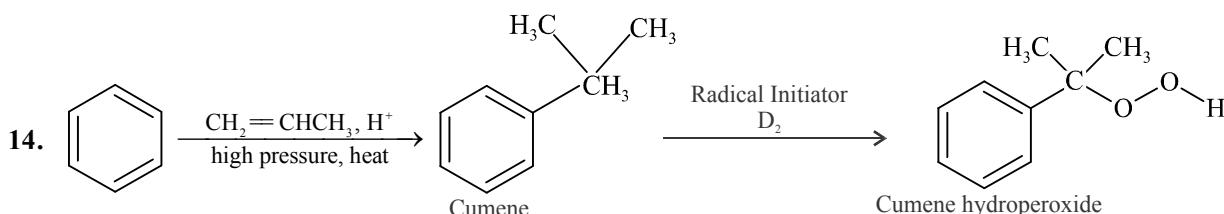




10. Methyl group activates benzene ring towards electrophilic substitution.  
Chlorine deactivates benzene ring less than the nitro group.
11. The phenyl group attached to the  $\text{—NH—}$  group gets activated and thus bromination at the *para* position occurs in this phenyl group.
12. The given reaction proceeds as follows.

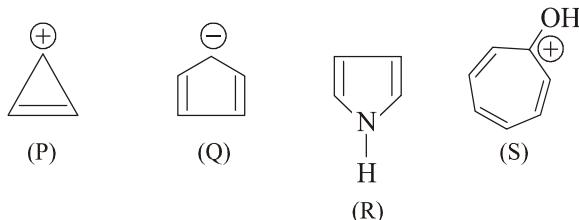


13. The benzene ring attached to  $\text{—NH—}$  group gets activated and thus will undergo nitration at the *para* position in preference to ring attached to  $\text{—CO—}$  group.



### Multiple Correct-Choice Type

- CH<sub>3</sub> group is *para* directing as it activates the benzene ring by hyperconjugation.
- The resultant compounds are as follows.



All these compounds satisfy  $4n + 2$  rule, where  $n$  is the number of  $\pi$ -electrons. Hence, all of them will be aromatic.

### True/False Type

- Benzene gets stabilised because of resonance.
- Both represent one and the same compound.
- Each carbon in benzene is sp<sup>2</sup> hybridised.
- An electron attracting group directs the incoming electrophilic group to *meta* position.



# ALCOHOLS

## Straight Objective Type

1. Ethyl alcohol is heated with concentrated  $H_2SO_4$ , the product formed is

- |                        |              |
|------------------------|--------------|
| (a) $CH_3—C=O—OC_2H_5$ | (b) $C_2H_6$ |
|                        |              |
| O                      |              |
| (c) $C_2H_4$           | (d) $C_2H_2$ |

(1980)

2. Which of the following is soluble in water?

- (a)  $CS_2$       (b)  $C_2H_5OH$       (c)  $CCl_4$       (d)  $CHCl_3$

(1980)

3. The compound which reacts fastest with Lucas reagent at room temperature is

- |                      |                         |
|----------------------|-------------------------|
| (a) 1-butanol        | (b) 2-butanol           |
| (c) 2-methylpropanol | (d) 2-methylpropan-2-ol |

(1981)

4. An industrial method of preparation of methanol is

- |  |  |
|--|--|
| (a) catalytic reduction of carbon monoxide in presence of $ZnO-Cr_2O_3$ .    |  |
| (b) by reacting methane with steam at $900\ ^\circ C$ with a nickel catalyst |  |
| (c) by reducing formaldehyde with lithium aluminium hydride                  |  |
| (d) by reaction of formaldehyde with aqueous sodium hydroxide solution       |  |

(1984)

5. HBr reacts fastest with

- |                         |                         |
|-------------------------|-------------------------|
| (a) 2-methylpropan-2-ol | (b) propan-1-ol         |
| (c) propan-2-ol         | (d) 2-methylpropan-1-ol |

(1984)

6. Hydrogen bonding is maximum in

- (a) ethanol      (b) diethylether      (c) ethyl chloride      (d) triethylamine

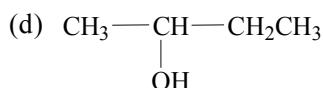
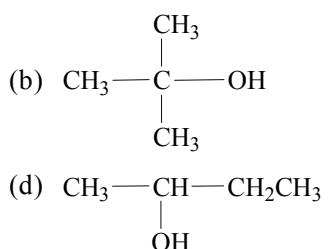
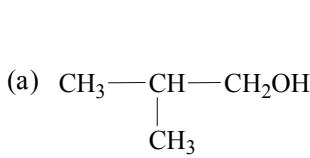
(1987)

7. Which of the following compounds is oxidised to prepare methyl ethyl ketone?

- (a) 2-Propanol      (b) 1-Butanol      (c) 2-Butanol      (d) *tert*-Butyl alcohol

(1987)

8. The compound which gives the most stable carbonium ion on dehydration is



(1989)

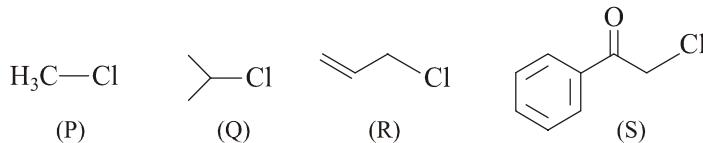
9. Butanonitrile may be prepared by heating

- |                               |                                |
|-------------------------------|--------------------------------|
| (a) propyl alcohol with $KCN$ | (b) butyl alcohol with $KCN$   |
| (c) butylchloride with $KCN$  | (d) propyl chloride with $KCN$ |

(1992)

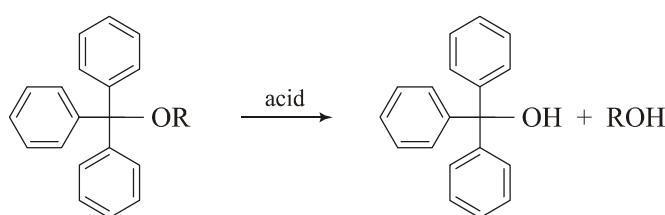


19. KI in acetone undergoes  $S_N2$  reaction with each of P, Q, R and S.



The rates of the reaction vary as

- (a) P > Q > R > S      (b) S > P > R > Q      (c) P > R > Q > S      (d) R > P > S > Q      (2013)
20. The acidic hydrolysis of ether (X) shown below is fastest when:



- (a) One phenyl group is replaced by a methyl group  
 (b) One phenyl group is replaced by a *para*-methoxyphenyl group.  
 (c) two phenyl groups are replaced by two *para*-methoxyphenyl groups  
 (d) no structural change is made to X.      (2014)

### Multiple Correct-Choice Type

- Aryl halides are less reactive towards nucleophilic substitution as compared to alkyl halides due to
  - the formation of less stable carbonium ion
  - resonance stabilisation
  - the inductive effect
  - $sp^2$ -hybridised carbon attached to the halogen(1990)
- The correct combination of names for isomeric alcohols with molecular formula  $C_4H_{10}O$  is/are
 

(a) <i>tert</i> -butanol and 2-methylpropan-2-ol	(b) <i>tert</i> -butanol and 1, 1-dimethylethan-1-ol
(c) <i>n</i> -butanol and butan-1-ol	(d) isobutyl alcohol and 2-methylpropan-1-ol

(2014)

### Fill-in-the-Blanks Type

- Ethanol vapour is passed over heated copper and the product is treated with aqueous sodium hydroxide. The final product is \_\_\_\_\_.      (1983)
- Aliphatic ethers are purified by shaking with a ferrous salt to remove \_\_\_\_\_ which are formed on prolonged standing in contact with air.      (1992)
- A \_\_\_\_\_ diol has two hydroxyl groups on \_\_\_\_\_ carbon atoms.      (1986)
- Glycerine contains one \_\_\_\_\_ hydroxy group.      (1997)

### True/False Type

- Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide.      (1986)
- The dipole moment of  $CH_3F$  is greater than that of  $CH_3Cl$ .      (1993)

3. The yield of ketone when a secondary alcohol is oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. (1983)

### Reasoning Type

In each subquestion below a statement (S) is given which may be correct or wrong.

For each statement an explanation (E) is given which may be correct or wrong.

Choose the correct answer from the code a, b, c, d given for each subsection.

1. Statement (S): Solubility of *n*-alcohols in water decreases with increase in molecular weight

Explanation (E): The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bonding with water.

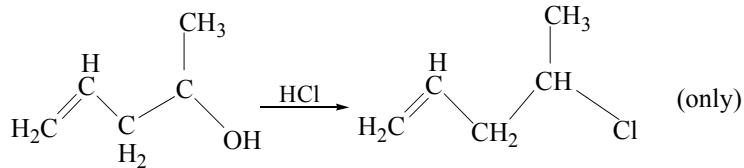
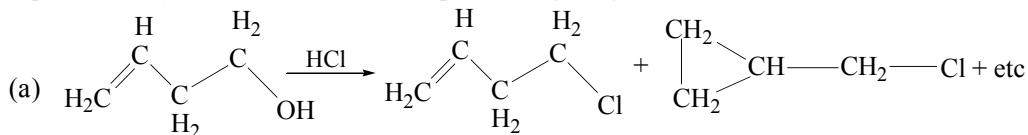
Code:

- (a) Both (S) and (E) are correct and (E) is the correct explanation of (S)
- (b) Both (S) and (E) are correct but (E) is not the correct explanation of (S)
- (c) (S) is correct but (E) is wrong
- (d) (S) is wrong but (E) is correct

(1988)

### Short Answer Type

- When *t*-butanol and *n*-butanol are separately treated with a few drops of dilute KMnO<sub>4</sub>, in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate? (1994)
- 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. (1996)
- Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. (1998)
- Explain briefly the formation of the products giving the structures of the intermediates.



(1999)

### ANSWERS

#### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (b)  | 3. (d)  | 4. (a)  | 5. (a)  | 6. (a)  | 7. (c)  |
| 8. (b)  | 9. (d)  | 10. (c) | 11. (d) | 12. (c) | 13. (a) | 14. (b) |
| 15. (a) | 16. (a) | 17. (d) | 18. (b) | 19. (b) | 20. (c) |         |

### Multiple Correct-Choice Type

1. (b), (d)      2. (a), (c), (d)

### Fill-in-the-Blanks Type

1. aldol      2. peroxide      3. vicinal, adjacent      4. secondary

### True/False Type

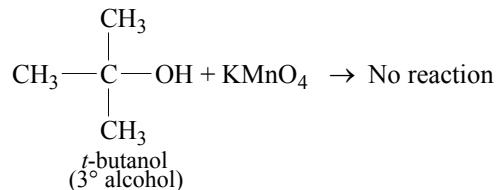
1. False      2. False      3. True

### Reasoning Type

1. (c)

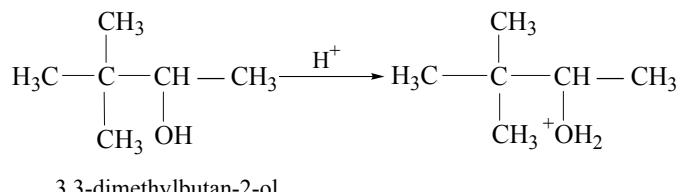
### Short Answer Type

1. *n*-Butanol is oxidised by KMnO<sub>4</sub> and not *t*-butanol as the latter does not contain H atom attached to carbinol carbon atom.

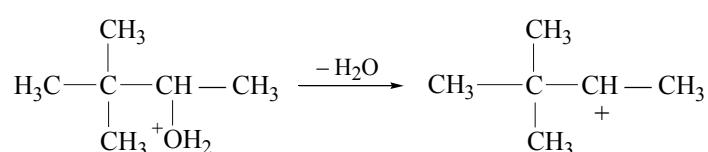


2. The steps involved in the suggested mechanism are as follows.

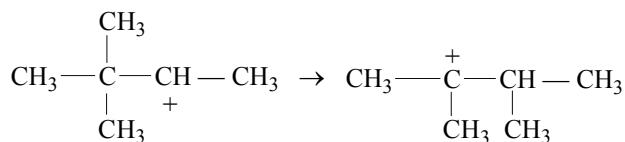
- (a) The protonation of hydroxyl group.



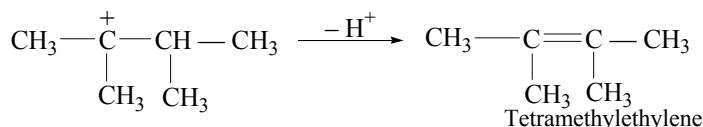
- (b) The removal of H<sub>2</sub>O to form a secondary (2°) carbonium ion



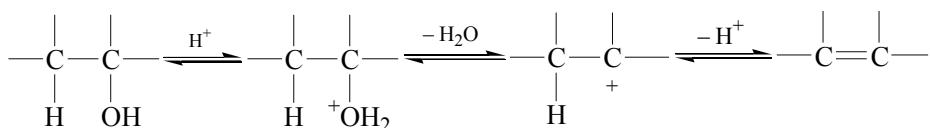
(c) The conversion of  $2^\circ$  carbonium to more stable  $3^\circ$  carbonium ion by the shift of  $\text{CH}_3$  group



(d) The removal of  $\text{H}^+$  to form a double bond

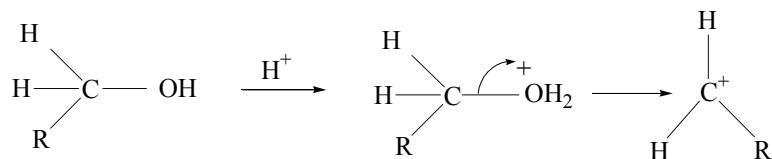


3. The acid catalysed dehydration of an alcohol proceeds via the formation of a carbocation:

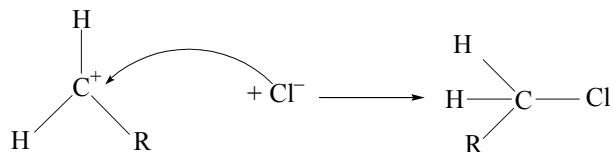


Since  $3^\circ$  carbocation is more stable than  $1^\circ$ , the dehydration in the former proceeds faster than in the latter.

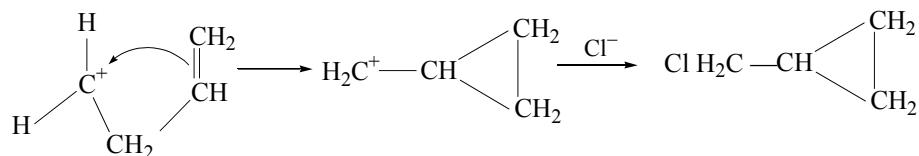
4. Because of the large propenyl group ( $-\text{CH}_2-\text{CH}=\text{CH}_2$ , represent as R) attached to the carbon bearing the hydroxyl group the nucleophilic substitution reaction probably proceeds via  $\text{S}_{\text{N}}1$  mechanism.



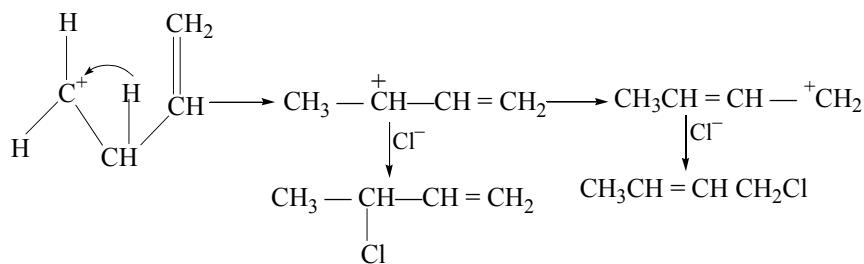
The attack of  $\text{Cl}^-$  produces the following product.



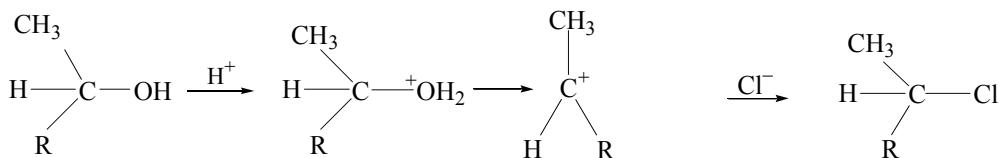
Due to the electron-rich double, bond the formed carbocation may also involve intramolecular rearrangement as shown below.



Other side products may be  $\text{CH}_3\text{CH}(\text{Cl})\text{CH}=\text{CH}_2$  and  $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$  as shown below.

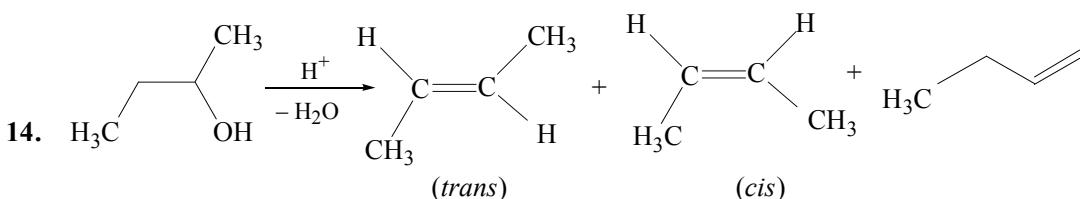


In the second reaction, the methyl group attached to the carbon bearing positive charge of the intermediate carbocation decreases its charge preventing the intermolecular rearrangements. This result into a single product.



## HINTS AND SOLUTIONS

## **Straight Objective Type**

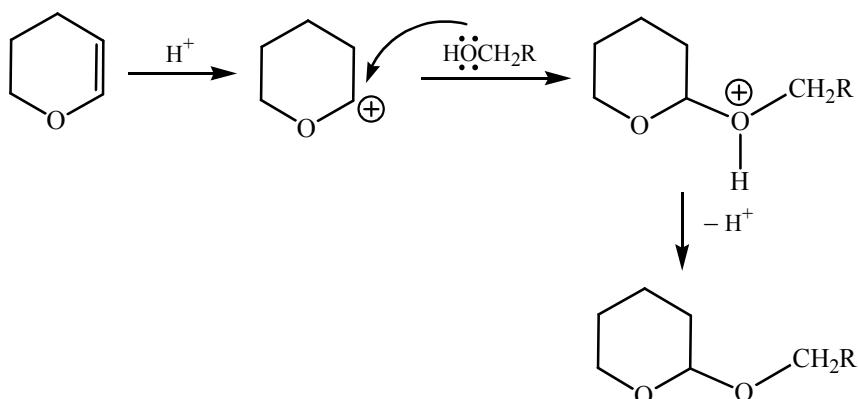


The addition of  $\text{Br}_2$  to *trans*-butene produces one compound, i.e. *meso*-2,3-dibromobutane.

The addition of  $\text{Br}_2$  to *cis*-butene produces two compounds (racemic mixture of 2,3-dibromobutane).

The addition of  $\text{Br}_2$  to but-1-ene produces two compounds (racemic mixture of 1, 2-dibromobutane).

15. The reaction is  $(\text{CH}_3)_3\text{COH} + \text{PhMgBr} \rightarrow \text{C}_6\text{H}_6 + (\text{CH}_3)_3\text{COMgBr}$
16.  $\text{Al}_2\text{O}_3$  at elevated temperature converts cyclohexanol to cyclohexene.
17. The cleavage of aryl ether yields alkyl halide and phenol.
18. The reaction proceeds as follows.

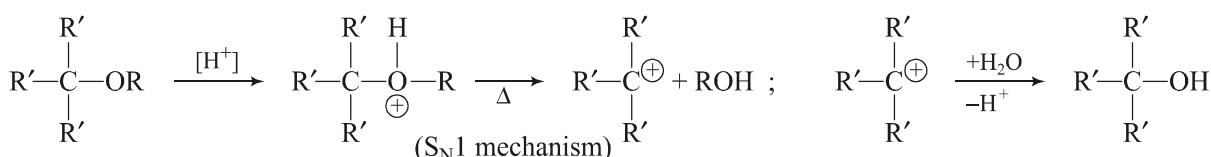


Hence, the **choice (b)** is correct.

19. The compound Q will have least rate of reaction as its transition state will be more crowded.

The compound S will have the maximum rate of reaction as the  $\pi$ -electronic cloud of  $\text{C}_6\text{H}_5\text{CO}-$  group reduces the energy of transition state. In the transition state, the carbon undergoing reaction changes from the  $\text{sp}^3$ -hybrid state to the  $\text{sp}^2$ -hybrid state and thus has a p orbital. This p orbital forms partial bonds with both the incoming nucleophile and the leaving group. The entire grouping of atoms carries a negative charge. Adjacent p orbitals of  $\text{C}_6\text{H}_5\text{CO}-$  or  $\text{CH}_2=\text{CH}-$  group undergo partial overlap with the transitional p orbital. In this way, negative charge is delocalized resulting lowering of energy of the transition state and thus enhancing the rate of reaction.

20. The reaction proceeds via the formation of oxonium salt. Ether linkage is cleaved by heating to form a carbocation which combines with water to give the given product.



The stability of the intermediate carbocation decides the rate of reaction. The larger the stability of carbocation, larger the rate of reaction.

*p*-Methoxyphenyl is the electron releasing group and thus helps stabilising the carbocation. The replacement of two phenyl groups by two *p*-methoxy groups stabilises the carbocation better than any other choice given in (a), (b) and (d).

### Multiple Correct-Choice Type

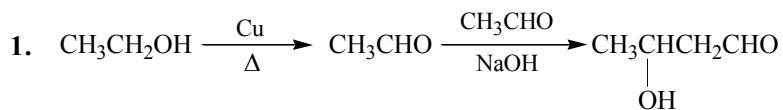
1. The lesser reactivity of aryl halide is due to resonance stabilisation and  $\text{sp}^2$  hybridised carbon attached to the halogen.

2. Tertiary butanol is  $\begin{matrix} & \text{CH}_3 \\ & | \\ \text{CH}_3 & - \text{C}^{\oplus} & - \text{OH} \\ & | \\ & \text{CH}_3 \end{matrix}$ . Its IUPAC name is 2-methylpropan-2-ol

*n*-Butanol is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ . Its IUPAC name is butan-1-ol.

Isobutyl alcohol is  $\begin{array}{c} ^3\text{CH}_3 \\ | \\ ^2\text{CH}-\text{CH}_2\text{OH} \end{array}$ . Its IUPAC name is 2-methylpropan-1-ol.

### Fill-in-the-Blanks Type



### True/False Type

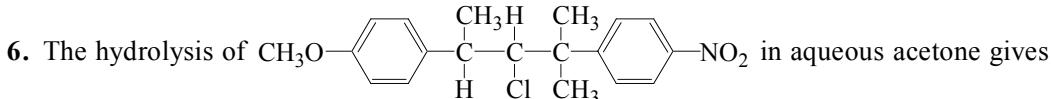
2.  $\text{CH}_3\text{F}$  involves lesser C—F distance but more charge separation as compared to those in  $\text{CH}_3\text{Cl}$ . Here, bond distance has more dominating effect causing dipole moment of  $\text{CH}_3\text{Cl}$  greater than that of  $\text{CH}_3\text{F}$ .



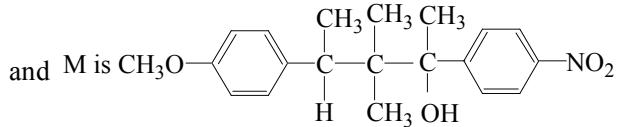
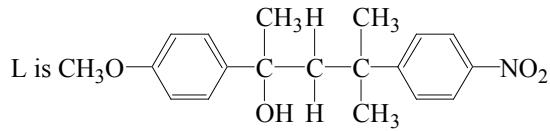
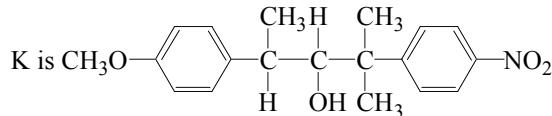
# ALKYL AND ARYL HALIDES

26

## Straight Objective Type

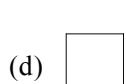
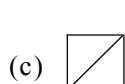
1.  $(\text{CH}_3)_3\text{CMgCl}$  on reaction with  $\text{D}_2\text{O}$  produces:  
(a)  $(\text{CH}_3)_3\text{CD}$       (b)  $(\text{CH}_3)_3\text{OD}$       (c)  $(\text{CD}_3)_3\text{CD}$       (d)  $(\text{CD}_3)_3\text{OD}$       (1997)
2. Which of the following has the highest nucleophilicity?  
(a)  $\text{F}^-$       (b)  $\text{OH}^-$       (c)  $\text{CH}_3^-$       (d)  $\text{NH}_2^-$       (2000)
3. The order of reactivities of the following alkyl halides for a  $\text{S}_{\text{N}}2$  reaction is  
(a)  $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$       (b)  $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$   
(c)  $\text{RCl} > \text{RBr} > \text{RF} > \text{RI}$       (d)  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$       (2000)
4. Diethyl ether on heating with concentrated  $\text{HI}$  gives two moles of  
(a) ethanol      (b) ethyl iodide      (c) iodoform      (d) methyl iodide      (1982)
5. Which of the following molecules having tetrahedral structures is expected to have maximum value of dipole moment?  
(a)  $\text{CH}_3\text{Cl}$       (b)  $\text{CH}_2\text{Cl}_2$       (c)  $\text{CHCl}_3$       (d)  $\text{CCl}_4$       (2003)
6. The hydrolysis of  $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)(\text{CH}_3\text{H})-\text{C}(\text{CH}_3)(\text{CH}_3)-\text{C}_6\text{H}_4-\text{NO}_2$  in aqueous acetone gives  
  
(a) K and L      (b) Only K      (c) L and M      (d) Only M

where



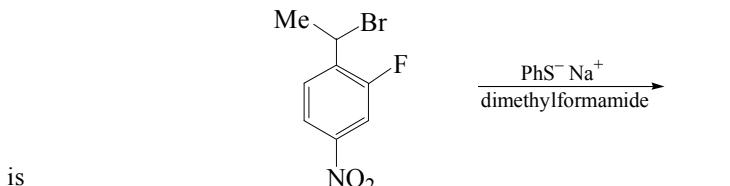
(2005)

7. 1-Bromo-3-chlorocyclobutane when treated with two equivalents of Na in the presence of ether results into

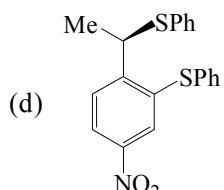
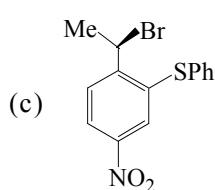
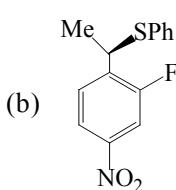
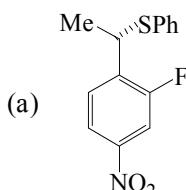


(2005)

8. The major product of the following reaction



is



(2008)

## **Multiple Correct-Choice Type**

1. The products of reaction of alcoholic silver nitrite with ethyl bromide are



(1991)

## **Fill-in-the-Blanks Type**

1. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as \_\_\_\_\_.

— (1982).

2. The interaction of elemental sulphur with Grignard reagent gives

(1991)

- $$3. \text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{AgCN}}$$

(1997)

### **True/False Type**

1. Carbon tetrachloride is inflammable (1985)

2. Carbon tetrachloride burns in air when lighted to give phosgene.

(1983)

## **Reasoning Type**

In each subquestion below are given a STATEMENT (S) in the left hand column and an EXPLANATION (E) in the right hand column. Ascertain the relationship between S and E and select the correct code among **a**, **b**, **c** and **d** which are defined below.

Code

- (a) Both **S** and **E** are true, and **E** is the correct explanation of **S**.
  - (b) Both **S** and **E** are true but **E** is not the correct explanation of **S**.
  - (c) **S** is true but **E** is false.
  - (d) **S** is false but **E** is true.

STATEMENT(S)	EXPLANATION (E)
1. Aryl halides undergo nucleophilic substitution with ease.	The carbon-halogen bond in aryl halides has partial double bond character. (1991)
2. Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide	Cyanide ( $\text{CN}^-$ ) is a strong nucleophile. (1998)

## Matching Type

1. Match the entries on the left with most appropriate choice(s) given on the right

(a) $\text{C}_6\text{H}_5\text{CH}_2\text{CD}_2\text{Br}$ on reaction with $\text{C}_2\text{H}_5\text{O}^-$ gives $\text{C}_6\text{H}_5-\text{CH}=\text{CD}_2$	(p) $\text{E}_1$
(b) $\text{C}_6\text{H}_5\text{CHBrCH}_3$ and $\text{C}_6\text{H}_5\text{CHBrCD}_3$ both react with the same rate	(q) $\text{E}_2$
(c) $\text{C}_6\text{H}_5\text{CHDCH}_2\text{Br}$ on treatment with $\text{C}_2\text{H}_5\text{O}^-$ and $\text{C}_2\text{H}_5\text{OD}$ gives $\text{C}_6\text{H}_5\text{CD}=\text{CH}_2$	(r) $\text{E}_{1,\text{cb}}$
(d) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$ reacts faster than $\text{C}_6\text{H}_5\text{CD}_2\text{CH}_2\text{Br}$ on reaction with $\text{C}_2\text{H}_5\text{O}^-$ in ethanol	(s) First order reaction

(2006)

## Short Answer Type

1. Show, by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis.
- (i) Hexachloroethane,  $\text{C}_2\text{Cl}_6$ , from calcium carbide
  - (ii) Chloroform from carbon disulphide (1979)
2. Aryl halides are less reactive than alkyl halides nucleophilic reagents. (1994)
3. Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why?
- (i)  $(\text{CH}_3)_3\text{CBr} + \text{NaOMe} \rightarrow$
  - (ii)  $\text{CH}_3\text{Br} + \text{NaO-}t\text{-Bu} \rightarrow$  (1997)
4. Give the reactions of  $\text{R'MgX}$  with (i)  $\text{RCOOEt}$  and (ii)  $\text{RCN}$ . Explain the difference between the two reactions. (2004)
5. Equations for the preparation of
- (i) lead tetraethyl from sodium – lead alloy.
  - (ii) methyl chloride from aluminium carbide (1983)

## ANSWERS

### Straight Objective Type

- |        |        |        |        |        |        |
|--------|--------|--------|--------|--------|--------|
| 1. (a) | 2. (c) | 3. (d) | 4. (b) | 5. (b) | 6. (a) |
| 7. (c) | 8. (a) |        |        |        |        |

### Multiple Correct-Choice Type

1. (c), (e)

### Fill-in-the-Blanks Type

1. Grignard reagent                            2. An adduct R-S-MgX (which on hydrolysis produces thioalcohols)  
3.  $\text{CH}_3\text{CH}_2\text{NC}$

### True/False Type

1. False    2. False

### Reasoning Type

1. (d)    2. (d)

### Matching Type

1. (a)-(q);                                    (b)-(p),(s);                                    (c)-(q);                                    (d)-(q)

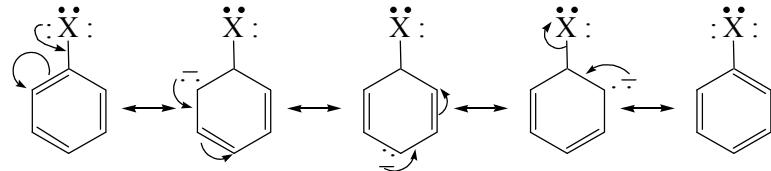
### Short Answer Type

1. (i)  $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$   
 $\text{C}_2\text{H}_2 \xrightarrow{\text{H}_2/\text{Ni}} \text{CH}_3\text{CH}_3 \xrightarrow[\text{excess}]{\text{Cl}_2} \text{CCl}_3 - \text{CCl}_3$   
(ii)  $\text{CS}_2 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{S}_2\text{Cl}_2$   
 $\text{CS}_2 + 2\text{S}_2\text{Cl}_2 \rightarrow \text{CCl}_4 + 6\text{S}$   
 $\text{CCl}_4 + 2 [\text{H}] \xrightarrow{\text{Fe}/\text{H}_2\text{O}} \text{CHCl}_3 + \text{HCl}$

2. Aryl halide are less reactive and more stable than alkyl halides due to two reasons.

(a) *Delocalization of electrons*

In aryl halides the delocalization of electron pairs occur as shown below.

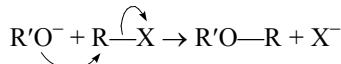


The delocalization imparts a partial double bond character to C—X bond making it stronger than C—X bond in alkyl halides.

(b) Difference in hybridisation of carbon.

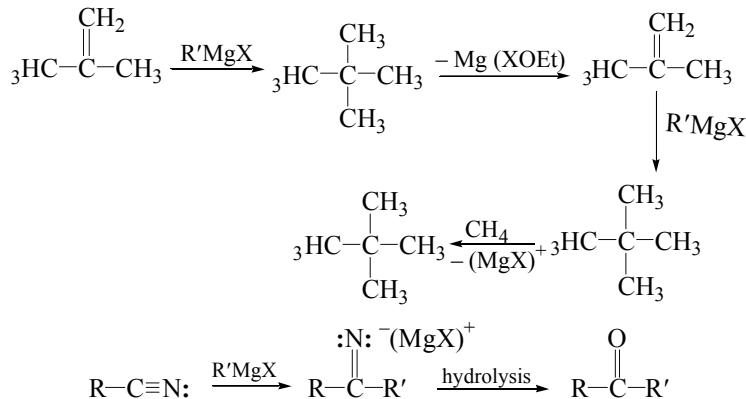
In alkyl halides, the carbon to which the halogen is attached is  $\text{sp}^3$  hybridised while in aryl halide it is  $\text{sp}^2$  hybridised. Therefore, the C—X bond in latter is shorter than in former.

3. The ether formation involves nucleophilic substitution of alkoxide ion for halide ion



3° alkyl halide can also involve elimination of HX to give alkene in the presence of a base. So, it is better to start with 3° alkoxide and 1° alkyl halide.

4. The reactions are



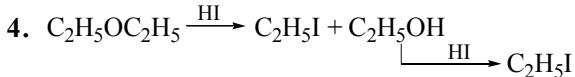
In the reaction between  $\text{R}-\text{C}\equiv\text{N}$  and  $\text{R}'\text{MgX}$ , the end product is  $\text{RCOR}'$ . A second equivalent of  $\text{R}'\text{MgX}$  does not react because the intermediate imine salt bears a negative charge. Elimination of charge by the removal of  $\text{R}'$  merely reverses the reaction to give  $\text{R}-\text{C}\equiv\text{N}$ .

5. (i)  $4\text{C}_2\text{H}_5\text{Br} + 4(\text{Na}/\text{Pb}) \rightarrow \text{Pb}(\text{C}_2\text{H}_5)_4 + 4\text{NaBr} + 3\text{Pb}$   
(ii)  $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4$ ;  $2\text{CH}_4 + 2\text{Cl}_2 \rightarrow 2\text{CH}_3\text{Cl} + 2\text{HCl}$   
(limited)

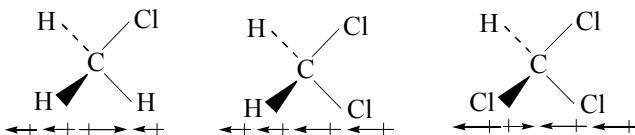
## HINTS AND SOLUTIONS

### Straight Objective Type

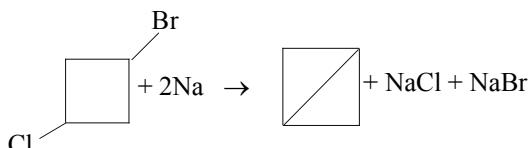
- The product is  $(\text{CH}_3)_3\text{CD}$ .
- More the electronegativity of the atom to which H is attached, lesser the nucleophilicity of the anion. Thus  $\text{CH}_3^-$  has the highest nucleophilicity.
- Stronger the C — X bond, lesser the reactivity of the alkyl halides for a  $\text{S}_{\text{N}}2$  reaction. Of the halogens, an iodide ion is the best leaving group and a fluoride ion is the poorest. Thus, the correct order is  $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$ .



- In  $\text{CH}_2\text{Cl}_2$  all bond moments reinforce each other, while in  $\text{CH}_3\text{Cl}$  and  $\text{CHCl}_3$  only one CCl and CH bond moments reinforce each other as shown in the following figure.



- With acetone as solvent, the reaction proceeds with the characteristics of both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanisms. The  $\text{S}_{\text{N}}1$  involves hydride shift giving structure L.
- The reaction involves intramolecular elimination of halogens by using sodium. (Wurtz reaction).



- The reaction involves nucleophilic substitution of a halogen by  $\text{PhS}^-$ . It is easy to carry such substitution in alkyl halide than in aryl halide. The substitution will proceed via  $\text{S}_{\text{N}}2$  mechanism, which results into the inversion of configuration of carbon atom at which substitution reaction occurs.

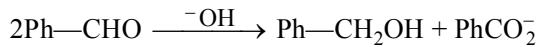


# ALDEHYDES AND KETONES

27

## Straight Objective Type

1. The reagent with which both acetaldehyde and acetone react easily is  
(a) Fehling's reagent (b) Grignard reagent (c) Schiff's reagent (d) Tollens reagent (1981)
2. The compound that gives a positive iodoform test is  
(a) 1-pentanol (b) 2-pentanone (c) 3-pentanone (d) pentanal (1982)
3. When acetaldehyde is heated with Fehling's solution it gives a precipitate of  
(a) Cu (b) CuO (c) Cu<sub>2</sub>O (d) Cu + Cu<sub>2</sub>O + CuO (1983)
4. The Cannizzaro reaction is not given by  
(a) trimethylalactaldehyde (b) benzaldehyde  
(c) acetaldehyde (d) formaldehyde (1983)
5. The compound that will not give iodoform on treatment with alkali and iodine is  
(a) acetone (b) ethanol (c) diethyl ketone (d) isopropyl alcohol (1985)
6. Polarization of electrons in acrolein may be written as  
(a)  $\delta^- \text{CH}_2=\text{CH}-\delta^+ \text{CH=O}$  (b)  $\delta^- \text{CH}_2=\text{CH}-\text{CH}=\delta^+ \text{O}$   
(c)  $\delta^- \text{CH}_2=\delta^+ \text{CH}-\text{CH=O}$  (d)  $\delta^+ \text{CH}_2=\text{CH}-\delta^- \text{CH=O}$  (1988)
7. The formation of cyanohydrin from a ketone is an example of  
(a) electrophilic addition (b) nucleophilic addition  
(c) nucleophilic substitution (d) electrophilic substitution (1990)
8. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives  
(a) potassium *m*-chlorobenzoate and *m*-hydroxybenzaldehyde  
(b) *m*-hydroxybenzaldehyde and *m*-chlorobenzyl alcohol  
(c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol  
(d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol (1991)
9. In the Cannizzaro reaction given below,



the slowest step is

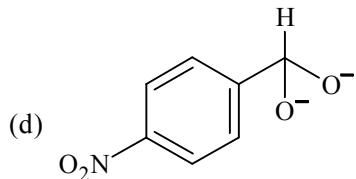
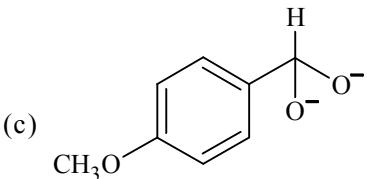
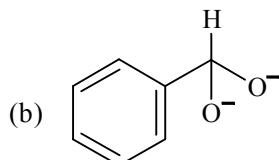
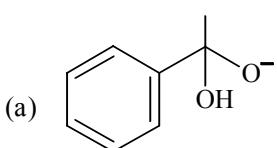
- (a) the attack of  $-\text{OH}$  at the carbonyl group,  
(b) the transfer of hydride to the carbonyl group,  
(c) the abstraction of proton from the carboxylic acid,  
(d) the deprotonation of  $\text{Ph}-\text{CH}_2\text{OH}$  (1996)

10. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is

- (a)  $\text{CH}_3\text{COCl}$       (b)  $\text{CH}_3\text{CHO}$       (c)  $\text{CH}_3\text{COOCH}_3$       (d)  $\text{CH}_3\text{COOCOCH}_3$

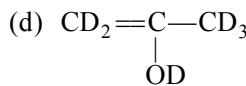
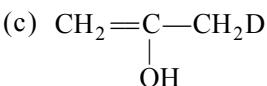
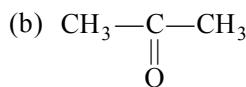
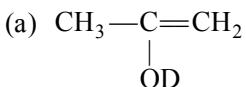
(1997)

11. In a Cannizaro reaction, the intermediate that will be the best hydride donor is



(1997)

12. The enol form of acetone, after treatment with  $\text{D}_2\text{O}$ , gives



(1999)

13. Which of the following has the most acidic hydrogen?

- (a) 3-Hexanone

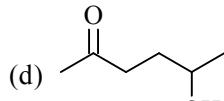
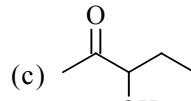
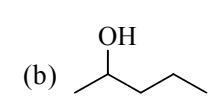
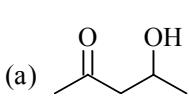
- (b) 2, 4-Hexanedione

- (c) 2, 5-Hexanedione

- (d) 2, 3-Hexanedione

(2000)

14. Which one of the following will most readily be dehydrated in acidic condition?



(2000)

15. Which of the following will react with water?

- (a)  $\text{CHCl}_3$

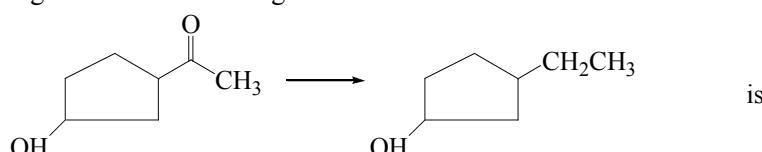
- (b)  $\text{Cl}_3\text{CCHO}$

- (c)  $\text{CCl}_4$

- (d)  $\text{ClCH}_2\text{CH}_2\text{Cl}$

(1998)

16. The appropriate reagent for the following transformation



- (a)  $\text{Zn}(\text{Hg}), \text{HCl}$       (b)  $\text{NH}_2\text{NH}_2, \text{OH}^-$       (c)  $\text{H}_2/\text{Ni}$       (d)  $\text{NaBH}_4$

(2000)

17. A mixture of benzaldehyde and formaldehyde on heating with aqueous  $\text{NaOH}$  solution gives

- (a) benzyl alcohol and sodium formate

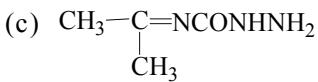
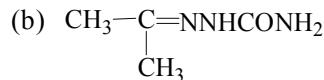
- (b) sodium benzoate and methyl alcohol

- (c) sodium benzoate and sodium formate

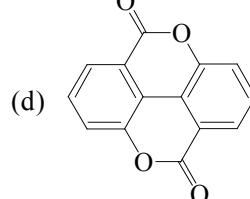
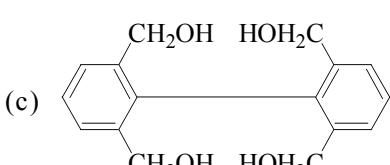
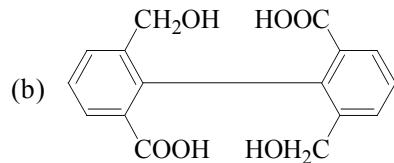
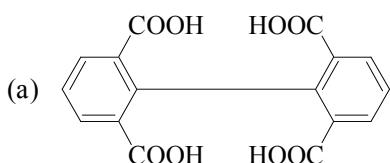
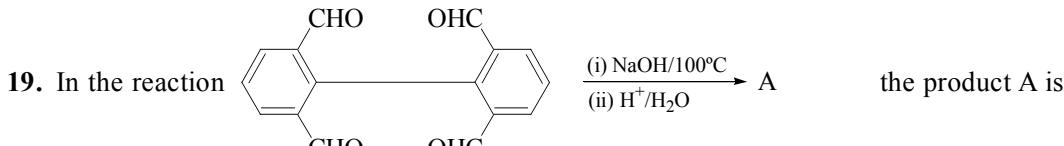
- (d) benzyl alcohol and methyl alcohol

(2001)

18. Compound 'A' (molecular formula  $\text{C}_3\text{H}_8\text{O}$ ) is treated with acidified potassium dichromate to form a product 'B' (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ). 'B' forms a shining silver mirror on warming with ammoniacal silver nitrate. 'B' when treated with an aqueous solution of  $\text{H}_2\text{NCONHNH}_2 \cdot \text{HCl}$  and sodium acetate gives a product 'C'. Identify the structure of 'C'.



(2002)

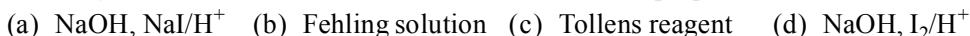


(2003)

20. The correct order of reactivity of  $\text{PhMgBr}$  with  $\text{PhCOPh}$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  is

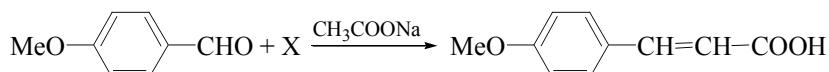
(2004)

21. The reagent that can be used to convert butan-2-one to propanoic acid is

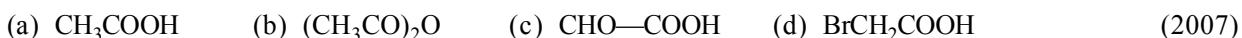


(2005)

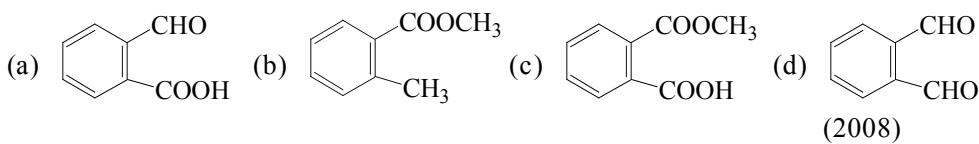
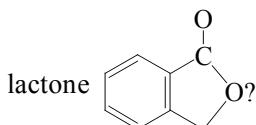
22. In the reaction



the species X is

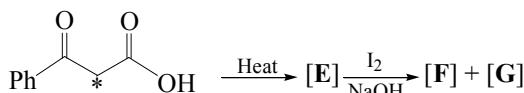


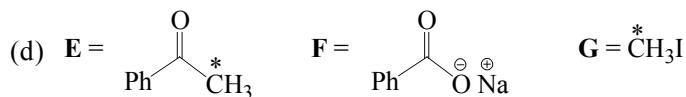
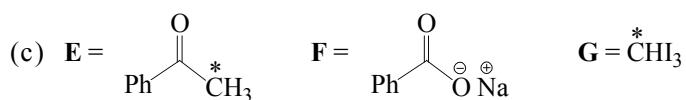
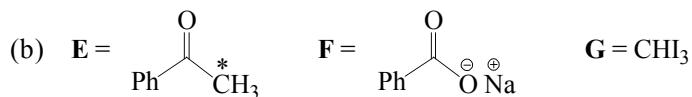
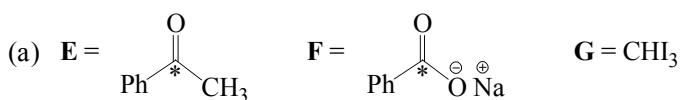
23. Which of the following compound(s) on treatment with aqueous alkali followed by acidification gives the



(2008)

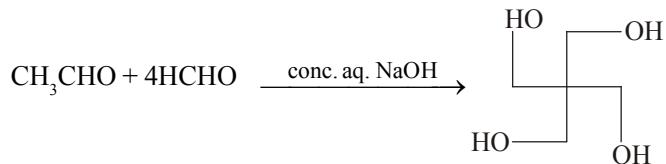
24. In the following reaction sequence, the correct structures of E, F and G are

(\* implies  $^{13}\text{C}$  labelled carbon)



(2008)

**25.** The number of aldol reaction(s) that occurs in the given transformation



15



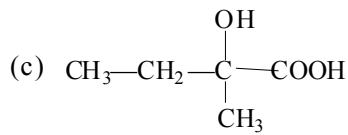
(2012)

**26.** The major product H in the given reaction sequence



is

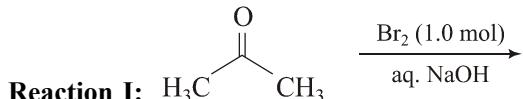
- |   |   |
|---|---|
| (a) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\overset{ }{\text{C}}}-\text{COOH}$ | (b) $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\overset{ }{\text{C}}}-\text{CN}$ |
|---|---|



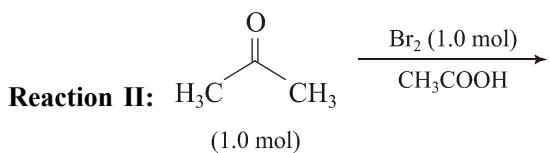
- (d)  $\text{CH}_3-\text{CH}=\underset{\text{CH}_3}{\overset{|}{\text{C}}}-\text{CO}-\text{NH}_2$

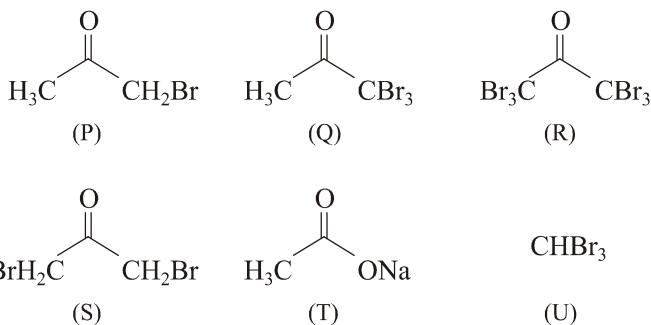
(2012)

27. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are)



(1.0 mol)

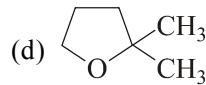
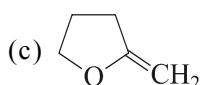
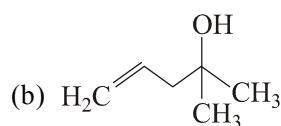
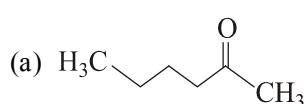
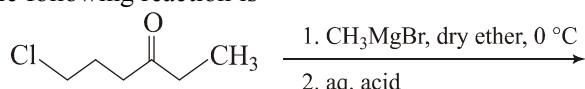




- (a) Reaction I: P and Reaction II : P
  - (b) Reaction I : U, acetone and Reaction II: Q, acetone
  - (c) Reaction I: T, U, acetone and Reaction II : P
  - (d) Reaction I: R and Reaction II: S, acetone.

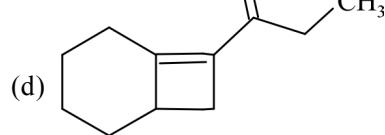
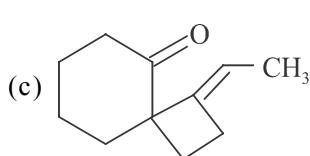
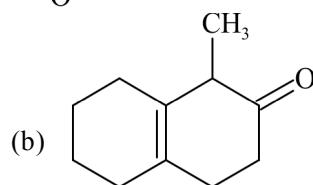
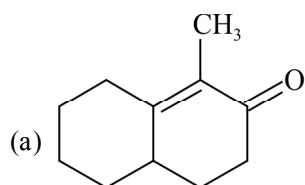
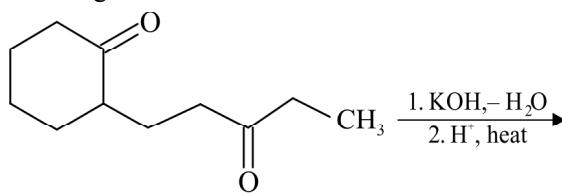
(2013)

**28.** The major product in the following reaction is



(2014)

**29.** The major product of the following reaction is



(2015)

## **Multiple Correct-Choice Type**

1. Base catalysed aldol condensation occurs with

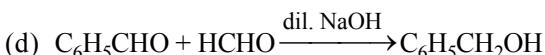
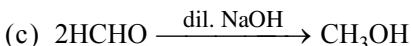
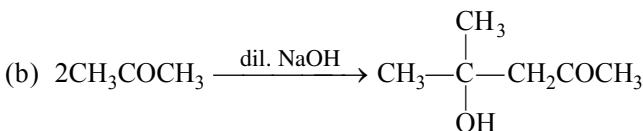
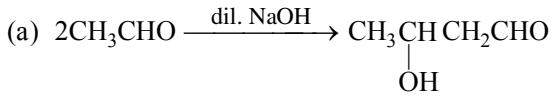


(1984)

3. Which of the following compounds will react with ethanolic KCN?

- (a) Ethyl chloride (b) Acetyl chloride (c) Chlorobenzene (d) Benzaldehyde (1989)  
4. Which of the following are the examples of aldol condensation?

4. Which of the following are the examples of aldol condensation?



5. A new carbon-carbon bond formation is possible in



6. Among the following compounds, which will react with acetone to give a product containing  $\text{C}=\text{N}-$ ?

- (a)  $C_6H_5NH_2$       (b)  $(CH_3)_3N$       (c)  $C_6H_5NHC_6H_5$       (d)  $C_6H_5NHNH_2$       (1998)

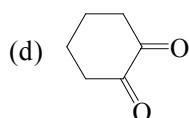
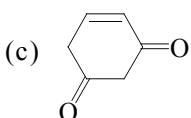
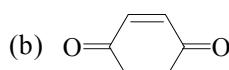
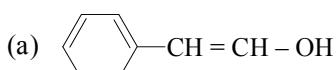
7. Which of the following will undergo aldol condensation?



8. Which of the following will give yellow precipitate with  $I_2/NaOH$ ?

- (a)  $\text{ICH}_2\text{COCH}_2\text{CH}_3$       (b)  $\text{CH}_3\text{COOCOCH}_3$   
 (c)  $\text{CH}_2\text{CONH}_2$       (d)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$       (1997)

9. Tautomerism is exhibited by



**10.** Which of the following compounds form(s) two isomeric oximes on reacting with  $\text{NH}_2\text{OH}$ ?

- (a) RCHO              (b) RCOR              (c) RCOR'              (d) HCHO              (2006)

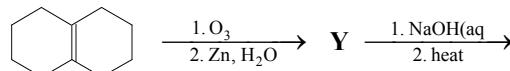
### **Fill-in-the-Blanks Type**

1. The product obtained when methanal reacts with ammonia is \_\_\_\_\_. (1981)
  2. Paraldehyde is a \_\_\_\_ of acetaldehyde and its structure is \_\_\_\_\_. (1981)
  3. Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide and the reaction mixture is poured into water. The main product obtained in this process is \_\_\_\_\_. (1981)

4. Fehling's solution A consists of an aqueous solution of copper sulphate while Fehling's solution B consists of an alkaline solution of \_\_\_\_\_. (1990)
5. The structure of the enol form of  $\text{CH}_3\text{—CO—CH}_2\text{—CO—CH}_3$  with intramolecular hydrogen bonding is \_\_\_\_\_. (1993)

### Integer Answer Type

1. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is \_\_\_\_\_. (2010)



2. Consider all possible isomeric ketones including stereo isomers of relative molar mass of 100. All these isomers are independently reacted with  $\text{NaBH}_4$  (Note: stereo isomers are also reacted separately). The total number of ketones that give a racemic product(s) is/are \_\_\_\_\_. (2014)

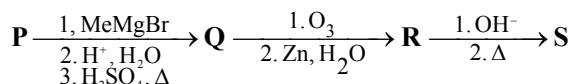
### True/False Type

1. Benzaldehyde undergoes aldol condensation in an alkaline medium. (1982)
2. Hydrazones of aldehydes and ketones are prepared in highly acidic medium. (1986)
3. The reaction of methyl magnesium iodide with acetone followed by hydrolysis gives secondary butanol. (1987)

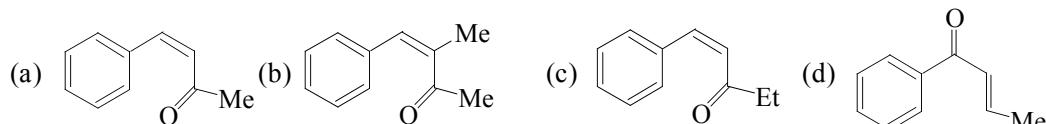
### Linked-Comprehension Type

#### Passage 1

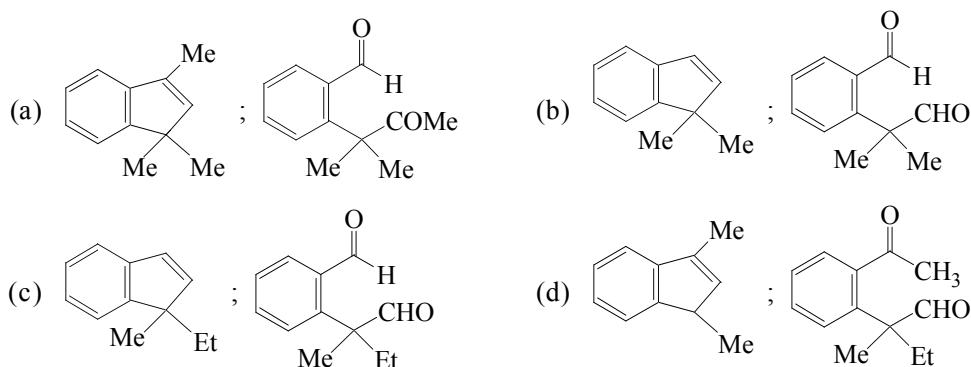
A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with  $\text{MeMgBr}$  followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R** which undergoes intramolecular aldol reaction to give predominantly **S**.



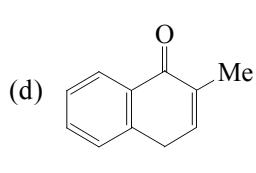
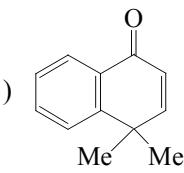
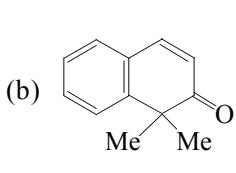
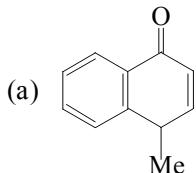
1. The structure of the carbonyl compound **P** is



2. The structures of the products **Q** and **R**, respectively, are



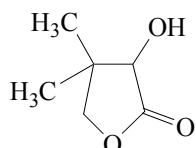
3. The structure of product S is



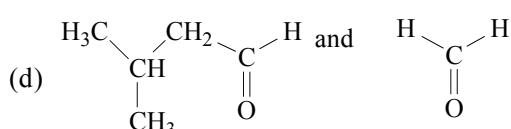
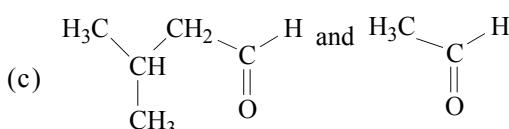
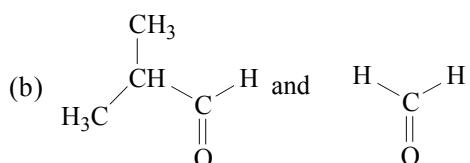
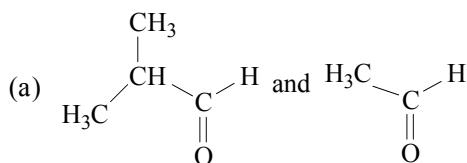
(2009)

**Passage 2**

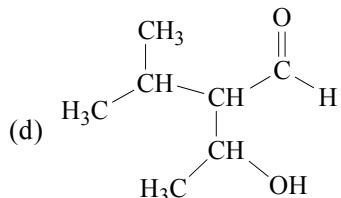
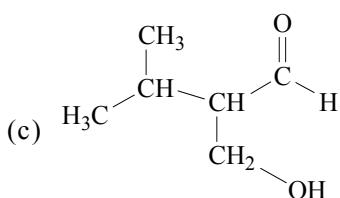
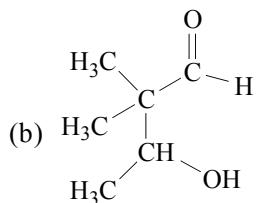
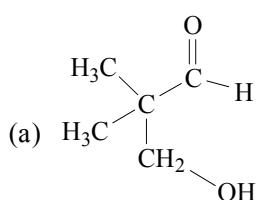
Two aliphatic aldehydes P and Q react in the presence of aqueous  $\text{K}_2\text{CO}_3$  to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below:



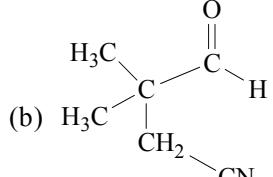
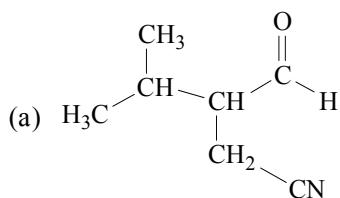
1. The compounds P and Q respectively are

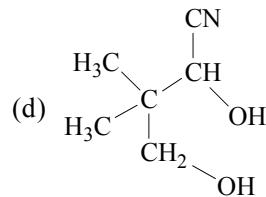
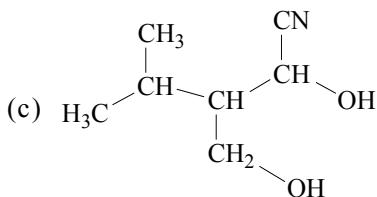


2. The compound R is



3. The compound S is





(2010)

### Short Answer Type

- Hydrazone of aldehydes and ketones are not prepared in highly acidic medium (1986)
- Iodoform is obtained by the reaction of acetone with hypoiodite but not with iodide. (1991)
- Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes. (1997)
- Explain why *o*-hydroxybenzaldehyde is a liquid at room temperature while *p*-hydroxybenzaldehyde is a high melting solid. (1999)
- State with balance equation, what happens when chloral is heated with aqueous sodium hydroxide. (1984)

### ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (b)  | 3. (c)  | 4. (c)  | 5. (c)  | 6. (d)  | 7. (b)  |
| 8. (d)  | 9. (b)  | 10. (a) | 11. (c) | 12. (a) | 13. (b) | 14. (a) |
| 15. (b) | 16. (b) | 17. (a) | 18. (a) | 19. (b) | 20. (c) | 21. (d) |
| 22. (b) | 23. (d) | 24. (c) | 25. (c) | 26. (a) | 27. (c) | 28. (d) |
| 29. (a) |         |         |         |         |         |         |

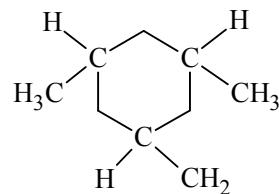
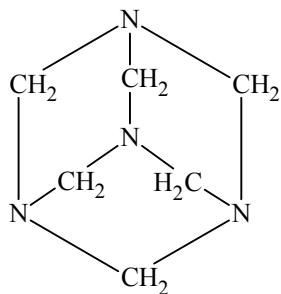
### Multiple Correct-Choice Type

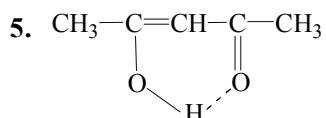
- |             |                  |             |                  |              |
|-------------|------------------|-------------|------------------|--------------|
| 1. (a), (c) | 2. (a), (b)      | 3. (a), (d) | 4. (a), (b)      | 5. (b), (d)  |
| 6. (a), (d) | 7. (a), (b), (d) | 8. (a), (d) | 9. (a), (c), (d) | 10. (a), (c) |

### Fill-in-the-Blanks Type

1. Urotropine,  $(\text{CH}_2)_6\text{N}_4$ 

2. Trimer,

3.  $(\text{C}_2\text{H}_5)_3\text{COH}$ .4. Rochelle salt (sodium potassium tartrate —  $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ).



## **Integer Answer Type**



## **True/False Type**

1. False                    2. False                    3. False

## **Linked-Comprehension Type**

## Passage 1

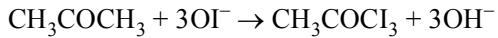
- 1.** (b)                    **2.** (a)                    **3.** (b)

## Passage 2

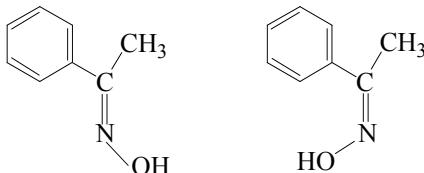
1. (b)                    2. (a)                    3. (d)

## **Short Answer Type**

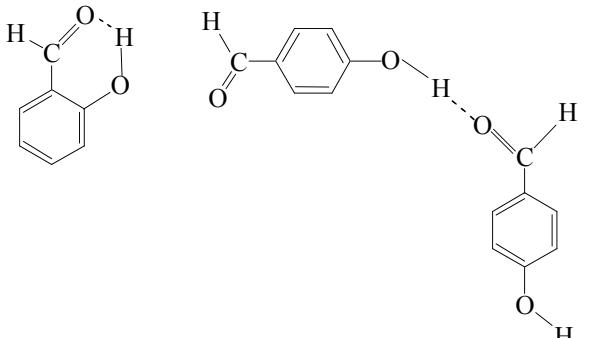
1. In strongly acidic medium, hydrazine gets easily protonated which lowers its nucleophilicity. That is why hydrazone of aldehyde and ketones are not prepared in highly acidic medium.
  2. The reaction is initiated by the replacement of methyl protons (as  $H^+$ ) by  $I^+$



3. The structures of two isomeric oximes are



4. The molecule *o*-hydrobenzaldehyde involves intramolecular hydrogen bonding while those of *p*-hydroxybenzaldehyde involves intermolecular hydrogen bondings (Fig. C2)



Single entity makes  
*o*-hydroxybenzaldehyde  
a liquid at room temperature

Giant molecules make  
*p*-hydroxybenzaldehyde  
a high melting solid.

**Fig. C.2**

5. The reaction is  $\text{Cl}_3\text{CHO} + \text{NaOH} \rightarrow \text{CHCl}_3 + \text{HCOONa}$

## HINTS AND SOLUTIONS

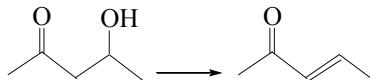
### Straight Objective Type

- Grignard reagent reacts both with acetaldehyde and acetone.
- A compound containing  $\text{CH}_3\text{CO}-$  or  $\text{CH}_3\text{CH}(\text{OH})-$  shows iodoform test.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$  (2-pentanone) shows this test.
- The red precipitates are due to  $\text{Cu}_2\text{O}$ .
- A ketone with no  $\alpha$ -hydrogen shows Cannizzaro reaction. Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) contains  $\alpha$ -hydrogen. It will not show this test.
- Diethyl ketone ( $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ ) will not show iodoform test.
- Polarization in acrolein may be represented as  $\overset{\delta+}{\text{CH}_2}=\overset{\delta-}{\text{CH}}-\overset{\delta-}{\text{O}}$ .
- The formation of cyanohydrin from a ketone is an example of nucleophilic addition reaction.
- m*-Chlorobenzaldehyde in the presence of concentrated alkali will undergo Cannizzaro reaction. The products will be potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.
- The slowest step in Cannizzaro reaction is the transfer of hydride to the carbonyl group.
- $\text{CH}_3\text{COCl}$  is the most susceptible to nucleophilic attack at the carbonyl group. This is due to  $-\text{Cl}$  which stabilises the transition state.
- The methoxy group being electron-releasing group makes the release of hydride group more easy.
- The enolic form of acetone ( $\text{CH}_3-\underset{\text{OH}}{\overset{|}{\text{C}}}=\text{CH}_2$ ) contains active hydrogen, replaceable by deuterium.

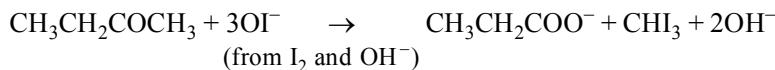
13. 2,4-Hexanedione

$(\text{H}_3\text{C}-\overset{\parallel}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\parallel}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\text{CH}_3)$  has the most acidic hydrogen attached to  $\text{C}^3$  carbon atom. The methylene group has two neighbouring carbonyl groups.

- The compound  $\text{CH}_3\text{COCH}_2\text{CH}(\text{OH})\text{CH}_3$ , a  $\beta$ -ketohydroxy compound, will be most readily dehydrated. Dehydration occurs readily because of the acidity of a hydrogens and also the product is stabilised by having conjugate double bonds.

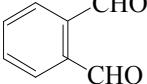


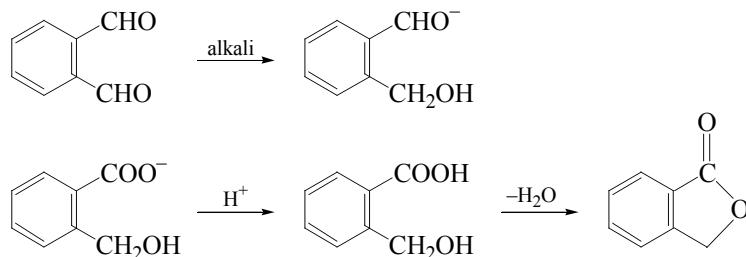
- Chloral,  $\text{CCl}_3\text{CHO}$ , reacts with water forming chloral hydrate,  $\text{CCl}_3\text{CH}(\text{OH})_2$ .
- The Wolff-Kishner reduction takes place in strongly basic solutions and can be used for those compounds that are sensitive to acid.
- Formaldehyde is always converted into formic acid.
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   $\xrightarrow[\text{(A)}]{\text{K}_2\text{Cr}_2\text{O}_7 \text{ acidified}}$   $\text{CH}_3\text{CH}_2\text{CHO}$   $\xrightarrow[\text{(B)}]{\text{sodium acetate}, \text{H}_2\text{NCONHNH}_2 \cdot \text{HCl}}$   $\text{CH}_3\text{CH}_2\text{CH}=\text{NNHCONH}_2$   $\text{(C)}$
- There occurs intramolecular Cannizzaro reaction.
- Aldehydes generally undergo nucleophilic addition more readily than ketones as the former involve lesser crowding at the transition state.
- Butanone is  $\text{CH}_3\text{CH}_2\text{COCH}_3$ . It contains  $-\text{COCH}_3$  group which can be converted to  $-\text{COOH}$  by carrying out the iodoform test. The reagent used is  $\text{NaOH}$ ,  $\text{I}_2/\text{H}^+$ .



- The reaction is called a Perkin condensation.

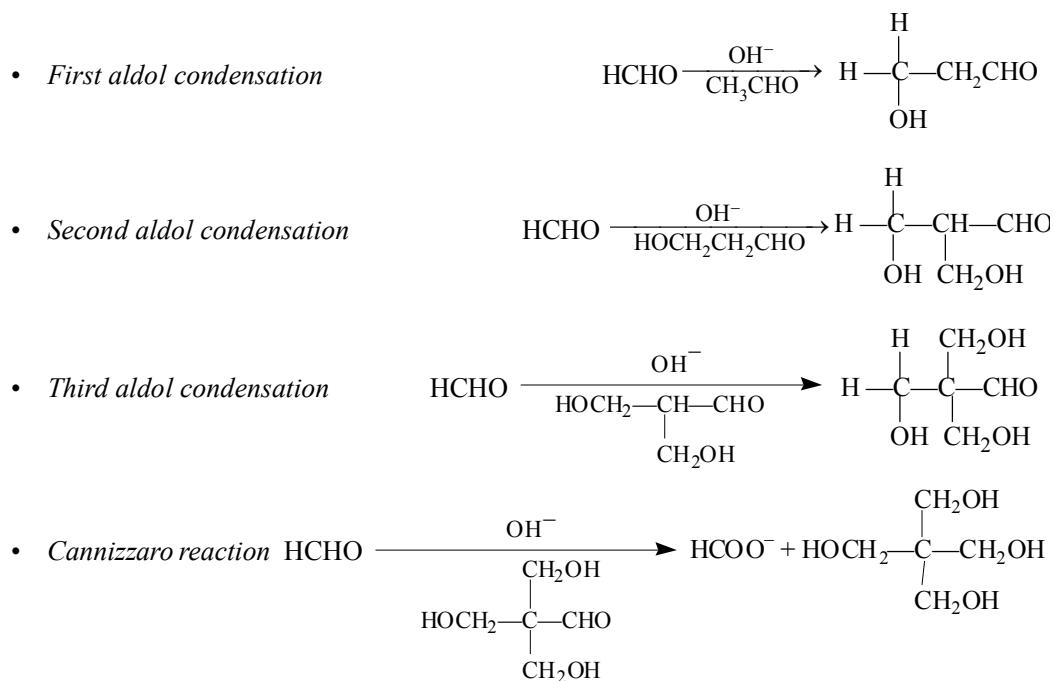
23. Carboxylic acid whose molecule has a hydroxyl group on a  $\gamma$  or  $\delta$  carbon undergoes an intramolecular esterification to give cyclic esters known as  $\gamma$ - or  $\delta$ -lactone. This reaction is acid catalysed.

Of the given compounds,  will satisfy the above requirement after it has undergone intramolecular Cannizzaro reaction in the presence of alkali.



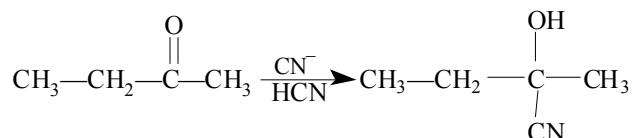
24. First reaction involves decarboxylation and thus E is  $\text{Ph CO}^*\text{CH}_3$ . The second reaction is iodoform reaction giving  $\text{PhCOO}^- \text{Na}^+$  (F) and  $\overset{*}{\text{CHI}}_3$  (G).

25. The given reaction may be formulated as follows.

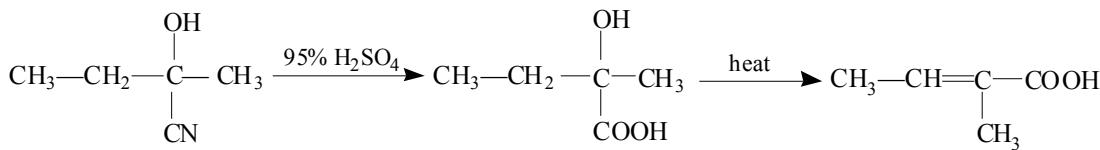


There are three aldol condensations and one Cannizzaro reaction.

26. The first reaction is nucleophilic addition reaction across the  $-\text{C}=\text{O}$  bond.

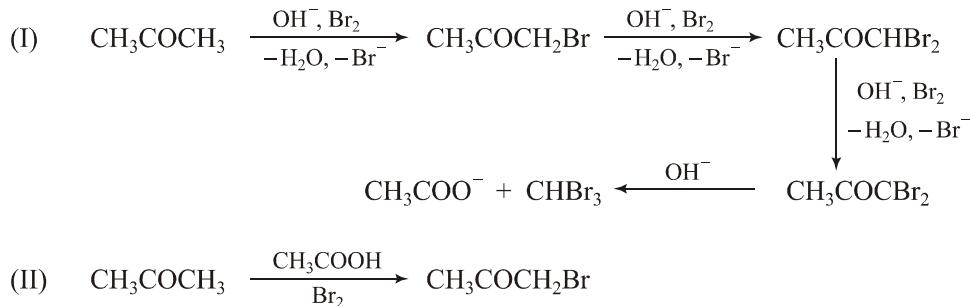


In the second reaction,  $-\text{CN}$  is hydrolysed to  $-\text{COOH}$ . The resultant molecule undergoes dehydration on heating.

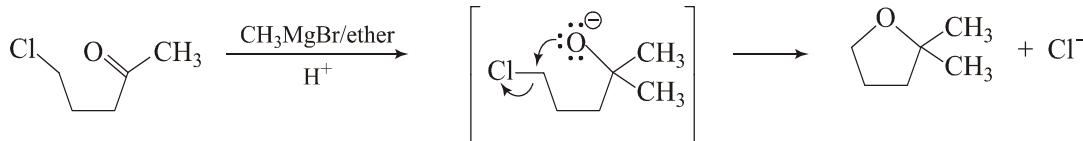


27. Since both acetone and  $\text{Br}_2$  are present in equal amounts, it is expected that the product P would be formed in both the cases. However, in the base-promoted  $\alpha$ -halogenation, the second and third halogenation occur with much faster than the first one. Consequently, the product T, U and remaining acetone will be found in the reaction I.

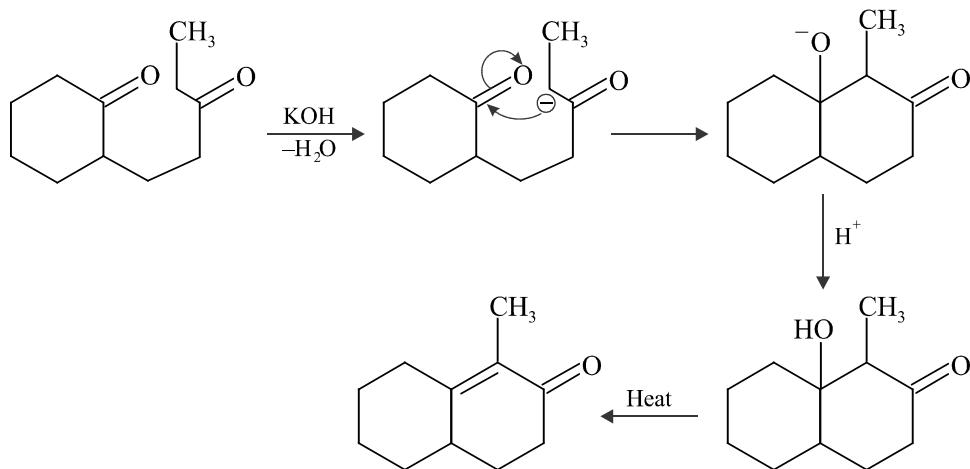
This does not occur in the acid-catalysed halogenation of ketone because the second and third halogenation occur with much slower speed than the first one. The reaction are :



28. The given reaction may be formulated as follows.



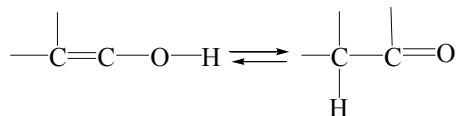
29. The molecule undergoes intramolecular aldol condensation.



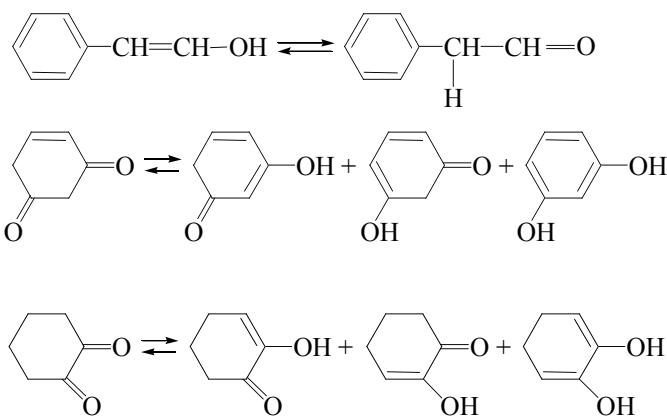
### Multiple Correct-Choice Type

1. Aldol condensation is shown by an aldehyde or ketone with  $\alpha$ -hydrogen atom. Propanal ( $\text{CH}_3\text{CH}_2\text{CHO}$ ) and 2-methylpropanal ( $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHO}$ ) will show this condensation.

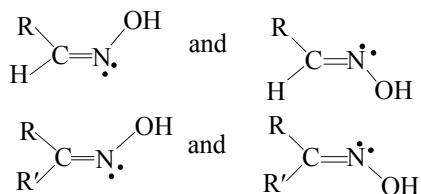
2. Acetophenone ( $C_6H_5COCH_3$ ) contains  $CH_3CO-$  group. This will show iodoform test. Also 2-hydroxypropane ( $CH_3CHOHCH_3$ ) which contains  $CH_3CHO-$  group will show iodoform test.
3. Ethyl chloride and benzaldehyde will react with ethanolic KCN.
4. Aldehydes and ketones containing  $\alpha$ -hydrogen atom show aldol condensation. Thus, the compounds  $CH_3CHO$  and  $CH_3COCH_3$  show these condensation.
5. Friedel-Crafts alkylation and Reimer-Tiemann reaction involves the formation of C—C bond.
6. Primary amines ( $C_6H_5NH_2$  and  $C_6H_5NNH_2$ ) on reacting with acetone will give products containing  $\text{C}=\text{N}-$  group.
7. Compounds containing  $\alpha$ -hydrogen (or deuterium) undergo aldol condensation. Acetaldehyde, propanaldehyde and trideuteroacetaldehyde will undergo aldol condensation.
9. Keto-enol tautomerism involves the following equilibrium.



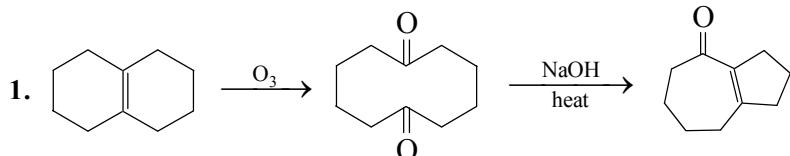
This equilibrium can exist in the following molecules.



10. Two isomeric oximes are formed when an aldehyde (other than formaldehyde) or a nonsymmetrical ketone reacts with hydroxylamine.



### Integer Answer Type



Since the dicarbonyl formed in the first step is symmetrical, the intramolecular aldol condensation would lead to only one product.

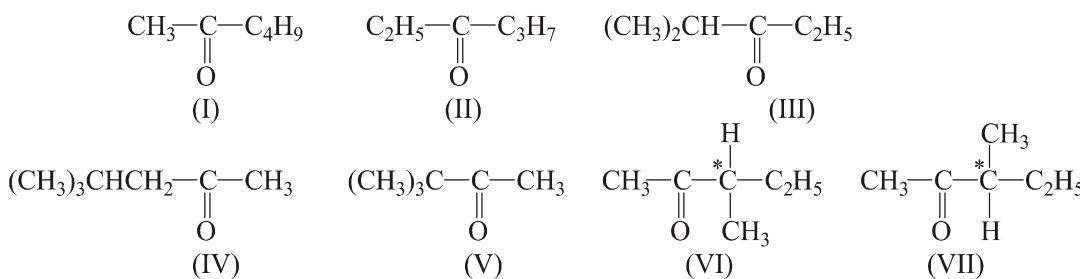
Hence, there is only **one** product.

2. The general formula of ketons is  $C_n H_{2n}O$ . The given relative molar mass is 100. Thus

$$12 + n + 2n \times 1 + 16 = 100$$

$$\text{This gives } 14n = 84 \Rightarrow n = 6$$

The ketone is  $C_6H_{12}O$ . The possible ketones are:

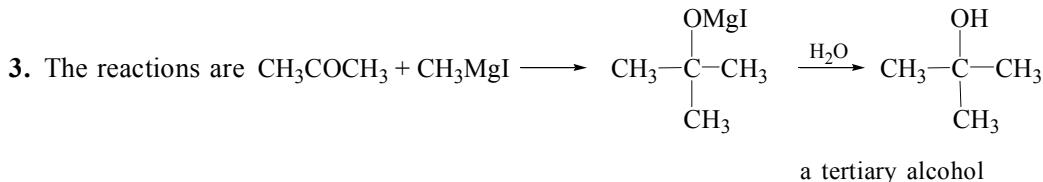


The isomers (VI) and (VII) are optically active enantiomers.

All ketones except (VI) and (VII) (which are optically active) give racemic mixture of alcohols as on reduction carbon bearing—OH group becomes chiral carbon. Thus, the number of ketones that give racemic products are **Five**.

### True/False Type

1. Benzaldehyde does not possess  $\alpha$ -hydrogen atom. It does not undergo aldol condensation but undergoes Cannizzaro reaction giving benzoic acid and benzyl alcohol.
2. Hydrazine gets protonated in highly acidic medium. Due to this, its nucleophilicity is decreased.



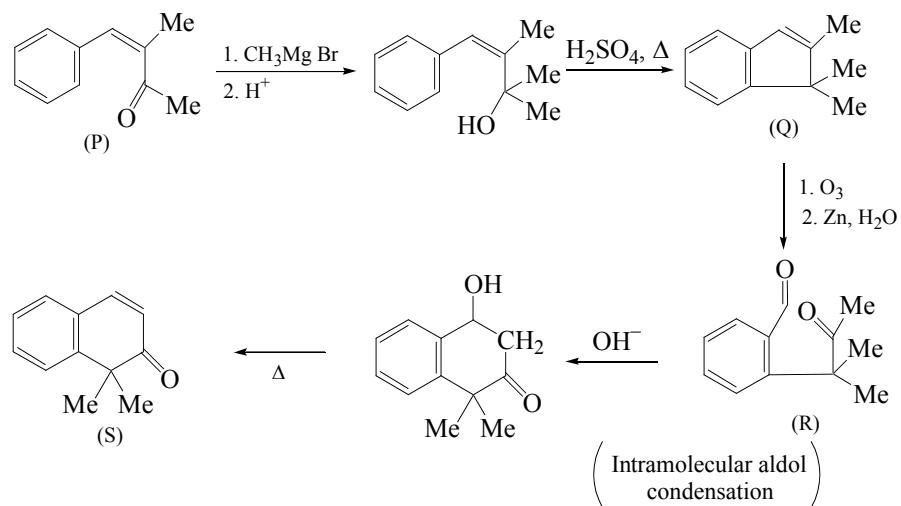
### Linked-Comprehension Type

#### Passage 1

1. The choices (c) and (d) are excluded on the basis that these compounds will not exhibit iodoform test as there exists no  $-\text{COCH}_3$  group.

Both the compounds (a) and (b) will exhibit the reactions  $P \rightarrow Q \rightarrow R$ . However, the reaction  $R \rightarrow S$  will be shown only when a methyl group is present adjoining the CO group produced in the reaction  $Q \rightarrow R$ .

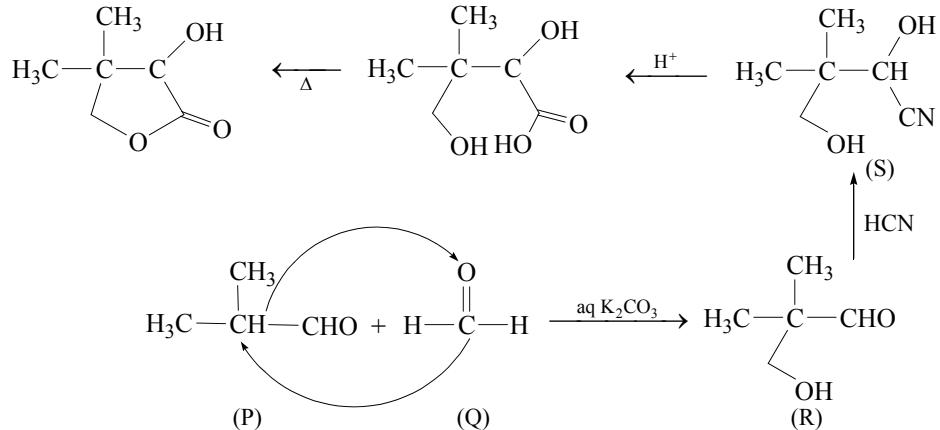
The given reactions are as follows.



2. From the reactions shown in Q.1, it follows that the choice (a) is correct.
3. From the reactions shown in Q.1, it follows that the choice (b) is correct.

### Passage 2

Writing the reactions in the reverse direction, we have



Hence, we have

1. The Choice (b) represents the compounds P and Q.
2. The Choice (a) represents the compound R.
3. The Choice (d) represents the compound S.

# CARBOXYLIC ACIDS

## Straight Objective Type

- When propionic acid is treated with aqueous sodium bicarbonate,  $\text{CO}_2$  is liberated. The C form  $\text{CO}_2$  comes from
 

(a) methyl group	(b) carboxylic acid group
(c) methylene group	(d) bicarbonate

(1999)
- Which of the following carboxylic acids undergoes decarboxylation easily?
 

(a) $\text{C}_6\text{H}_5\text{—CO—CH}_2\text{—COOH}$	(b) $\text{C}_6\text{H}_5\text{—CO—COOH}$
(c) $\text{C}_6\text{H}_5\text{—CH(OH)—COOH}$	(d) $\text{C}_6\text{H}_5\text{—CH(NH}_2\text{—COOH}$

(1995)
- In the following groups,
 

$\text{—OAc}$	$\text{—OMe}$	$\text{—OSO}_2\text{Me}$	$\text{—OSO}_2\text{CF}_3$
I	II	III	IV

 the order of leaving group ability is
 

(a) I > II > III > IV	(b) IV > III > I > II
(c) III > II > I > IV	(d) II > III > IV > I

(1997)
- Benzoyl chloride is prepared from benzoic acid by
 

(a) $\text{Cl}_2, h\nu$	(b) $\text{SO}_2\text{Cl}_2$	(c) $\text{SOCl}_2$	(d) $\text{Cl}_2, \text{H}_2\text{O}$
-------------------------	------------------------------	---------------------	---------------------------------------

(2000)
- Which of the following acids has the smallest dissociation constant?
 

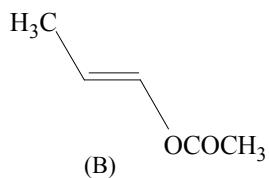
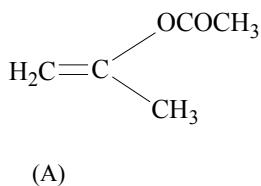
(a) $\text{CH}_3\text{CHFCOOH}$	(b) $\text{FCH}_2\text{CH}_2\text{COOH}$
(c) $\text{BrCH}_2\text{CH}_2\text{COOH}$	(d) $\text{CH}_3\text{CHBrCOOH}$

(2002)
- Identify the correct order of boiling points of the following compounds:
 

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
1	2	3

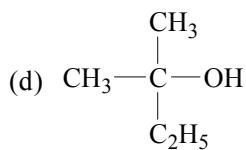
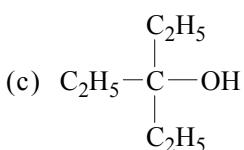
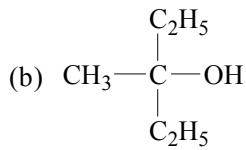
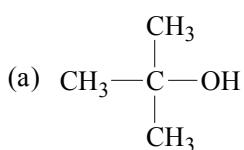
(a) 1 > 2 > 3	(b) 3 > 1 > 2
(c) 1 > 3 > 2	(d) 3 > 2 > 1

(2002)
- Given are the two organic compounds A and B:



Which of the following reagents can distinguish between the products of acid hydrolysis of the two compounds?

- |                        |                      |
|------------------------|----------------------|
| (a) Lucas reagent      | (b) 2,4-DNP          |
| (c) Fehling's solution | (d) $\text{NaHSO}_3$ |
8. Methyl acetate on treating with excess of  $\text{C}_2\text{H}_5\text{MgBr}$  produces (2003)



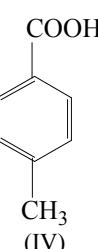
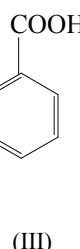
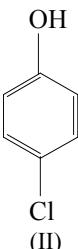
(2003)

9. The correct sequence regarding the activity of the given acid derivatives is

- |   |   |
|---|---|
| (a) $\text{RCOCl} > (\text{RCO})_2\text{O} > \text{RCON}_3$ | (b) $\text{RCOCl} > \text{RCON}_3 > (\text{RCO})_2\text{O}$ |
| (c) $\text{RCON}_3 > \text{RCOCl} > (\text{RCO})_2\text{O}$ | (d) $\text{RCON}_3 > (\text{RCO})_2\text{O} > \text{RCOCl}$ |

(2004)

10. The correct acidity order of the compounds



is

- |                               |                               |
|-------------------------------|-------------------------------|
| (a) (III) > (IV) > (II) > (I) | (b) (IV) > (III) > (I) > (II) |
| (c) (III) > (II) > (I) > (IV) | (d) (II) > (III) > (IV) > (I) |

(2009)

11. Among the following compounds, the most acidic is

- |                                   |                                   |
|-----------------------------------|-----------------------------------|
| (a) <i>p</i> -nitrophenol         | (b) <i>p</i> -hydroxybenzoic acid |
| (c) <i>o</i> -hydroxybenzoic acid | (d) <i>p</i> -toluic acid         |

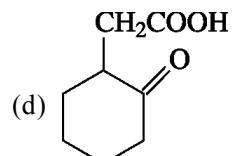
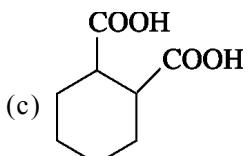
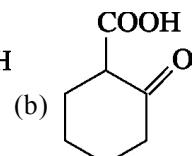
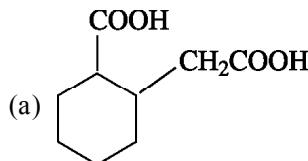
(2011)

12. The carboxylic functional group ( $-\text{COOH}$ ) is present in

- |                   |                     |
|-------------------|---------------------|
| (a) picric acid   | (b) barbituric acid |
| (c) ascorbic acid | (d) aspirin         |

(2012)

13. The compound that undergoes decarboxylation most readily under mild condition is



(2012)

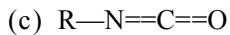
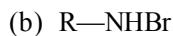
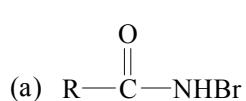
14. The compound that does not liberate  $\text{CO}_2$  on treating with aqueous sodium bicarbonate solution is

- |                     |                              |
|---------------------|------------------------------|
| (a) Benzoic acid    | (b) Benzene sulphonic acid   |
| (c) Salicyclic acid | (d) Carboxylic acid (phenol) |

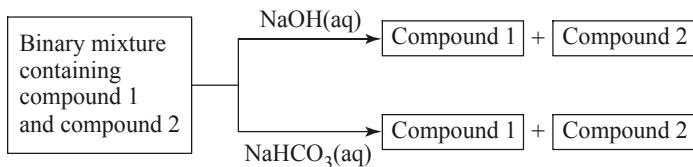
(2013)

### Multiple Correct-Choice Type

1. Reaction of  $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $\text{R}-\text{NH}_2$  as the main product. The intermediates involved in this reaction are



2. Identify the binary mixture(s) that can be separated into individual compounds by differential extraction as shown in the scheme.



- (a)  $\text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{COOH}$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{OH}$

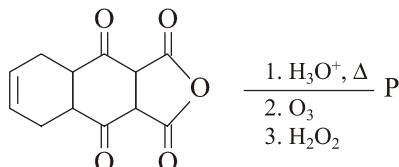
- (b)  $\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
 (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$  (2012)

### Fill-in-the-Blanks Type

1. Formic acid when heated with concentrated  $\text{H}_2\text{SO}_4$  produces \_\_\_\_\_. (1983)

### Integer Answer Type

1. The Total number of carboxylic acid groups in the product P is \_\_\_\_\_. (2013)



### True/False Type

- Formic acid like acetic acid can be halogenated in the presence of red phosphorus and  $\text{Cl}_2$ . (1983)
- Formic acid is a stronger acid than acetic acid. (1985)
- The boiling point of propanoic acid is less than that of *n*-butyl alcohol, an alcohol of comparable molar mass. (1991)
- Hydrolysis of an ester in presence of a dilute acid is known as saponification. (1983)
- Acetic acid can be halogenated in the presence of red P and  $\text{Cl}_2$  but formic acid cannot be halogenated in the same way. (1983)

### Reasoning Type

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subsection.

#### Code

- (a) If both assertion and statement are true and statement is an explanation of assertion.
- (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
- (c) If assertion is wrong and statement is correct, statement is an explanation of assertion.
- (d) If both assertion and statement are wrong and statement is not explanation of assertion.

#### Assertion (Column 1)

1. Acetate ion is more basic than the methoxide ion
2. Acetic acid does not undergo haloform reaction.
3. STATEMENT-1: *p*-Hydroxybenzoic acid has a lower boiling point than *o*-hydroxybenzoic acid.  
because

STATEMENT-2: *o*-Hydroxybenzoic acid has intramolecular hydrogen bonding.

#### Reason (Column 2)

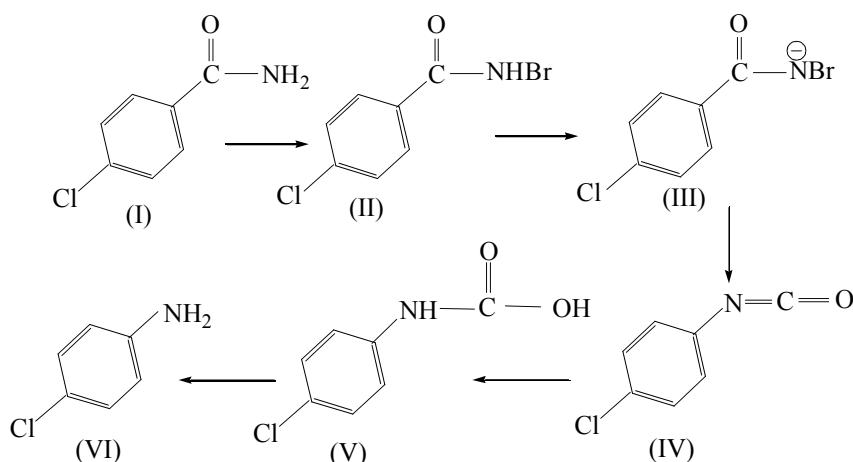
- The acetate ion is resonance stabilised (1994)
- Acetic acid has no alpha hydrogens. (1998)

- (a) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
- (b) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (c) Statement-1 is True, Statement-2 is False
- (d) Statement-1 is False, Statement-2 is True

(2007)

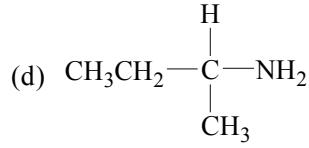
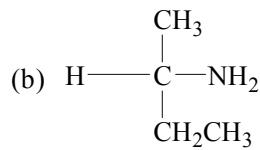
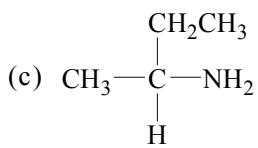
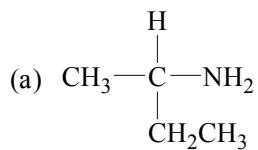
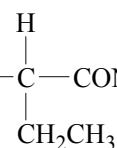
### Linked-Comprehension Type

Mechanism of Hofmann degradation of amide goes as follows.



1. The reagent used to convert I into II is
  - (a) NaBr + NaOH (b) Br<sub>2</sub> + NaOH (c) NaBr + NaHCO<sub>3</sub> (d) NBS
2. The rate determining step is conversion of
  - (a) I → II (b) II → III (c) III → IV (d) IV → V

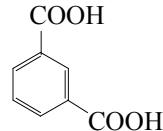
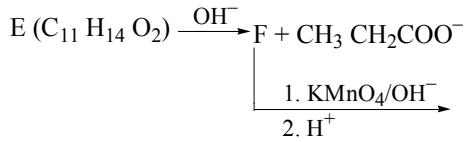
3. The Hofmann degradation of  $\text{CH}_3\text{---C}(\text{H})\text{---CONH}_2$  produces



(2006)

### Short Answer Type

1. Write down the structures of E and F.



(1997)

2. Write the structures of the products A and B.



(2000)

3. Match the following  $pK_a$  values with the corresponding acids

	$pK_a$
X is	
— OH	3.55
— CN	4.55
— Cl	4.46
— H	3.96
— OCH <sub>3</sub>	4.19

(2003)

### ANSWERS

#### Straight Objective Type

1. (d)      2. (a)      3. (b)      4. (c)      5. (c)      6. (b)

7. (c)      8. (b)      9. (b)      10. (a)      11. (c)      12. (d)  
13. (b)      14. (d)

## **Multiple Correct-Choice Type**

- 1.** (a), (c) **2.** (b), (d)

### **Fill-in-the-Blanks Type**

1. CO

## Integer Answer Type

- 1, 2

## **True/False Type**

- 1.** False                    **2.** True                    **3.** False  
**4.** False                    **5.** True

## **Reasoning Type**

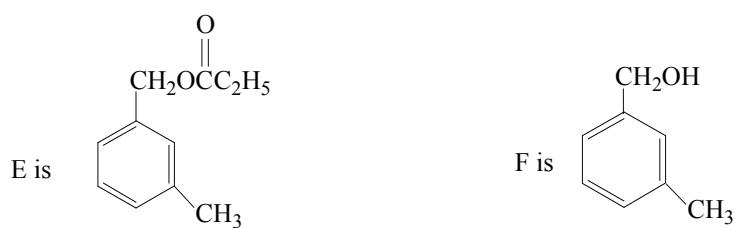
1. (d)                    2. (c)                    3. (d)

## **Linked-Comprehension Type**

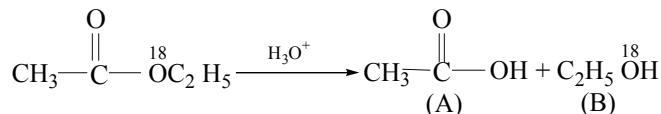
- 1. (b)**                           **2. (c)**                           **3. (a)**                           **(2006)**

## **Short Answer Type**

1.



2. The cleavage of ester occurs between oxygen and the acyl group.



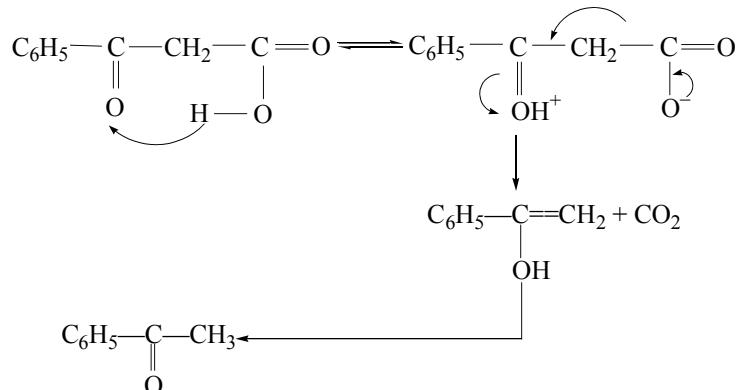
3. Electron releasing group makes the acid weaker ( $pK_a$ ) and electron attracting group makes the acid stronger ( $pK_a$ ). Hence, the correct order is

$-\text{OH}$	4.55	weakest acid
$-\text{CN}$	3.55	strongest acid
$-\text{Cl}$	3.96	
$-\text{H}$	4.19	
$-\text{OCH}_3$	4.46	

## HINTS AND SOLUTIONS

### Straight Objective Type

- $\text{CO}_2$  comes from bicarbonate.
- $\beta$ -Ketoacids are unstable acids. These readily undergo decarboxylation through a cyclic transition state.



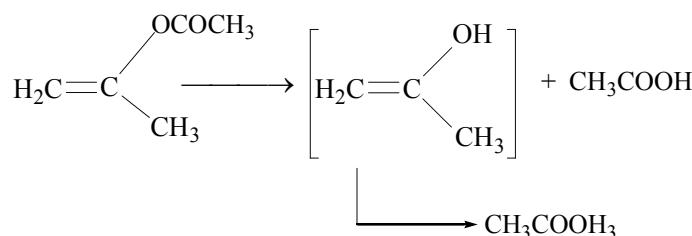
- The weaker the base, the greater its leaving-group ability. Alternatively, the stronger the conjugate acid, the greater the leaving-group ability of the base. The strength of the conjugate acid is

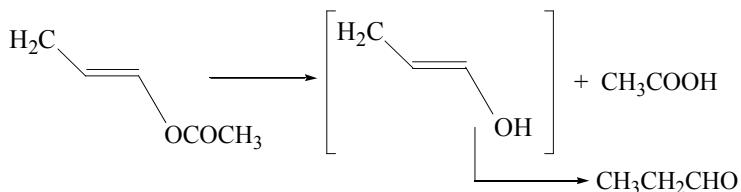


The same is the order of leaving-group ability of the base, i.e.,



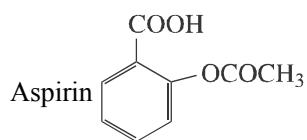
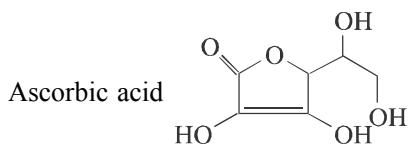
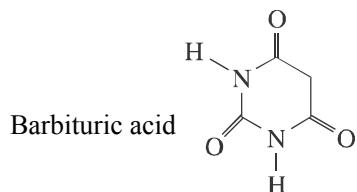
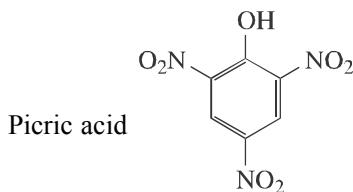
- Bromine is lesser electronegative than fluorine. Bromine attached to  $\beta$ -carbon will cause least enhancement in the dissociation of halo substituted propanoic acid.
- Carboxylic acids have relatively high boiling points because of hydrogen bonds. Their boiling points are somewhat higher than those of alcohols of comparable molar masses. Since there exists no hydrogen bonding in aldehydes, their boiling points are lower than those of corresponding alcohols.
- The products of acid hydrolysis are:



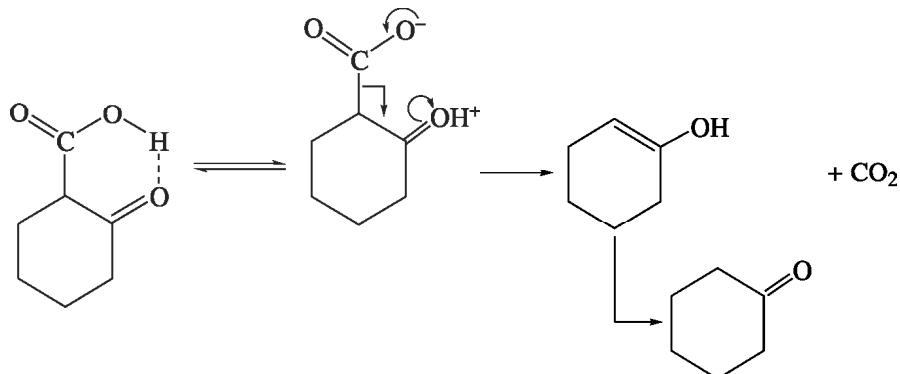


Only Fehling's solution can distinguish between aldehyde and ketone.

8. The reaction may be represented as  $\text{R}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OR}' \xrightarrow{2\text{R}''\text{Mg X}} \begin{array}{c} \text{R}'' \\ | \\ \text{R}-\overset{\text{C}}{\underset{|}{\text{OH}}} \\ | \\ \text{R}'' \end{array}$
9.  $\text{HN}_3$  is slightly more acidic than  $\text{CH}_3\text{COOH}$ .  $\text{N}_3^-$  is slightly less basic than  $\text{CH}_3\text{COO}^-$ , and is slightly better-leaving group. Thus,  $\text{RCON}_3$  is less reactive than  $\text{RCOCl}$  but a little more reactive than the anhydride  $(\text{RCO})_2\text{O}$ .
10. Carboxylic acids are stronger acids than phenols.  
Methyl group is an electron-releasing group, it weakens the acidity of carboxylic acid.  
Chlorine is electron-attracting group, it strengthens the acidity of phenol. Hence, the correct acidity order of the given compounds is (III) > (IV) > (II) > (I)
11. Because of the ortho effect, ortho isomer of hydroxybenzoic acid is the strongest acid. Phenols are weaker acids than benzoic acids.
12. The structures of the given compounds are as follows.



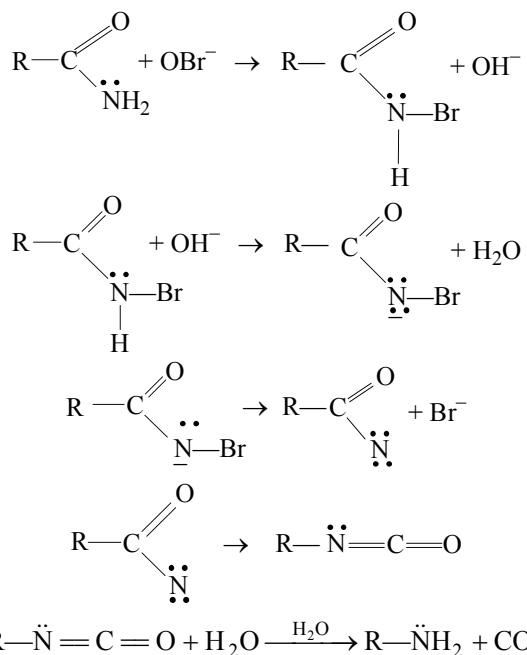
13.  $\beta$ -Ketocarboxylic acid is unstable acid. It readily undergoes decarboxylation through a cyclic transition state.



14. The compound containing —COOH group or —SO<sub>3</sub>H group react with NaHCO<sub>3</sub>, liberating CO<sub>2</sub>. Phenol does not react with NaHCO<sub>3</sub> because it is a weaker acid as compared to H<sub>2</sub>CO<sub>3</sub>.

### Multiple Correct-Choice Type

1. The mechanism is



2. We have the following facts.

$\text{C}_6\text{H}_5\text{OH}$  is soluble in  $\text{NaOH(aq)}$  and not in  $\text{NaHCO}_3(\text{aq})$ .  $\text{C}_6\text{H}_5\text{COOH}$  is soluble in both  $\text{NaOH(aq)}$  and  $\text{NaHCO}_3(\text{aq})$ .  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  is insoluble in both  $\text{NaOH(aq)}$  and  $\text{NaHCO}_3(\text{aq})$ .  $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$  is soluble in both  $\text{NaOH(aq)}$  and  $\text{NaHCO}_3(\text{aq})$ . Thus, we have

Only in the choices (b) and (d), one compound is soluble and the other one is insoluble in both  $\text{NaOH(aq)}$  and  $\text{NaHCO}_3(\text{aq})$  solutions.

In choice (a),  $\text{C}_6\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{COOH}$  are soluble in  $\text{NaOH(aq)}$  while  $\text{C}_6\text{H}_5\text{OH}$  is insoluble and  $\text{C}_6\text{H}_5\text{COOH}$  is soluble in  $\text{NaHCO}_3(\text{aq})$ .

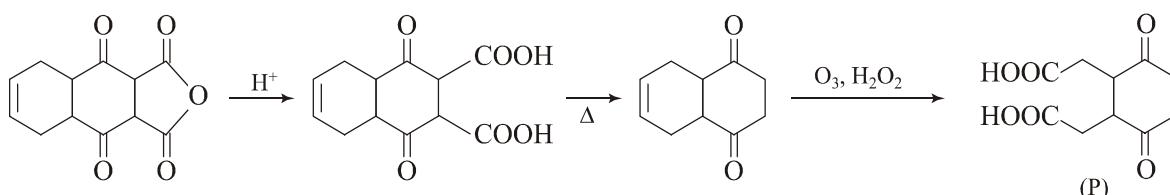
In choice (c),  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  and  $\text{C}_6\text{H}_5\text{OH}$  are insoluble in  $\text{NaHCO}_3(\text{aq})$  while  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  is insoluble and  $\text{C}_6\text{H}_5\text{OH}$  is soluble in  $\text{NaOH(aq)}$ .

Thus, only in choices (b) and (d), the two components can be separated as one is soluble while the second one is insoluble in both  $\text{NaOH(aq)}$  and  $\text{NaHCO}_3(\text{aq})$ .

### Integer Answer Type

1. The treatment with  $\text{H}_3\text{O}^+$  will cause the opening of anhydride bonds. The resultant compound contains two  $\beta$ -keto-carboxylic acids. These are easily decarboxylated by heating. The resultant compound undergoes ozonolysis followed by oxidation of  $-\text{CHO}$  groups to give  $-\text{COOH}$  groups.

The reactions are



Therefore, the total number of carboxylic acid in the compound is 2.

### True/False Type

1. Formic acid does not contain  $\alpha$ -hydrogen atom.
3. The boiling point of carboxylic acid is higher than that of alcohol of comparable molar mass because of more extensive hydrogen bonding.
4. Hydrolysis of an ester in presence of alkali is known as saponification.
5. Acetic acid has an  $\alpha$ -hydrogen atom while formic acid does not have  $\alpha$ -hydrogen atom.

### Reasoning Type

3. *p*-Hydroxybenzoic acid involves intermolecular hydrogen bonding while *o*-hydroxybenzoic acid involves intramolecular hydrogen bonding. The former involves more than one molecule linked through hydrogen bondings while the latter involves a single molecule. This results in the higher boiling point in case of *p*-hydroxybenzoic acid.

### Linked-Comprehension Type

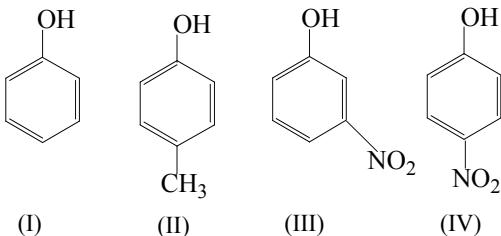
#### Passage-I

1. The reagent used is  $\text{Br}_2 + \text{NaOH}$ .
2. The rate determine step is the conversion of III into IV which involves the migration of R group.
3. The migration of alkyl group to nitrogen occurs with the retention of its configuration.

# **PHENOLS**

29

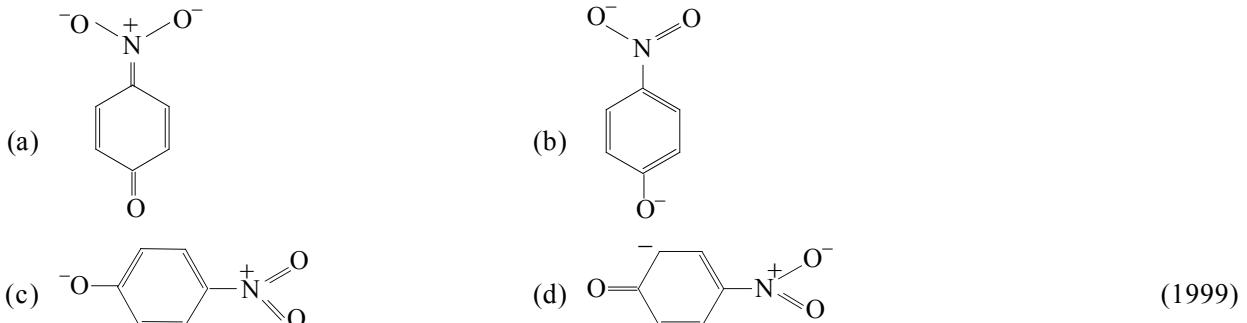
## **Straight Objective Type**



the order of acidity is

- (a) III > IV > I > II (b) I > IV > III > II (c) II > I > III > IV (d) IV > III > I > II      (1996)

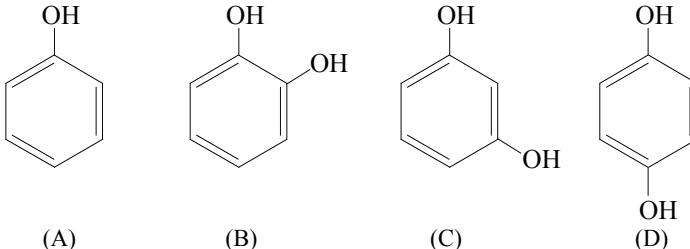
4. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is



5. In the reaction  the product A is

6. Benzene sulphonic acid and 2,4-dinitrophenol on reaction with sodium bicarbonate respectively liberate  
 (a)  $\text{SO}_2$ ,  $\text{NO}_2$       (b)  $\text{SO}_2$ ,  $\text{CO}_2$       (c)  $\text{CO}_2$ ,  $\text{NO}_2$       (d)  $\text{CO}_2$ ,  $\text{CO}_2$       (2006)  
 7. The increasing order of the boiling points of the compounds

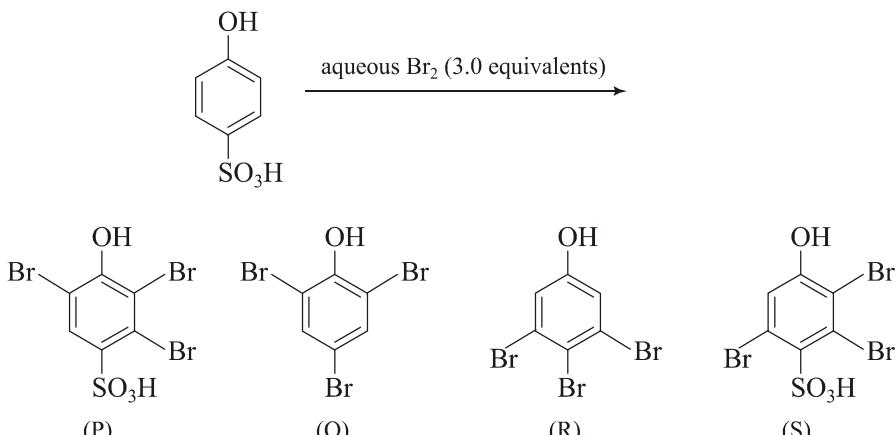
7. The increasing order of the boiling points of the compounds



is

- (a) A < B < C < D    (b) A < B < D < C    (c) D < C < B < A    (d) D < A < B < C

8. The major product(s) of the following reaction is (are).



(a) (F)

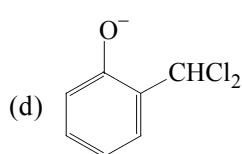
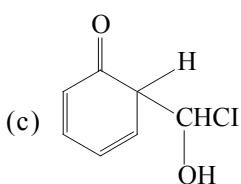
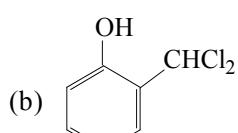
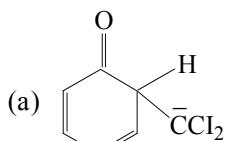
(b) O

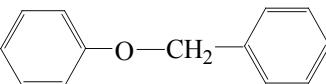
(c) R

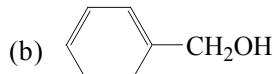
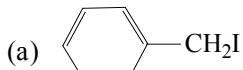
(d) S

(2013)

## **Multiple Correct-Choice Type**

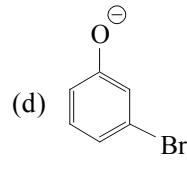
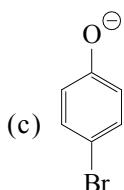
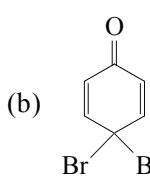
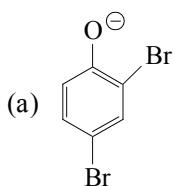


3. The ether  when treated with HI produces



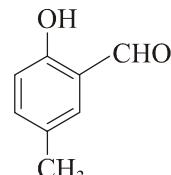
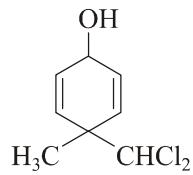
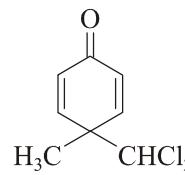
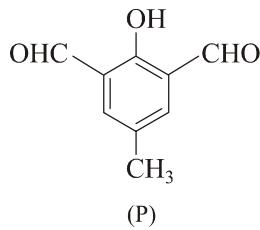
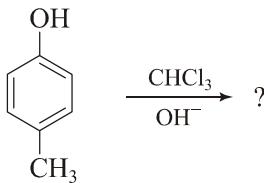
(1991)

4. In the reaction   $\xrightarrow{\text{NaOH(aq)}/\text{Br}_2}$  the intermediate(s) is(are)



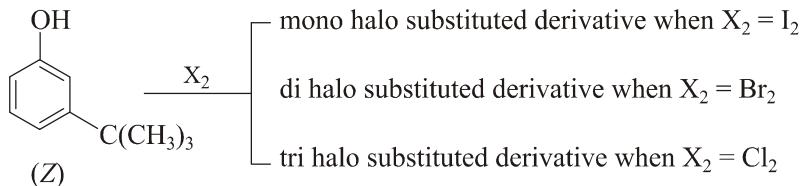
(2010)

5. In the following reaction, the product(s) formed is (are)



(a) (P) major      (b) (Q) minor      (c) R (minor)      (d) S (major)      (2013)

6. The reactivity of compound Z with different halogens under appropriate conditions is given below.



The observed pattern of electrophilic substitution can be explained by

- |   |  |
|---|--|
| (a) the steric effect of the halogen            | (b) the steric effect of the <i>tert</i> -butyl group      |
| (c) the electronic effect of the phenolic group | (d) the electronic effect of the <i>tert</i> -butyl group. |

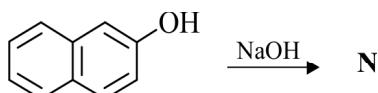
(2014)

**Fill-in-the-Blanks Type**

- The acidity of phenol is due to the \_\_\_\_\_ of its anion. (1984)
- Formation of phenol from chlorobenzene is an example of \_\_\_\_\_ aromatic substitution. (1989)
- Phenol is acidic because of resonance stabilisation of its conjugate base, namely \_\_\_\_\_. (1990)
- Among the three isomers of nitrophenol, the one that is least soluble in water is \_\_\_\_\_. (1992)

**Integer Answer Type**

- The number of resonance structures for N is



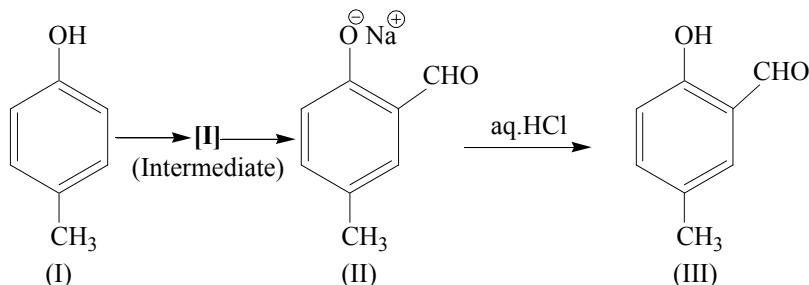
(2015)

**True/False Type**

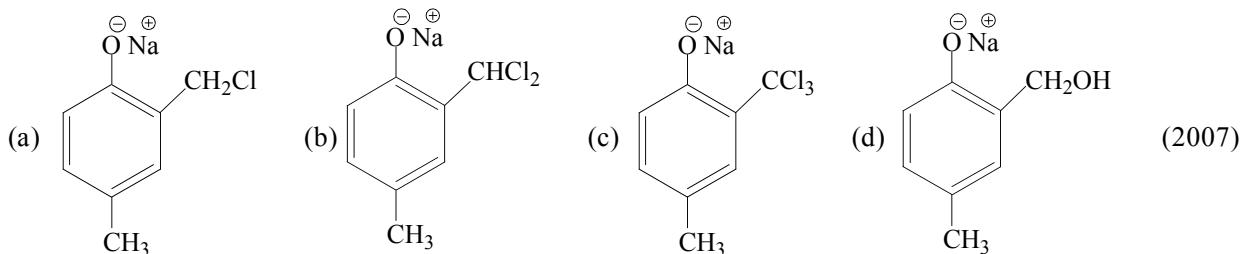
- o*-Nitrophenol is steam volatile whereas *p*-nitrophenol is not. (1995)

**Linked-Comprehension Type**

Riemer-Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, *ortho* to the hydroxyl group. The reaction involves electrophilic aromatic substitution. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



- Which one of the following reagents is used in the above reaction?
  - (a) aq. NaOH + CH<sub>3</sub>Cl
  - (b) aq. NaOH + CH<sub>2</sub>Cl<sub>2</sub>
  - (c) aq. NaOH + CHCl<sub>3</sub>
  - (d) aq. NaOH + CCl<sub>4</sub>
- The electrophile in this reaction is
  - (a) :CHCl
  - (b) <sup>+</sup>CHCl<sub>2</sub>
  - (c) :CCl<sub>2</sub>
  - (d) :CCl<sub>3</sub>
- The structure of the intermediate I is
  - (a)
  - (b)
  - (c)
  - (d)



## Reasoning Type

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subsection.

### Code

- (a) If both assertion and statement are true and statement is an explanation of assertion.
- (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
- (c) If assertion is wrong and statement is correct, statement is an explanation of assertion
- (d) If both assertion and statement are wrong and statement is not explanation of assertion.

### Assertion

1. *p*-Nitrophenol is a stronger acid than *o*-nitrophenol.
2. Phenol is more reactive than benzene towards electrophilic substitution reaction.

### Statement

- Intramolecular hydrogen bonding make the *o*-isomer weaker than the *p*-isomer. (1989)
- In the case of phenol, the intermediate carbocation is more resonance stabilised. (2000)

## Short Answer Type

1. Write tautomeric forms for phenol. (1992)

## ANSWERS

## Straight Objective Type

- |        |        |        |        |        |
|--------|--------|--------|--------|--------|
| 1. (d) | 2. (b) | 3. (d) | 4. (c) | 5. (b) |
| 6. (d) | 7. (a) | 8. (b) |        |        |

## Multiple Correct-choice Type

- |             |                  |             |             |
|-------------|------------------|-------------|-------------|
| 1. (a), (c) | 2. (a), (d)      | 3. (a), (d) | 4. (a), (c) |
| 5. (b), (d) | 6. (a), (b), (c) |             |             |

## Fill-in-the-Blanks Type

- |                            |                          |
|----------------------------|--------------------------|
| 1. resonance stabilization | 2. nucleophilic          |
| 3. phenoxide ion           | 4. <i>o</i> -nitrophenol |

## Integer Answer Type

1. 9

## True/False Type

1. True

## Linked-Comprehension Type

1. (c)
2. (c)
3. (b)

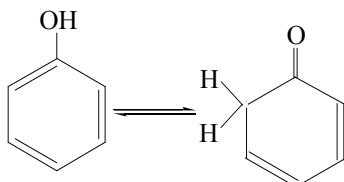
**Reasoning Type**

1. (a)

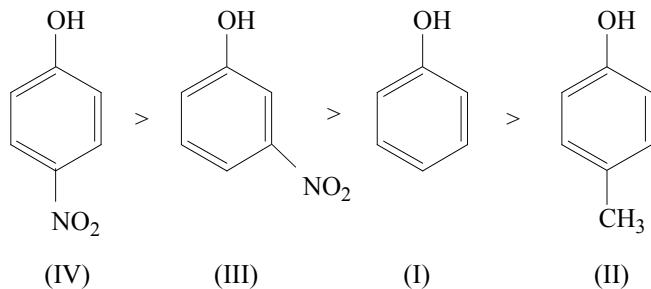
2. (c)

**Short Answer Type**

1. The tautomeric forms of phenol are

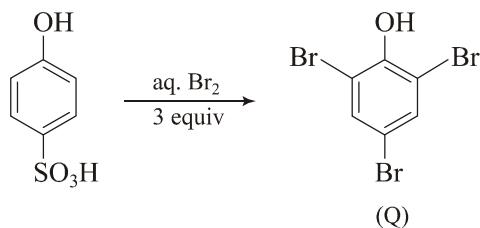
**HINTS AND SOLUTIONS****Straight Objective Type**

- The product formed is 2,4,6-tribromophenol.
- In less polar solvent, phenol reacts with bromine to give a mixture of *o*- and *p*-bromophenol.
- An electron-attracting substituent tends to disperse the negative charge of the phenoxide ion and thus, makes it more stable. This, in turn, increases the acid strength of phenol. The substituent in *para* position is more effective than in the *meta* position as the former involves a resonating structure bearing negative charge on the carbon attached to the electron-withdrawing substituent.  
An electron-releasing substituent tends to increase the negative charge of the phenoxide ion and thus makes it more unstable. This, in turn, decreases the acid strength of phenol. Hence, the order of acid strength is



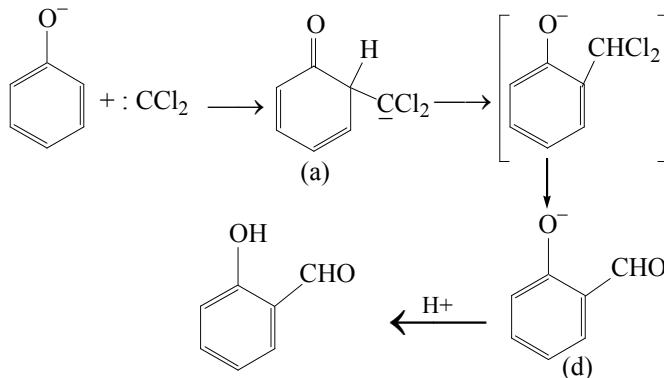
- The structure  $\text{^-\ddot{O}-C}_6\text{H}_4-\text{N}^+=\text{O}$  is most unlikely as N containing 5 valence electrons should not carry positive charge.
- Phenoxy ion is less reactive than alkoxide ion.
- Both benzene sulphonic acid and 2,4-dinitrophenol are stronger acid than carbonic acid. Both liberate  $\text{CO}_2$  on reaction with sodium bicarbonate.
- Phenol will have the lowest boiling point as it contains a single hydroxyl group. Of the dihydroxyl compounds, the *para* isomer will have maximum boiling point due to the more involved hydrogen bondings. The *ortho* isomer is expected to have lower boiling point than the *meta* isomer as former is expected to have lesser involved hydrogen bondings.

8. The reaction is



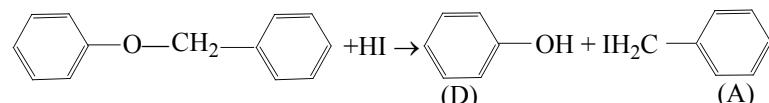
## **Multiple Correct-Choice Type**

1. Carboxylic acid is more acidic than phenol. Electron-attracting group also increases the acidity of phenol, thus, phenol is less acidic than acetic acid and *p*-nitrophenol.
  2. The mechanism of the reaction is

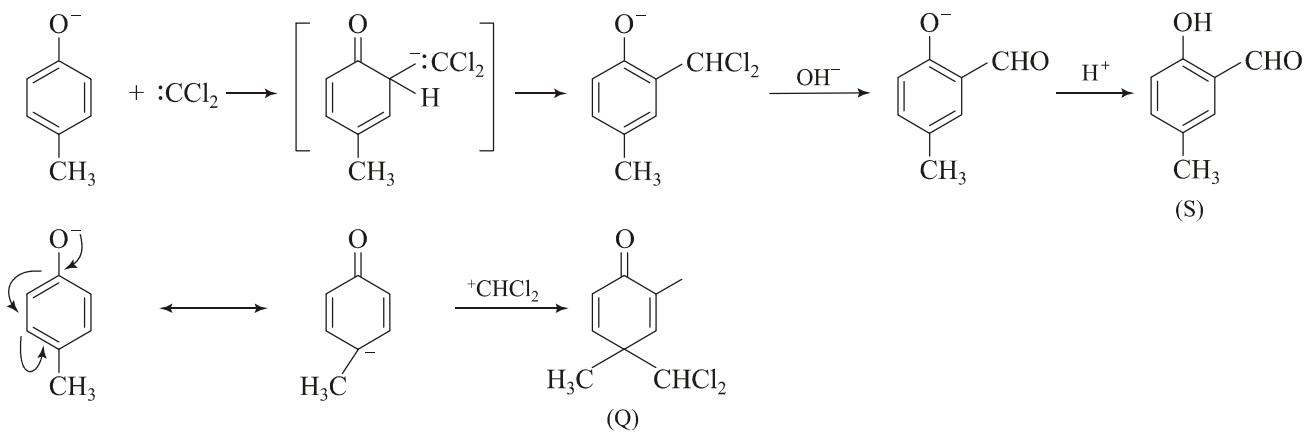


Thus, the species (a) and (d) are involved as the intermediates.

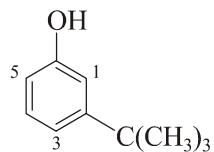
3. The aromatic ethers are cleaved to give phenol as one of the products.



4. The intermediates are given by the Choices (a) and (c). The final product is 2,4,6 tribromophenoxyde ion.  
 5. The reaction is known as Reimer – Tiemann reaction. It proceeds as follows.



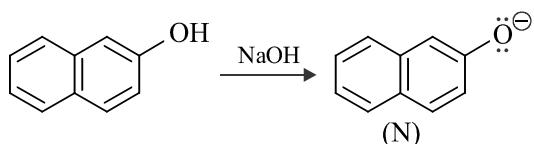
6. Halogen can be introduced at the positions 1, 3 and 5 as shown in the figure. This is due to *ortho*- and *para*-directing phenolic group



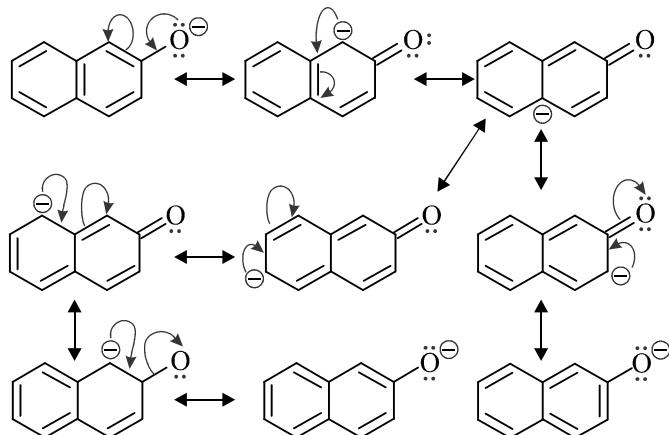
Because of steric effect of iodine and  $\text{—C}(\text{CH}_3)_3$ , the former can be inserted in position 5 only. Bromine, being less bulky, can be inserted at 3 and 5 positions. Chlorine can be inserted in all the three positions.

### Integer Answer Type

1. The reaction is



The resonating structures of N are follows:



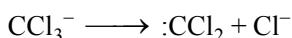
There are 9 resonating structures.

### True/False Type

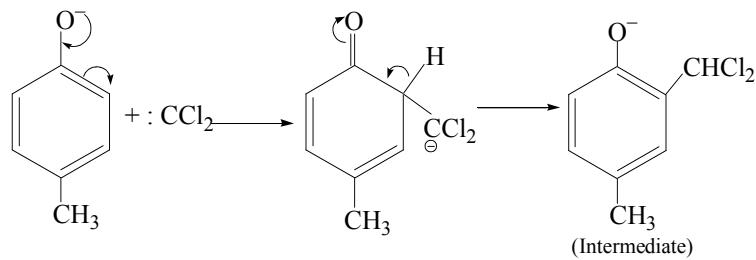
1. *o*-Nitrophenol involves intramolecular hydrogen bond whereas *p*-nitrophenol involves intermolecular hydrogen bond. Consequently, the former exists as single molecule whereas the latter exists as multimolecular form.

### Linked-Comprehension Type

1. The reagent used in the given Reimer-Tiemann reaction is aq.  $\text{NaOH} + \text{CHCl}_3$ .
2. The electrophile in the given reaction is  $\text{:CCl}_2$  generated from  $\text{CHCl}_3$  by aq.  $\text{NaOH}$ .



3. The reaction proceeds as follows.



### Reasoning Type

2. In the substitution reaction of phenol, The intermediates are hardly carbocation but rather oxonium ions.

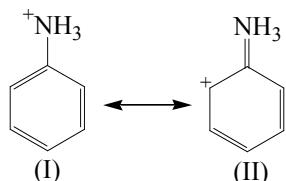


# AMINES

30

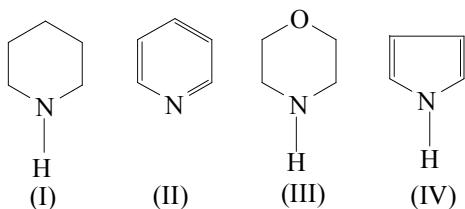
## **Straight Objective Type**

- The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is  
 (a) methylamine    (b) ethylamine    (c) diethylamine    (d) triethylamine    (1981)
  - Acetamide is treated separately with the following reagents. Which one of these would give methylamine?  
 (a)  $\text{PCl}_5$     (b) sodalime    (c)  $\text{NaOH} + \text{Br}_2$     (d) hot concentrated  $\text{H}_2\text{SO}_4$     (1983)
  - Carbylamine test is performed in alcoholic KOH by heating a mixture of  
 (a) chloroform and silver powder  
 (b) trihalogenated methane and a primary amine  
 (c) an alkyl halide and a primary amine  
 (d) an alkyl cyanide and a primary amine    (1984)
  - Chlorobenzene can be prepared by reacting aniline with  
 (a) hydrochloric acid  
 (b) cuprous chloride  
 (c) chlorine in the presence of anhydrous aluminium chloride  
 (d) nitrous acid followed by heating with cuprous chloride    (1984)
  - Amongst the following, the most basic compound is  
 (a) benzylamine    (b) aniline    (c) acetanilide    (d) *p*-nitroaniline    (1990)
  - Examine the following two structures for the anilinium ion and chose the correct statement from the ones given below.



- (a) II is not acceptable canonical structure because carbonium ions are less stable than ammonium ions
  - (b) II is not an acceptable canonical structure because it is nonaromatic
  - (c) II is not an acceptable canonical structure because nitrogen has 10 valence electrons
  - (d) II is an acceptable canonical structure

7. In the following compounds



the order of basicity is

- (a) IV > I > III > II (b) III > I > IV > II (c) II > I > III > IV (d) I > III > II > IV (1997)
8. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives

- (a) diphenyl ether (b) *p*-hydroxyazobenzene  
(c) chlorobenzene (d) benzene (1998)

9. A positive carbylamine test is given by

- (a) *N,N*-dimethylaniline (b) 2, 4-dimethylaniline  
(c) *N*-methyl-*o*-methylaniline (d) *p*-methylbenzylamine (1999)

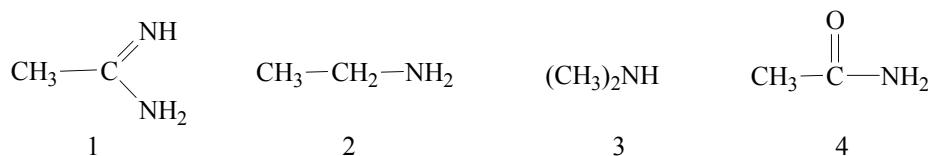
10. Among the following, the strongest base is

- (a) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> (b) *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>  
(c) *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (d) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub> (2000)

11. *p*-Chloroaniline and anilinium hydrochloride can be distinguished by

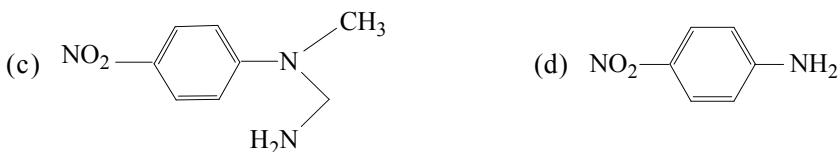
- (a) Sandmeyer reaction (b) NaHCO<sub>3</sub>  
(c) AgNO<sub>3</sub> (d) Carbylamine test (1998)

12. The correct order of basicities of the following compounds is



- (a) 2 > 1 > 3 > 4 (b) 1 > 3 > 2 > 4 (c) 3 > 1 > 2 > 4 (d) 1 > 2 > 3 > 4 (2001)

13. In the reaction F——NO<sub>2</sub>  $\xrightarrow[\text{DMF, } \Delta]{(\text{CH}_3)_2\text{NH}}$  A  $\xrightarrow[\text{(ii) H}_2/\text{Ni}]{\substack{\text{(i) NaNO}_2/\text{HCl} \\ 0^\circ\text{C} - 5^\circ\text{C}}}$  B the product B is

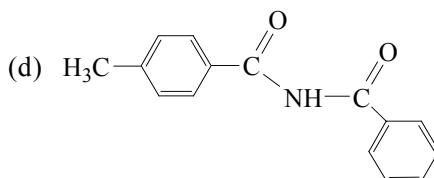
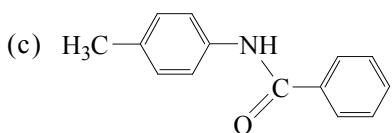
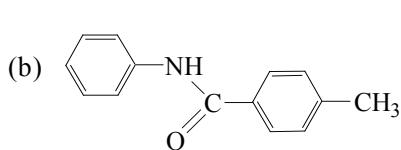
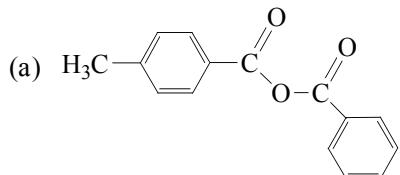


14. In the reaction RNH<sub>2</sub> + CHCl<sub>3</sub> + KOH  $\rightarrow$  A + 3KCl + H<sub>2</sub>O the compound A is

- (a) R—CN (b) R— $\overset{\ominus}{\underset{\oplus}{\text{N}\equiv\text{C}}}$   
(c) R— $\overset{\oplus}{\underset{\ominus}{\text{N}\equiv\text{C}}}$  (d) R—NHCl (2006)

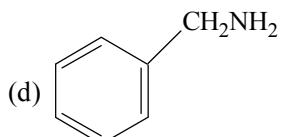
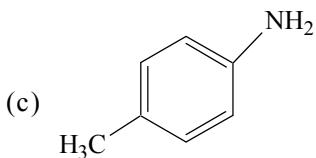
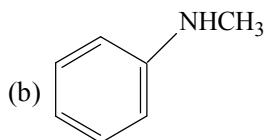
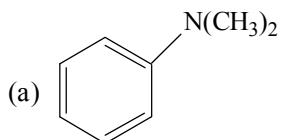
15. In the reaction  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{C}(=\text{O})\text{NH}_2 \xrightarrow{(1) \text{NaOH/Br}_2} \text{O} \xrightarrow{(2)} \text{T}$

the structure of the product  $\mathbf{T}$  is



(2010)

16. Among the following compounds, the one that would form brilliant coloured dye on treatment with  $\text{NaNO}_2$  in dilute HCl followed by addition of an alkaline solution of  $\beta$ -naphthol is

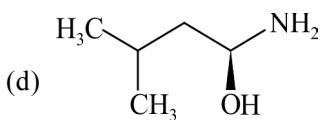
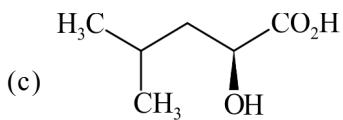
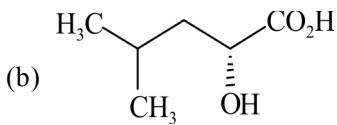
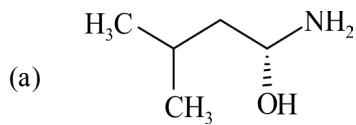
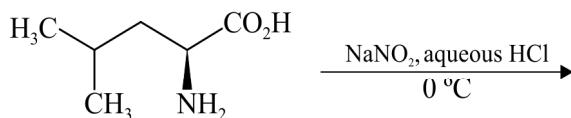


(2011)

17. For the identification of  $\beta$ -naphthol using dye test, it is necessary to use

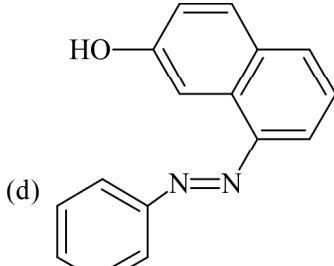
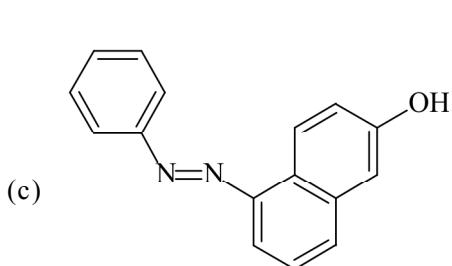
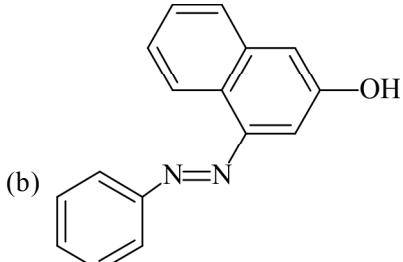
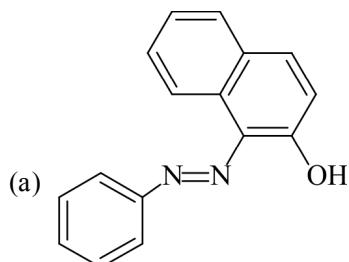
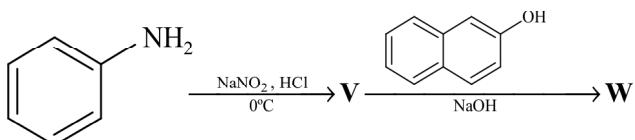
- (a) dichloromethane solution of  $\beta$ -naphthol      (b) acidic solution of  $\beta$ -naphthol  
(c) neutral solution of  $\beta$ -naphthol      (d) alkaline solution of  $\beta$ -naphthol

**18.** The major product of the reaction is



(2015)

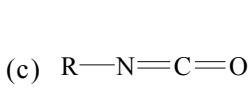
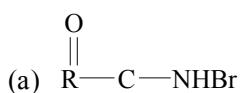
19. In the following reactions, the major product **W** is



(2015)

### Multiple Correct-Choice Type

1. Reaction of  $\text{RCONH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $\text{RNH}_2$  as the main product. The intermediates involved in the reaction are



(1993)

2. Among the following compounds, which will react with acetone to give a product containing  $\text{---C}=\text{N---}$  ?



### Fill-in-the-Blanks Type

1. The main product obtained in the reaction of chloroform with aniline in the presence of excess of alkali is \_\_\_\_\_.

(1981)

### Integer Answer Type

1. The total number of lone pairs in melamine is \_\_\_\_\_.

(2013)

## Reasoning Type

In each subquestion below an assertion in the left hand column and a statement in the right hand column are given. Select one of the correct codes from the following categories for each subsection.

### Code

- (a) If both assertion and statement are true and statement is an explanation of assertion.
- (b) If assertion is correct and statement is wrong and statement is not an explanation of assertion.
- (c) If assertion is wrong and statement is correct, statement is an explanation of assertion
- (d) If both assertion and statement are wrong and statement is not explanation of assertion.

### Assertion (column 1)

1. In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

### Reason (column 2)

The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance. (2001)

2. STATEMENT-1: Aniline on reaction with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol gives a dark blue coloured precipitate.

and

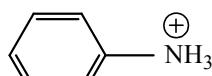
STATEMENT-2: The colour of the compound formed in the reaction of aniline with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  followed by coupling with  $\beta$ -naphthol is due to the extended conjugation.

- (a) STATEMENT-1 is True, STATEMENT-2 is true; STATEMENT-2 is correct explanation for STATEMENT-1
- (b) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT correct explanation for Statement-1
- (c) STATEMENT-1 is True, STATEMENT-2 is False
- (d) STATEMENT-1 is False, STATEMENT-2 is True

(2008)

## Short Answer Type

1. Cyclohexylamine is a stronger base than aniline (1982)
2. Dimethylamine is a stronger base than trimethylamine (1998)

3. Which one is more acidic? Explain  ; F (2004)

4. Write the structure of the foul-smelling compound obtained when aniline is treated with chloroform in the presence of KOH. (1982)

## ANSWERS

### Straight Objective Type

- |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|
| 1. (c)  | 2. (c)  | 3. (b)  | 4. (d)  | 5. (a)  | 6. (c)  | 7. (d)  |
| 8. (b)  | 9. (d)  | 10. (d) | 11. (c) | 12. (b) | 13. (a) | 14. (c) |
| 15. (c) | 16. (c) | 17. (d) | 18. (c) | 19. (a) |         |         |

### Multiple Correct-Choice Type

1. (a), (c)
2. (a), (d)

**Fill-in-the-Blanks Type**

1. benzeneisonitrile

**Integer Answer Type**

1. 6

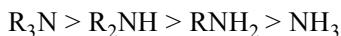
**Reasoning Type**

1. (d)                    2. (d)

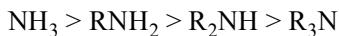
**Short Answer Type**

2. Two factors operate in deciding the basicity of alkylamines.

(i) *Inductive Effect* The alkyl group being electron releasing increases the charge density on nitrogen. This in turn increases the basicity of amines. The expected order of basicity is



(ii) *Solvantion Effect* Because of the positive charge carried by the conjugate acid of an amine, it is stabilised by the hydrogen bonding with the solvent water. The larger the number of hydrogens attached to the nitrogen in the conjugate acid, the larger its stability and thus larger is the basicity of the corresponding base. The expected order of basicity of the alkylamine will be



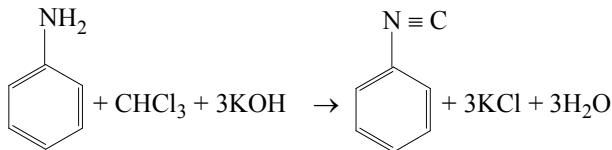
The inductive and solvent effects predict the opposite trend in the basicity of alkylamines. In going from  $\text{R}_2\text{NH}$  to  $\text{R}_3\text{N}$ , the solvation effect plays a more dominating role as compared to the inductive effect making  $\text{R}_2\text{NH}$  more basic than  $\text{R}_3\text{N}$ .

A simple explanation is that the steric factor in  $\text{R}_3\text{N}$  makes the availability of a lone pair of electrons on nitrogen poor than in the dialkylamine, predicting  $\text{R}_3\text{NH}$  a stronger base than  $\text{R}_3\text{N}$ .

3. Due to the electron withdrawal nature of fluorine, the negative charge on nitrogen atom in *p*-fluoroanilinium ion is less than that in anilinium ion. This facilitates the removal of  $\text{H}^+$  more easily in *p*-fluoroanilinium ion as compared to that in anilinium ion. Hence, *p*-fluoroanilinium ion is more acidic than anilinium ion.

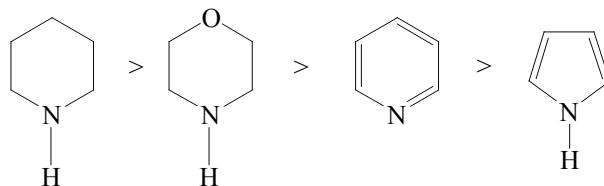
4. Ph—NC

The reaction is

**HINTS AND SOLUTIONS****Straight Objective Type**

- Secondary amines produce nitrosoamines with aqueous nitrous acid at low temperature.
- $\text{CH}_3\text{CONH}_2 \xrightarrow{\text{NaOH} + \text{Br}_2} \text{CH}_3\text{NH}_2$
- Carbylamine test is performed in alcoholic KOH by heating a mixture of trihalogenated methane (say,  $\text{CHCl}_3$ ) and a primary amine.
- Chlorobenzene can be prepared by reacting aniline with nitrous acid followed by heating with cuprous chloride.
- Alkyl amine (benzyl amine,  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ) is the most basic compound.

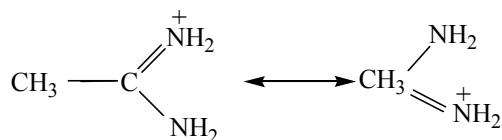
7. The order of basicity is



Pyrrole is a very weak base because the lone pair of electrons is involved in  $\pi$ -electron delocalisation and is not available for the protonation. Pyridine is less basic than alkyl amines as the N in pyridine is  $sp^2$  hybridised and its lone pair is more tightly held.

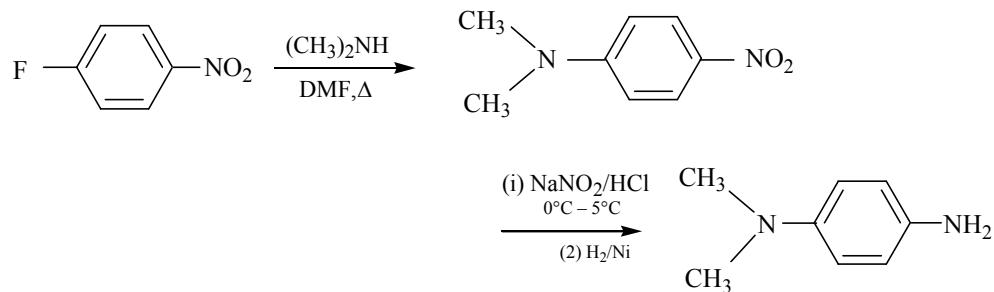
8. Benzenediazonium chloride on reacting with phenol produces *p*-hydroxyazobenzene.  
 9. *p*-Methylbenzylamine (a primary amine) shows carbylamine test.  
 10. Aliphatic amine ( $C_6H_5CH_2NH_2$ ) is the strongest base. Aliphatic amines are stronger bases than aromatic amines.  
 11. Anilinium hydrochloride will give white precipitates of  $AgCl$  with  $AgNO_3$ .

12.  $\text{CH}_3-\text{C}(\text{NH}_2)=\text{NH}_2$  is most basic as its protonation leads to resonating cation with a large delocalization energy.



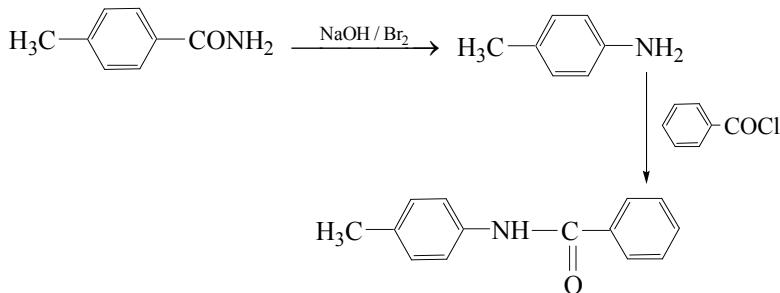
$2^\circ$  amine is more basic than  $1^\circ$  amine.

13. The reactions are

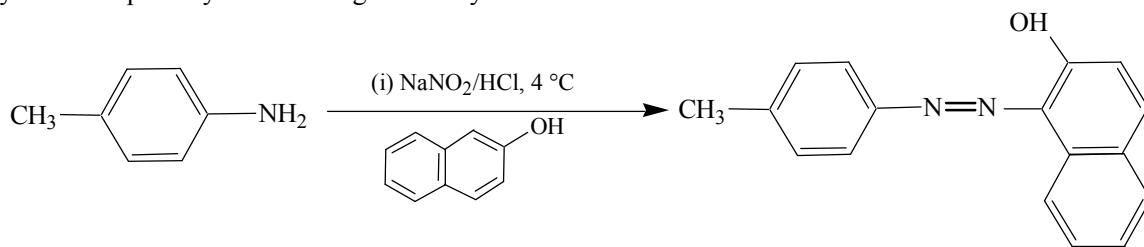


14. The compound A is alkyl isonitrile ( $R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}:)$

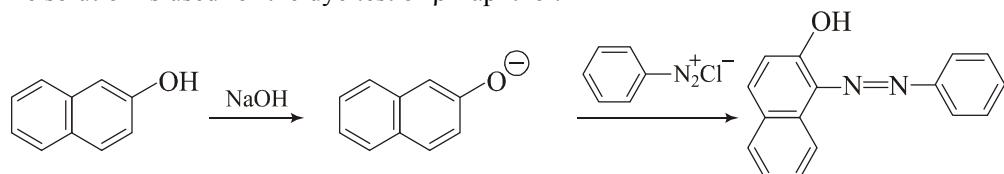
15. The reactions are



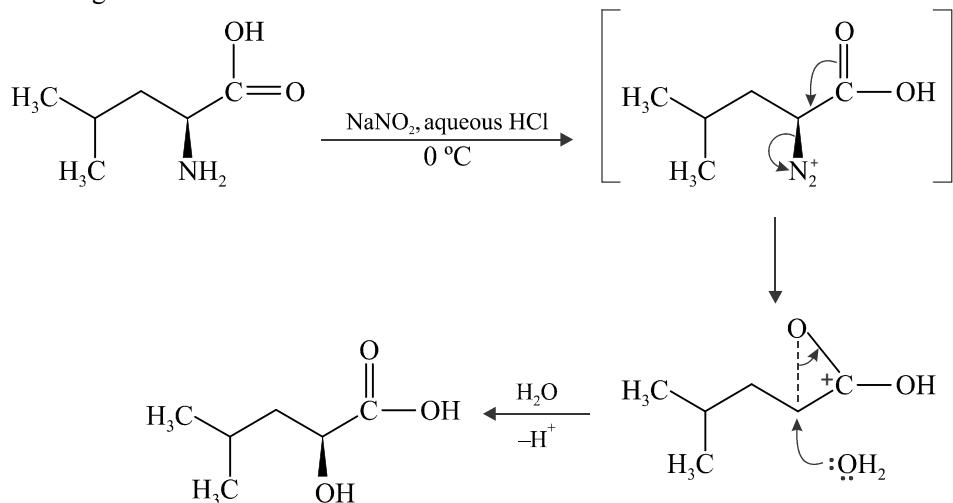
16. Only aromatic primary amine will give azo dye test.



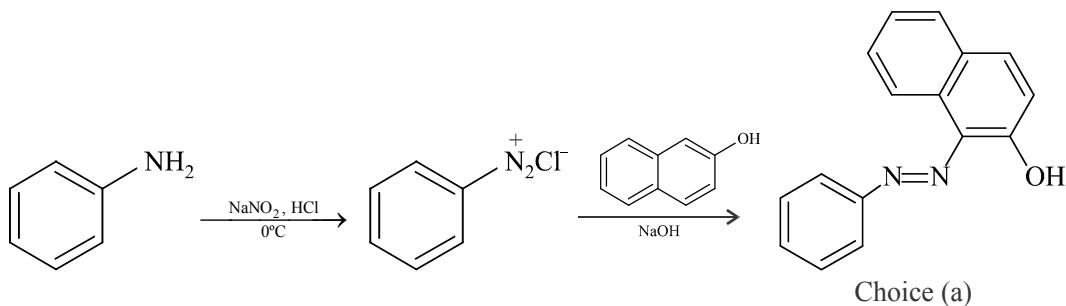
17. An alkaline solution is used for the dye test of  $\beta$ -naphthol.



18. The reaction involves neighbouring group participation in the  $S_N2$  substitution of  $-\text{NH}_2$  by  $-\text{OH}$ . The reaction proceeds through a new reaction intermediate by a substituent that bonds to the reaction centre involving intramolecular nucleophilic attack followed by intermolecular substitution. This results into the retention of configuration.

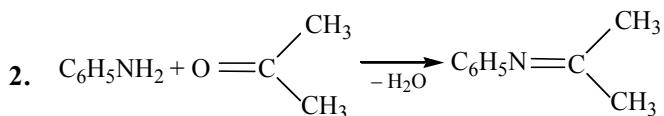


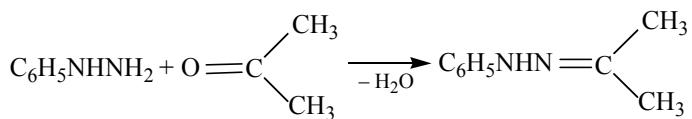
19. The reaction is



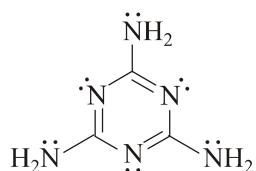
### Multiple Correct-Choice Type

1. The intermediates involved in the reaction are  $\text{RCONHBr}$  and  $\text{R}-\text{N}=\text{C}=\text{O}$ .



**Integer Answer Type**

1. The structure of melamine is



There are **six pairs** of lone pairs of electrons.

**Reasoning Type**

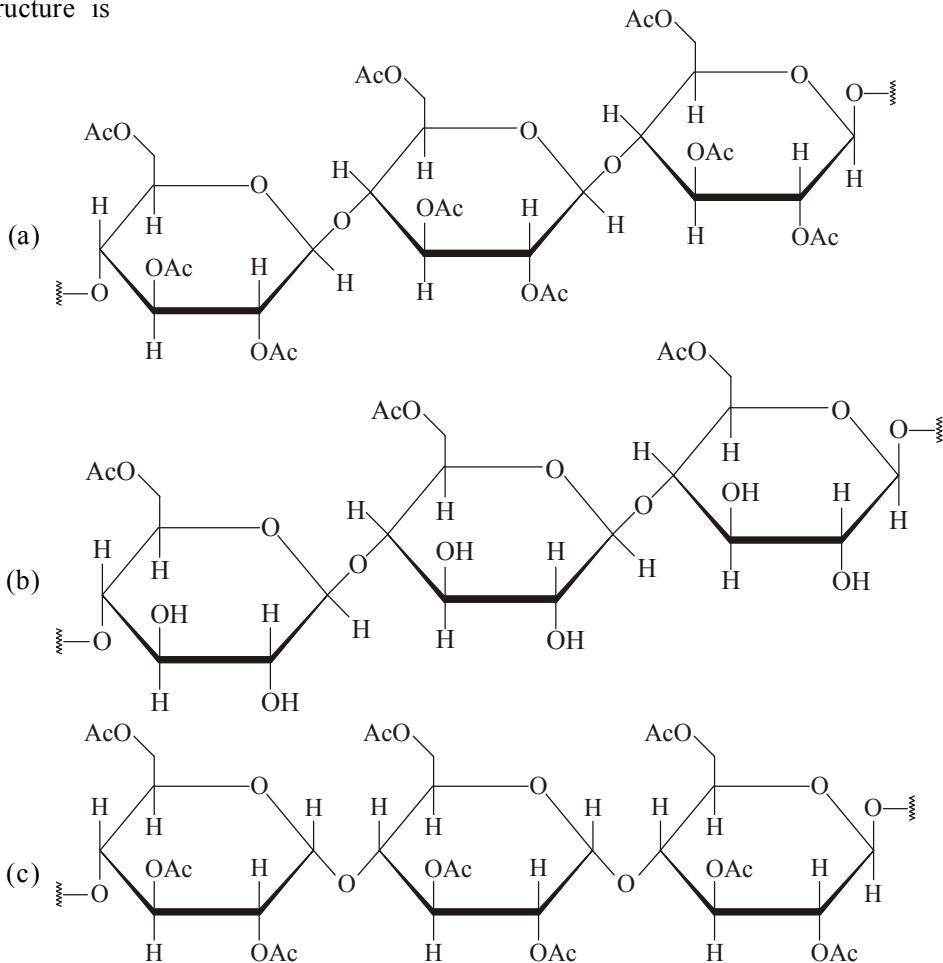
- Because of the protonation of  $-\text{NH}_2$  group, the resultant  $-\text{NH}_3^+$  becomes *meta* director.
- Statement-1 is false since red-coloured dye is formed. Statement-2 is true because the colour is due to extended conjugation.

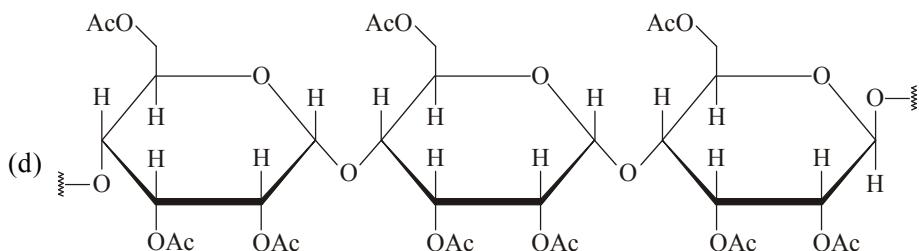
# CARBOHYDRATES

31

## Straight Objective Type

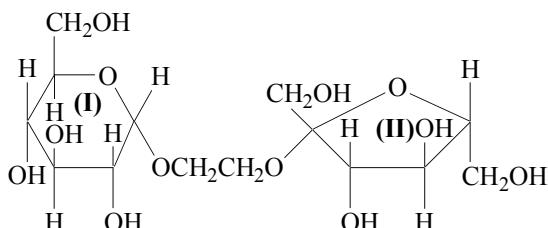
1. The pair of compounds showing positive Tollens reagent test is
  - (a) glucose and sucrose
  - (b) fructose and sucrose
  - (c) glucose and fructose
  - (d) acetophenone and pentanal(2004)
2. Two forms of D-glucopyranose are frequently called
  - (a) enantiomers
  - (b) anomers
  - (c) diastereomers
  - (d) stereoisomers(2005)
3. Cellulose upon acetylation with excess acetic anhydride /  $H_2SO_4$  (catalytic) gives cellulose triacetate whose structure is





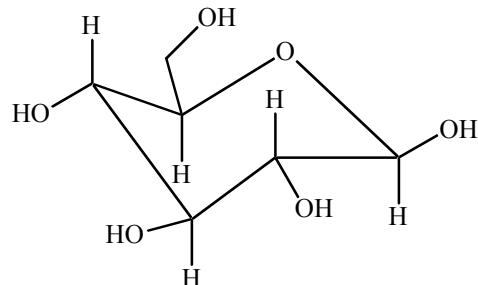
(2008)

4. The correct statement about the following disaccharide is



- (a) Ring (I) is pyranose with  $\alpha$ -glycosidic link
- (b) Ring (I) is furanose with  $\alpha$ -glycosidic link
- (c) Ring (II) is furanose with  $\alpha$ -glycosidic link
- (d) Ring (II) is pyranose with  $\beta$ -glycosidic link

5. The carbohydrate

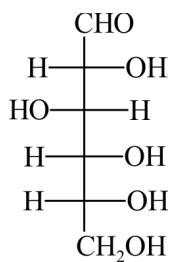


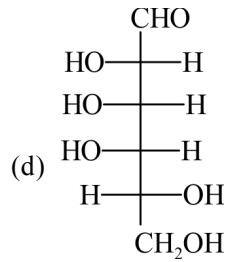
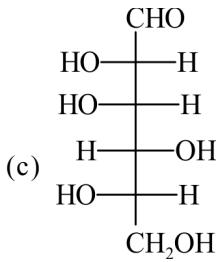
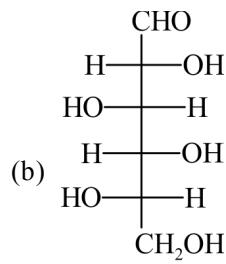
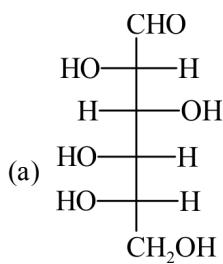
is

- (a) a ketohexose
- (b) an aldohexose
- (c) an  $\alpha$ -furanose
- (d) an  $\alpha$ -pyranose

(2011)

6. The structure of D-(+)-glucose is

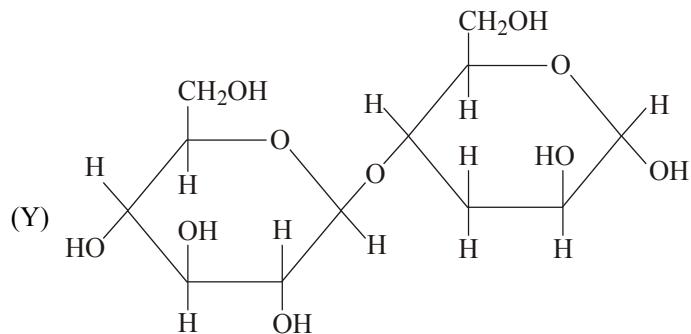
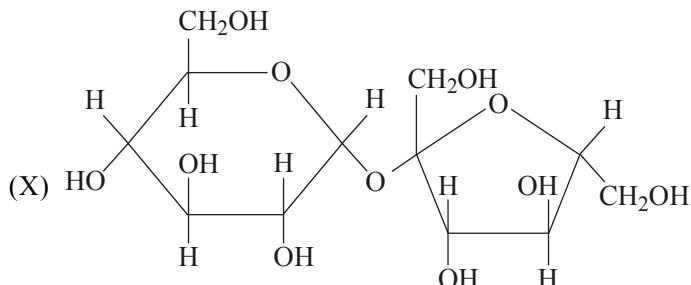




(2015)

### Multiple Correct-Choice Type

1. The correct statement(s) about the sugars



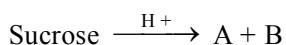
is are

- (a) X is a reducing sugar and Y is a nonreducing sugar
- (b) X is a nonreducing sugar and Y is a reducing sugar
- (c) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ ; respectively.
- (d) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively.

(2009)

### Fill-in-the-Blanks Type

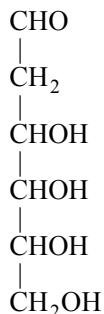
1. Give the structure of the products in each of the following reactions.



(2000)

**Integer Answer Type**

1. When the following aldohexose exists in D-configuration, the total number of stereoisomers in its pyranose form is



(2012)

**Reasoning Type**

STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which **ONLY ONE** is correct.

1. STATEMENT- 1: Glucose gives a reddish-brown precipitate with Fehling's solution.

**because**

STATEMENT- 2: Reaction of glucose with Fehling's solution gives CuO and gluconic acid.

- (a) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for statement-1
- (b) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1
- (c) Statement-1 is True, Statement-2 is False
- (d) Statement-1 is False, Statement-2 is True

**Short Answer Type**

- 2.(a) Write the Fischer projection formulae of L-glucose and D-glucose

- (b) Write the products of reaction of D-glucose with Tollens reagent and dilute nitric acid. (2004)

**ANSWERS****Straight Objective Type**

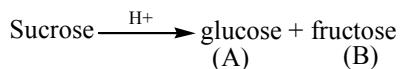
- |        |        |        |        |
|--------|--------|--------|--------|
| 1. (c) | 2. (b) | 3. (a) | 4. (a) |
| 5. (b) | 6. (a) |        |        |

**Multiple Correct-Choice Type**

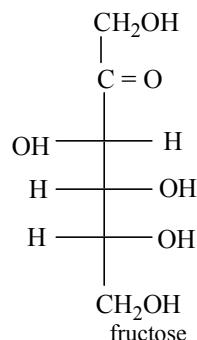
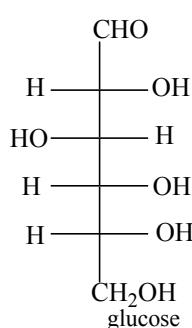
1. (b), (c)

### Fill-in-the-Blanks Type

1. The hydrolysis of sucrose produces glucose and fructose.



The structure of glucose and fructose are



### Integer Answer Type

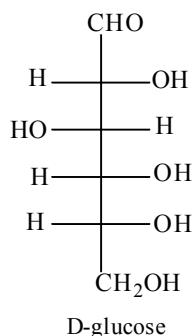
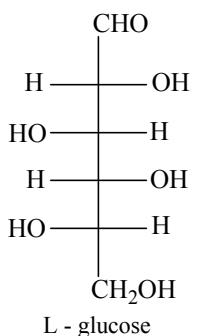
1. 8.

### Reasoning Type

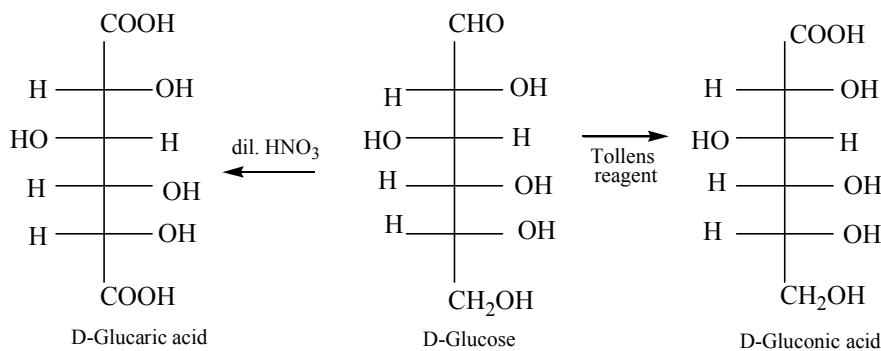
1. (c)

### Short Answer Type

2. (a) If the hydroxyl group at the asymmetric carbon placed at the bottom of Fischer projection lies to the left, the molecule is said to have L absolute configuration. For D configuration, the hydroxyl group lies to the right. Hence, the Fischer projection formulae of L-glucose and D-glucose are



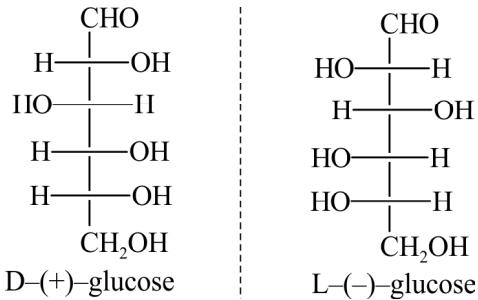
- (b) With Tollens reagent, the—CHO group is oxidised to—COOH giving D-gluconic acid. With dilute nitric acid, both the —CHO and —CH<sub>2</sub>OH groups are oxidised to —COOH giving D-glucaric acid.



## HINTS AND SOLUTIONS

### Straight Objective Type

- Both glucose and fructose are reducing sugars. Sucrose is a non-reducing sugar.  
Pentanal contains —CHO group. It shows the test. Acetophenone does not contain —CHO group. It does not show the test.
- The anomers are the cyclic hemiacetal structures in which carbon at C<sub>1</sub> is asymmetric. The anomers with the hydroxyl group projected above the ring is called  $\beta$ -anomer and the other as  $\alpha$ -anomer.
- Cellulose is formed from D-glucose via 1,4'- $\beta$ -glycoside bond and in each glucose unit there are three hydroxyl groups in the uncombined state which undergo acetylation.
- The six-membered ring (I) is the pyranose ring and the link at <sup>1</sup>C is below the ring, it is an  $\alpha$ -glycosidic link.
- The anomeric —OH group is above the plane of ring, thus it is a  $\beta$ -pyranose. The given carbohydrate is  $\beta$ -glucopyranose which is an aldohexose.
- If the —OH group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right, the molecule is said to have D absolute configuration and if it lies on left, the molecule is said to have L configuration.  
The dextrorotatory (rotating the light to right) and levorotatory (rotating the light to left) are indicated by plus and minus signs written within the parenthesis and inserted immediately after the symbol D and L  
Guided by these, we have

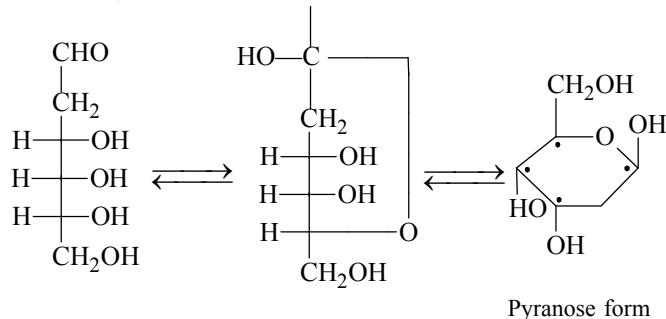


### Multiple Correct-Choice Type

- The structure Y is an aldose, hence it is a reducing sugar.  
The glycoside linkage in X is below the plane, hence it is an  $\alpha$ -glycoside.  
The glycoside linkage in Y is above the plane, hence it is a  $\beta$ -glycoside.

**Integer Answer Type**

1. In D-configuration, the hydroxyl group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right of the straight skeleton. Thus, we will have



There are four chiral carbon atoms in the pyranose form of the given aldohexose. Thus, there will be  $16 (= 2^4)$  stereoisomers, out of which 8 are of D-configurations (CH<sub>2</sub>OH group above the ring) and 8 are of L-configurations (CH<sub>2</sub>OH group below the ring).

Therefore, the correct answer is **8**.

**Reasoning Type**

1. Glucose contains an aldehyde group. It reduces Fehling's solution to give red precipitate of Cu<sub>2</sub>O. Thus, statement 1 is true and the statement 2 is false.

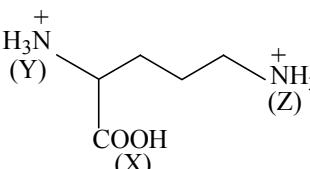




# AMINO ACIDS AND PEPTIDES

32

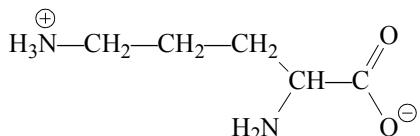
## Straight Objective Type

1. In the compound  the order of acidity of positions X, Y and Z is
- (a) X > Y > Z      (b) X > Z > Y      (c) Z > X > Y      (d) Y > X > Z      (2004)

## Fill-in-the-Blanks Type

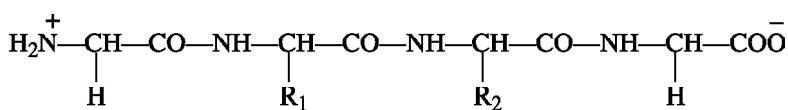
### Integer Answer Type

1. The total number of basic groups in the following form of lysine is \_\_\_\_\_.



(2010)

2. The substituents R<sub>1</sub> and R<sub>2</sub> for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0?

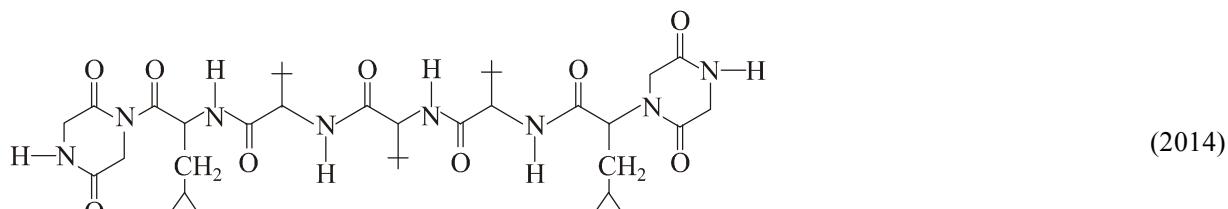


Peptide	R <sub>1</sub>	R <sub>2</sub>
I	H	H
II	H	CH <sub>3</sub>
III	CH <sub>2</sub> COOH	H
IV	CH <sub>2</sub> CONH <sub>2</sub>	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
V	CH <sub>2</sub> CONH <sub>2</sub>	CH <sub>2</sub> CONH <sub>2</sub>
VI	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
VII	CH <sub>2</sub> COOH	CH <sub>2</sub> CONH <sub>2</sub>
VIII	CH <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
IX	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	CH <sub>3</sub>

(2012)

3. A tetrapeptide has  $\text{—COOH}$  group on alanine. This produces glycine (Gly), valine (val), phenyl alanine (Phe) and alanine (Al), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structure) with  $\text{—NH}_2$  group attached to a chiral centre is \_\_\_\_\_. (2013)

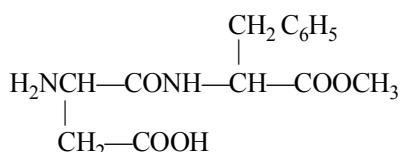
4. The total number of distinct naturally occurring amino acids obtained by complete acidic hydrolysis of the peptide shown as follows is \_\_\_\_\_.



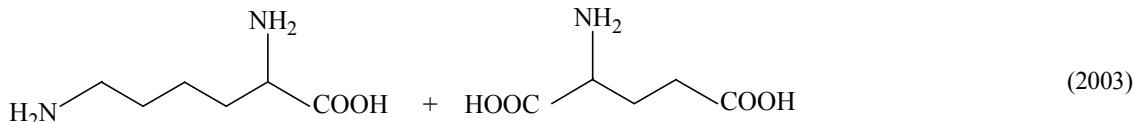
5. A decapeptide (relative molar mass 796) on complete hydrolysis gives glycine (relative molar mass 75), alanine and phenylalanine. Glycine constitutes 47.0% of the total mass of the hydrolysed products. The number of glycine units present in the decapeptide is . . . . . (2011)

## **Short Answer Type**

1. Write the structure of alanine at pH = 2 and pH = 10 (2000)  
2. Aspartame, an artificial sweetener, is a peptide and has the following structure:



- (i) Identify the four functional groups.  
(ii) Write the zwitter-ionic structure.  
(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.  
(iv) Which of the two amino acids is more hydrophobic? (2001)  
3. Following two amino acids liosine and glutamine form dipeptide. What are the possible dipeptides?



ANSWERS

## **Straight Objective Type**

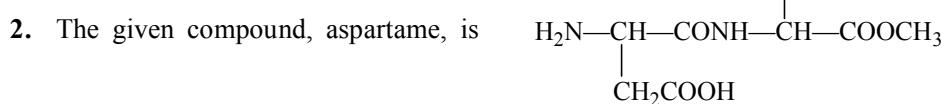
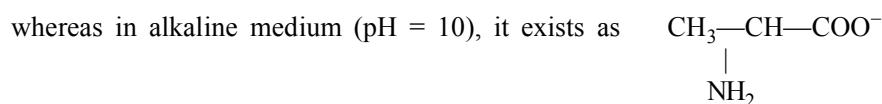
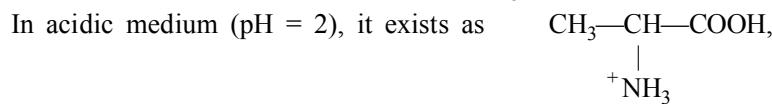
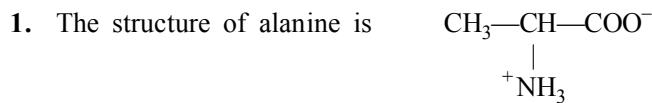
1. (a)

### **Fill-in-the-Blanks Type**

## Integer Type

1. 2      2. 4.      3. 4      4. 1      5. 6

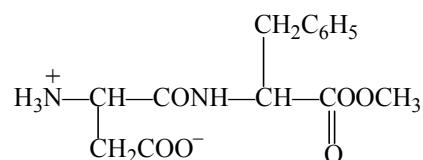
### Short Answer Type



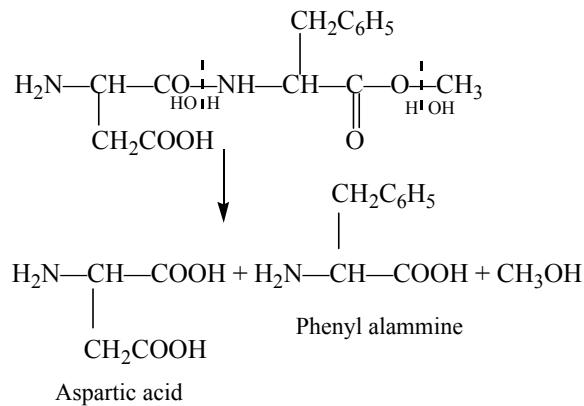
The four functional groups in this compound are

An amine group	$-\text{NH}_2$
A carboxlic group	$-\text{COOH}$
An amide group	$-\text{C}(=\text{O})-\text{NH}-$
An ester group	$-\text{C}(=\text{O})-\text{O}-$

(ii) The zwitter-ionic structure of aspartame is

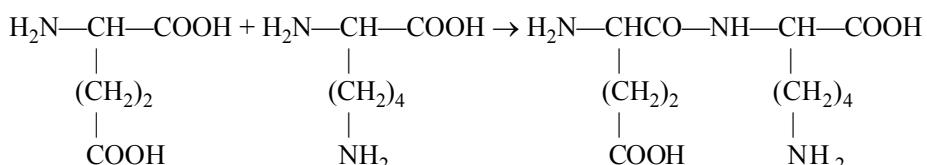
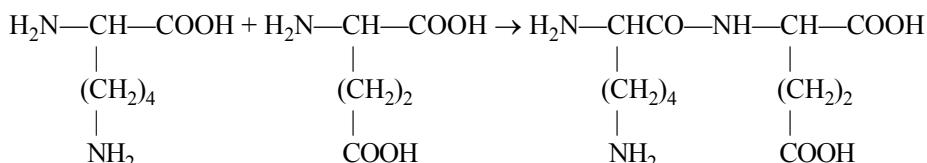


(iii) The hydrolysis of aspartame may be represented as follows:



(iv) Phenyl alamine will be more hydrophobic due to phenyl group present in it.

3. Two possible dipeptides are



## HINTS AND SOLUTIONS

## **Straight Objective Type**

1. The  $\text{—COOH}$  group has maximum acidity.  
The  $\text{H}_3\text{N}^+$  near to  $\text{COOH}$  group is more acidic than  $\text{NH}_3^+$  away from it.

## **Integer Answer Type**

- The number of basic groups is two. These are  $\text{—NH}_2$  and  $\text{—COO}^-$ .
  - In general, the pH of the solution at which amino acids exist as zwitterion follows the order :

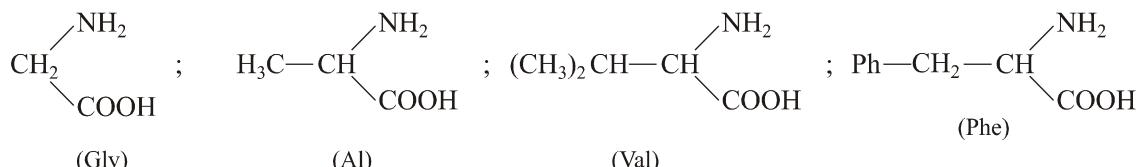
Acidic side chain < neutral chain < basic side chain  
 $(\text{pH} \approx 3)$                $(\text{pH} = 5.5 - 6.0)$        $(\text{pH} = 9 - 10)$

This pH is known as isoelectric point.

At pH = 7, the acidic side chain (for which isoelectric point < 7) exists as a negatively-charged species (e.g. —COO<sup>-</sup>) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g. —NH<sup>+</sup>). Since peptides IV, VI, VIII and IX contain —NH<sub>2</sub> group in R<sub>1</sub> or/and R<sub>2</sub> group(s), these are expected to exist as positively-charged species.

Therefore, the correct answer is 4.

3. The structures of four amino acids are as follows.



The given tetrapeptide has —COOH group on alanine. Thus, alanine occupy right-most position in tetrapeptide. Since —NH<sub>2</sub> group is attached to a chiral centre, the left-most position will not be occupied by glycine (which has no chiral centre). This left-most position will be occupied by any of the two remaining acids, i.e. valine and phenylalanine. Thus, the following will be the primary structures.

Val – Phe – Gly – Ala

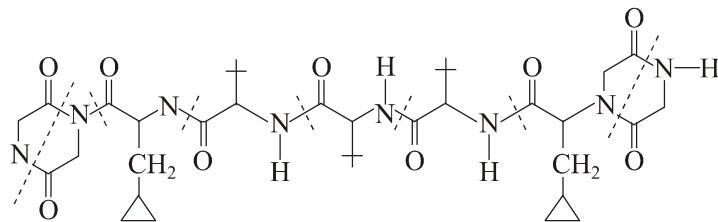
Val – Gly – Phe – Ala

Phe – Val – Gly – Ala

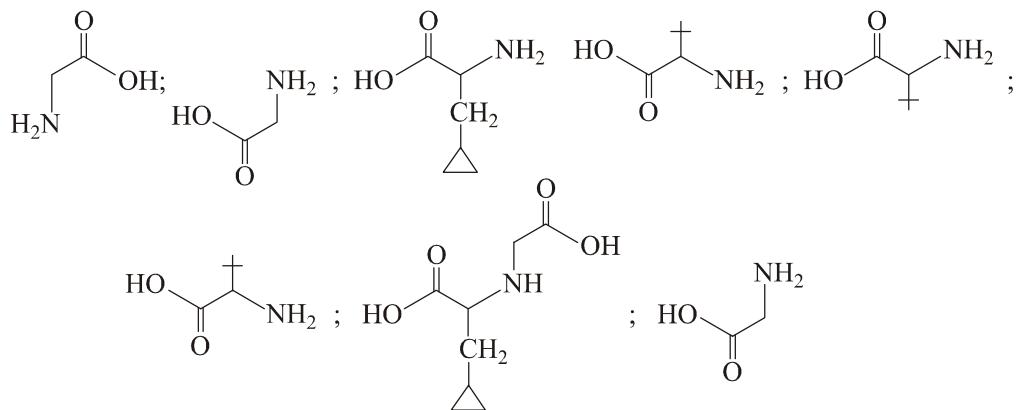
Phe – Gly – Val – Ala

Therefore, there are **4** primary structures.

4. The site of hydrolysis is shown by the broken lines in the following figures.

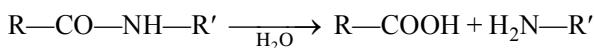


The products at each hydrolysis step are as follows.



Only naturally occurring amino acid is glycine ( $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ ).

5. A decapeptide is formed by 10 amino acids and it will contain 9 peptide linkages ( $\text{R}-\text{CO}-\text{NH}-\text{R}'$ ). The hydrolysis of a peptide linkage is



Thus, there will be consumption of 9 mol of water per mole of a decapeptide. Hence total mass of hydrolysed products from one mole of decapeptide will be

$$m = (796 + 18 \times 9) \text{ g} = 958 \text{ g}$$

Mass of glycine in the hydrolysed products will be

$$m = 47\% \text{ of } 958 \text{ g} = \left(\frac{47}{100}\right) (958 \text{ g}) = 450 \text{ g}$$

Number of glycine units in the hydrolysed products will be

$$N = \frac{m}{M} = \frac{450 \text{ g}}{75 \text{ g}} \approx 6$$

Hence, the correct answer is 6.



# POLYMERS

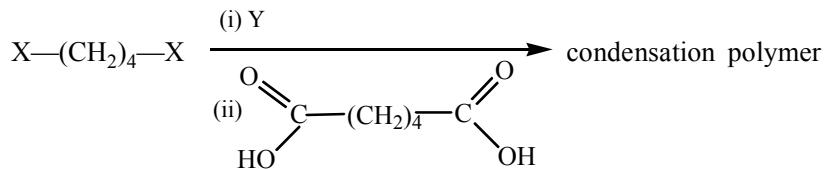
33

## **Straight Objective Type**



## **Multiple Correct-Choice Type**

1. The correct functional group X and the reagent/reaction conditions Y in the scheme



are

- (a)  $X = \text{COOCH}_3$ ,  $Y = \text{H}_2$  / Ni / heat      (b)  $X = \text{CONH}_2$ ,  $Y = \text{H}_2$  / Ni / heat  
 (c)  $X = \text{CONH}_2$ ,  $Y = \text{Br}_2$  / NaOH      (d)  $X = \text{CN}$ ,  $Y = \text{H}_2$  / Ni / heat      (2011)

## **Fill-in-the-Blanks Type**

1. Vinyl chloride on reaction with dimethyl copper gives \_\_\_\_\_.



## **Matrix Match Type**

1. Match the chemical substances in **Column I** with type of polymers/type of bond in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

**Column I**

- (a) cellulose
- (b) nylon-6,6
- (c) protein
- (d) sucrose

**Column II**

- (p) natural polymer
- (q) synthetic polymer
- (r) amide linkages
- (s) glycoside linkages

(2007)

**ANSWERS**

**Straight Objective Type**

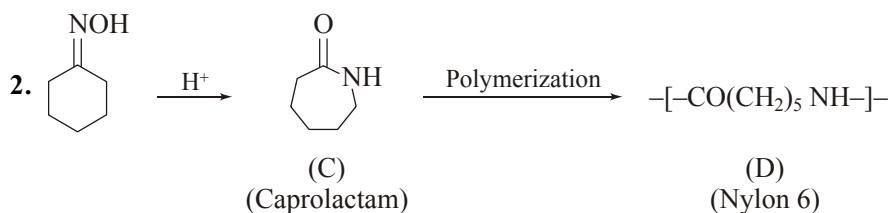
1. (d)

**Multiple Correct-Choice Type**

1. (a), (b), (c), (d)

**Fill-in-the-Blanks Type**

1. Polyvinyl chloride



**Matrix Match Type**

1. The correct-bubbled diagram is as follows.

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	○	●	○
d	○	○	○	●

## HINTS AND SOLUTIONS

### Straight Objective Type

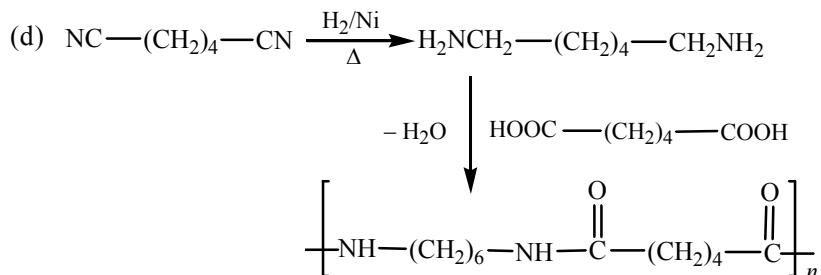
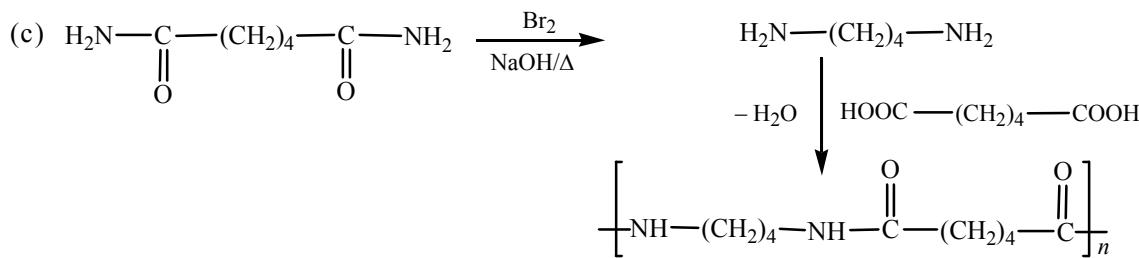
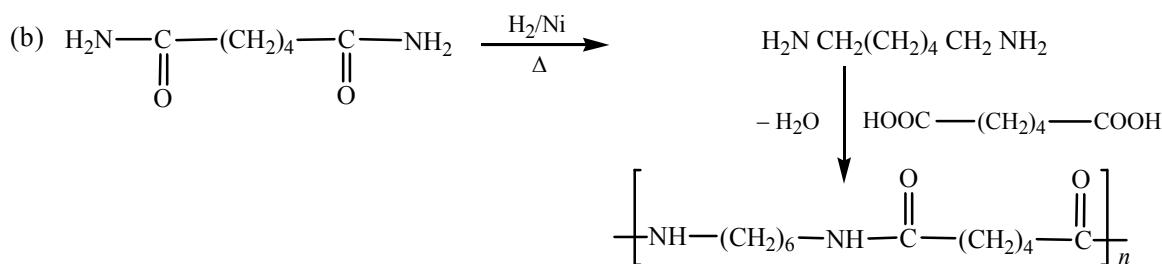
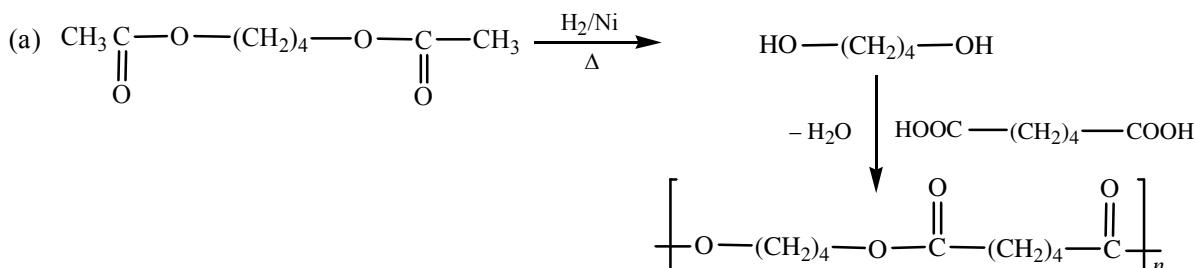
#### Solution

1. Natural rubber is an elastomer. The irregular geometry of the molecules involves weak van der Waals force of interactions.

### Multiple Correct-Choice Type

1. A condensation polymer is formed in a reaction between two functional groups and thereby eliminating small molecules during polymerization. Since one of the functional group involves carboxylic acid, the other one may involve hydroxyl or amino group to form an ester or amide linkages in the polymer.

The reactions with the given choices are as follows.



**Matrix Match Type**

1.

- (a) Cellulose is a natural polymer (choice p) and contains glycoside linkages (choice s).
- (b) Nylon-6, 6 is a synthetic polymer (choice q) and contains amide linkages (choice r).
- (c) Protein is a natural polymer (choice p) and contains amide linkages (choice r).
- (d) Sucrose contains glycoside linkage (choice s).

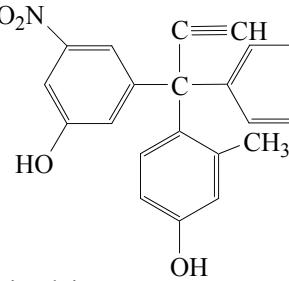
# EXERCISES IN ORGANIC CHEMISTRY

34

## Straight Objective Type

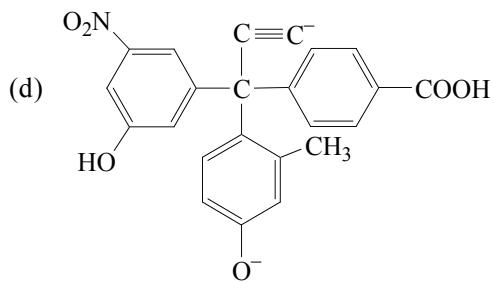
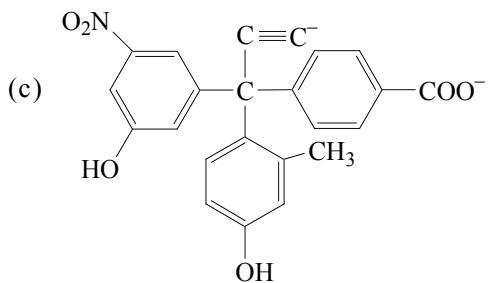
- Which of the following decolourises alkaline  $\text{KMnO}_4$  solution?  
 (a)  $\text{C}_2\text{H}_6$       (b)  $\text{C}_2\text{H}_4$       (c)  $\text{CH}_4$       (d)  $\text{CCl}_4$       (1980)
- Which of the following is basic ?  
 (a)  $\text{CH}_3\text{CH}_2\text{OH}$       (b)  $\text{HO—CH}_2\text{CH}_2\text{—OH}$       (c)  $\text{H—O—O—H}$   
 (d)  $\text{H}_3\text{C—COOH}$       (e) None      (1980)
- Which of the following compounds does not dissolve in concentrated  $\text{H}_2\text{SO}_4$  even on warming ?  
 (a) ethylene      (b) benzene      (c) hexane      (d) aniline      (1981)
- Hydrogenation of benzoyl chloride in the presence of Pd on  $\text{BaSO}_4$  gives  
 (a) benzyl alcohol      (b) benzaldehyde      (c) benzoic acid      (d) phenol      (1992)
- What is the decreasing order of strength of the bases  $\text{OH}^-$ ,  $\text{NH}_2^-$ ,  $\text{H—C}\equiv\text{C}^-$  and  $\text{CH}_3\text{—CH}_2^-$ ?  
 (a)  $\text{CH}_3\text{—CH}_2^- > \text{NH}_2^- > \text{H—C}\equiv\text{C}^- > \text{OH}^-$       (b)  $\text{H—C}\equiv\text{C}^- > \text{CH}_3\text{—CH}_2^- > \text{NH}_2^- > \text{OH}^-$   
 (c)  $\text{OH}^- > \text{NH}_2^- > \text{H—C}\equiv\text{C}^- > \text{CH}_3\text{—CH}_2^-$       (d)  $\text{NH}_2^- > \text{H—C}\equiv\text{C}^- > \text{OH}^- > \text{CH}_3\text{—CH}_2^-$       (1993)
- Which of the following is an organometallic compound ?  
 (a) Lithium methoxide      (b) Lithium acetate  
 (c) Lithium dimethylamide      (d) Methyl lithium.      (1997)

7. The compound



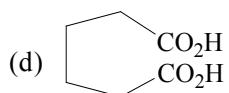
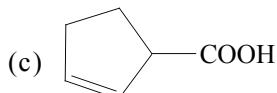
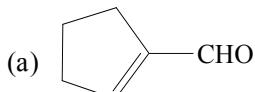
The product obtained is

- (a)
- 
- (b)
-



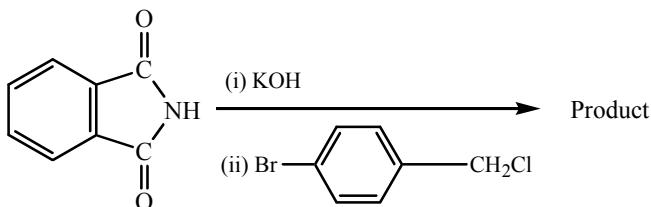
(2003)

8. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound **F** is

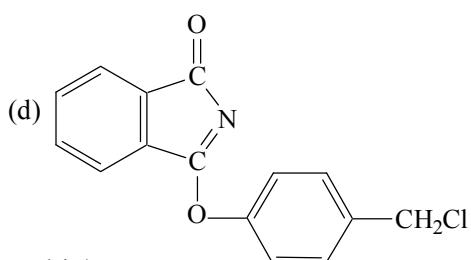
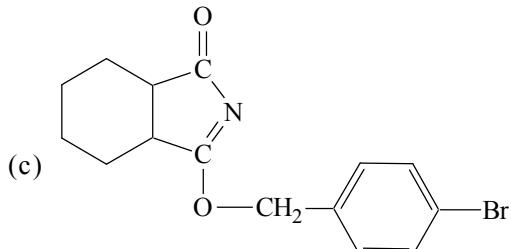
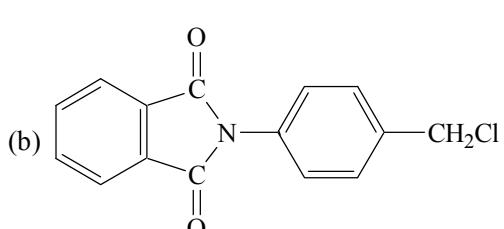
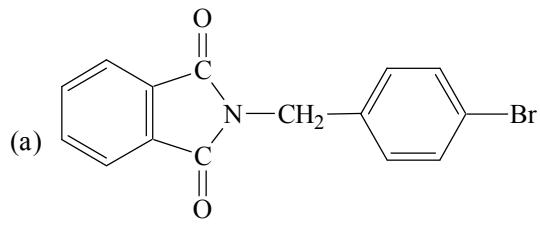


(2007)

9. The major product of the reaction

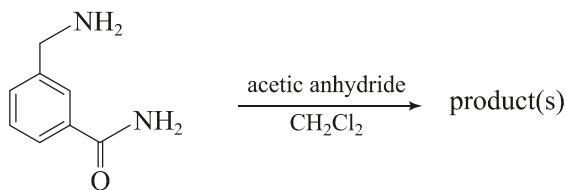


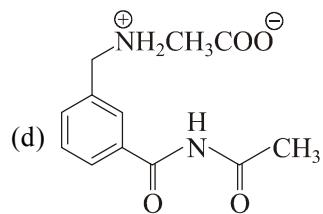
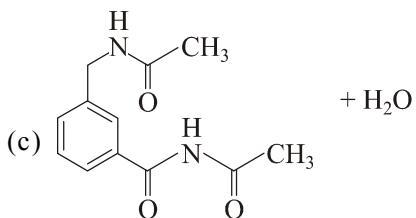
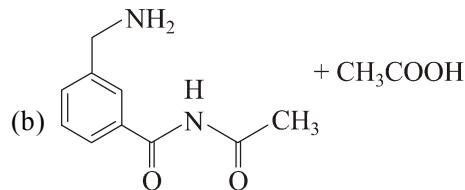
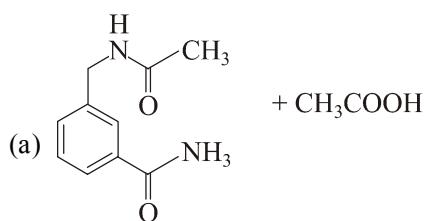
is



(2011)

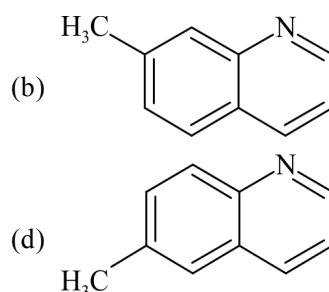
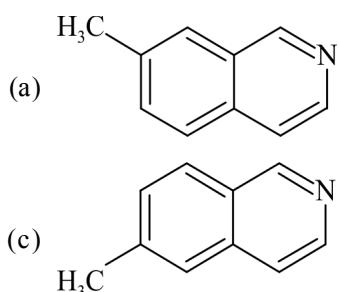
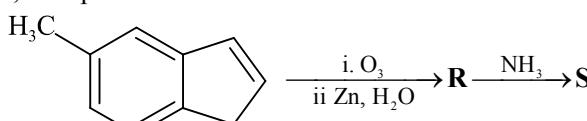
10. In the reaction shown below, the major product(s) formed is/are





(2014)

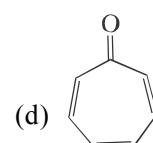
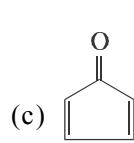
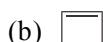
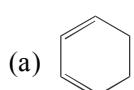
11. In the following reactions, the product S is



(2015)

### Multiple Correct-Choice Type

1. Which of the following molecules, in pure form, is (are) unstable at room temperature?



(2012)

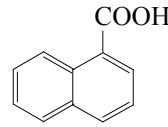
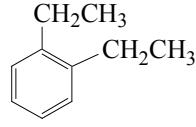
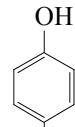
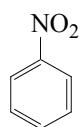
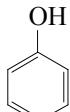
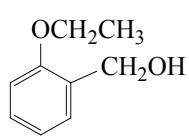
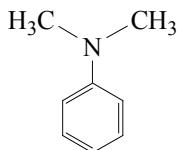
### Fill-in-the-Blanks Type

- In acidic medium \_\_\_\_\_ behaves as a strongest base. (nitrobenzene, aniline, phenol) (1981)
- Benzene  $\xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{CH}_2\text{COCl}}$  \_\_\_\_\_ (1985)
- Propanal  $\xrightarrow[\text{heat}]{\text{NaOH}}$  \_\_\_\_\_ (1985)
- Ethanol  $\xrightarrow[\text{I}_2]{\text{NaOH}}$  \_\_\_\_\_ (1985)
- Aliphatic ethers are purified by shaking with a solution of ferrous salt to remove \_\_\_\_\_ which are formed on prolonged standing in contact with air. (1992)

6. The high melting point and insolubility in organic solvents of sulphanilic acid are due to its \_\_\_\_\_ structure. (1994)

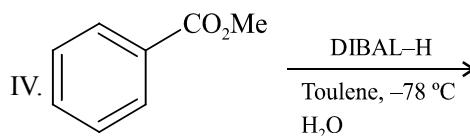
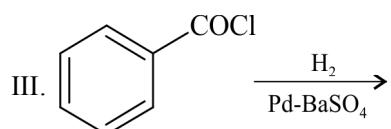
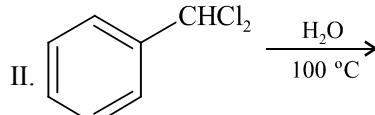
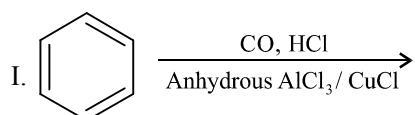
### Integer Answer Type

1. Amongst the following, the total number of compounds soluble in aqueous NaOH is \_\_\_\_\_.



(2010)

2. Among the following, the number of reaction(s) that produce(s) benzaldehyde is

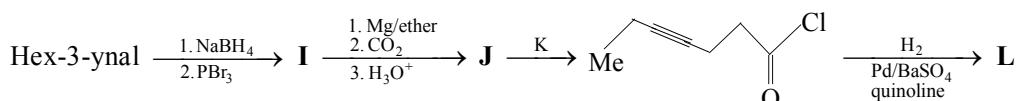


(2015)

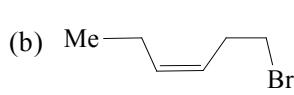
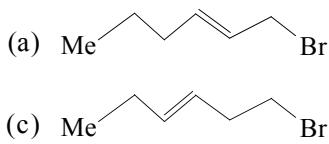
### Linked-Comprehension Type

#### Passage-1

In the following reaction sequence, products **I**, **J** and **L** are formed. **K** represents a reagent.



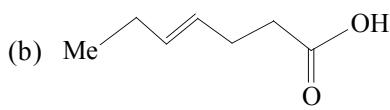
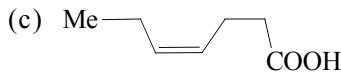
1. The structure of the product **I** is



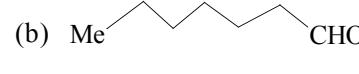
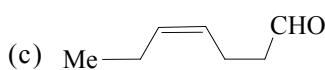
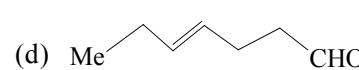
2. The structure of compounds **J** and **K** respectively, are



and  $\text{SOCl}_2$

- (b)  and  $\text{SO}_2\text{Cl}_2$
- (c)  and  $\text{SOCl}_2$
- (d)  and  $\text{CH}_3\text{SO}_2\text{Cl}$

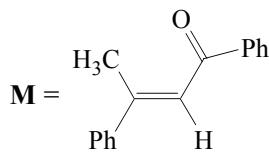
3. The structure of product **L** is

- (a)  (b) 
- (c)  (d) 

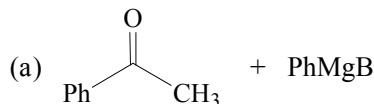
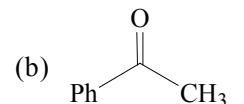
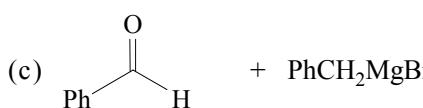
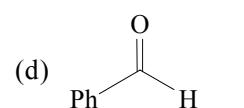
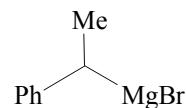
(2008)

### Passage-2

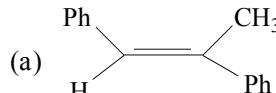
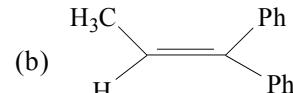
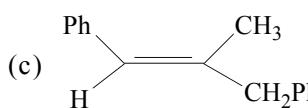
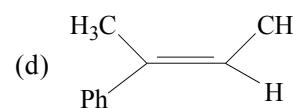
A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.



1. Compound **H** is formed by the reaction of

- (a)  +  $\text{PhMgBr}$  (b)  +  $\text{PhCH}_2\text{MgBr}$
- (c)  +  $\text{PhCH}_2\text{MgBr}$  (d)  + 

2. The structure of compound **I** is

- (a)  (b) 
- (c)  (d) 

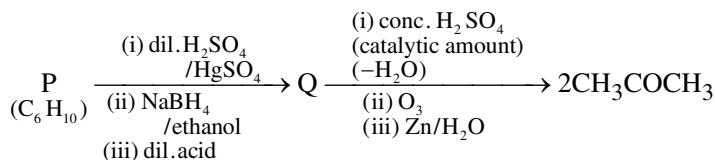
3. The structures of compounds **J**, **K** and **L**, respectively, are

- (a)  $\text{PhCOCH}_3$ ,  $\text{PhCH}_2\text{COCH}_3$  and  $\text{PhCH}_2\text{COO}^-\text{K}^+$   
 (b)  $\text{PhCHO}$ ,  $\text{PhCH}_2\text{CHO}$  and  $\text{PhCOO}^-\text{K}^+$   
 (c)  $\text{PhCOCH}_3$ ,  $\text{PhCH}_2\text{CHO}$  and  $\text{CH}_3\text{COO}^-\text{K}^+$   
 (d)  $\text{PhCHO}$ ,  $\text{PhCOCH}_3$  and  $\text{PhCOO}^-\text{K}^+$

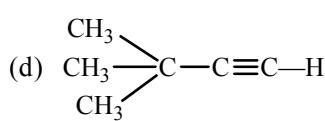
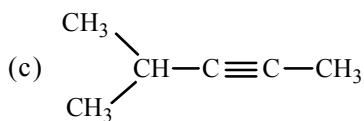
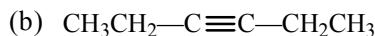
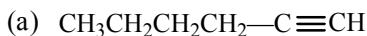
(2008)

**Passage-3**

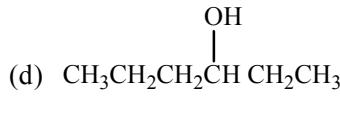
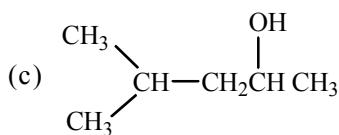
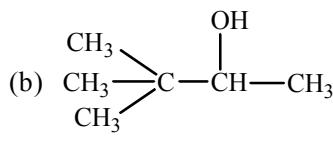
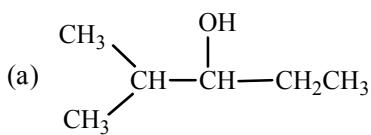
An acyclic hydrocarbon P, having molecular formula  $C_6H_{10}$ , gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.



1. The structure of the compound P is



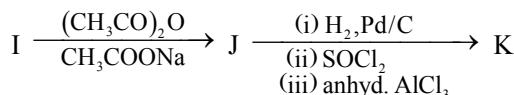
2. The structure of the compound Q is



(2011)

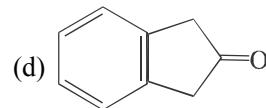
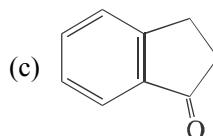
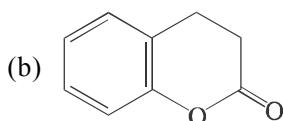
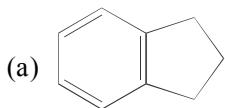
**Passage-4**

In the following reaction sequence, the compound J is an intermediate

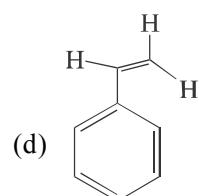
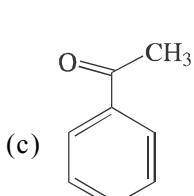
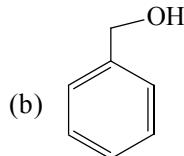
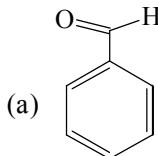


J( $C_9H_8O_2$ ) gives effervescence on treatment with  $NaHCO_3$  and positive Baeyer's test.

1. The compound K is



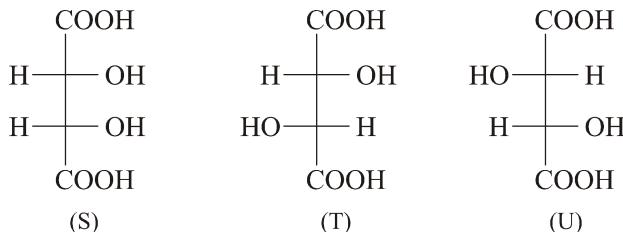
2. The compound I is



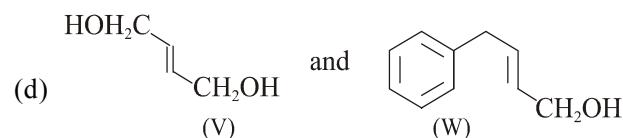
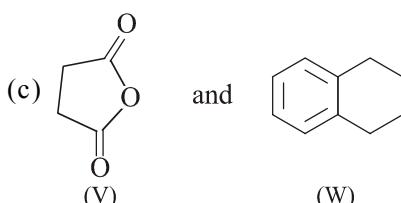
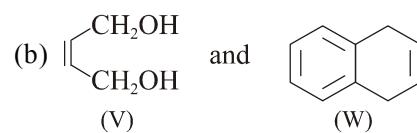
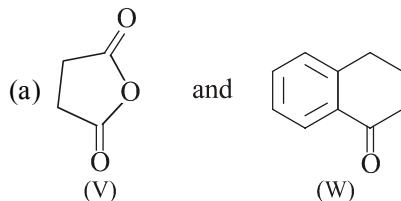
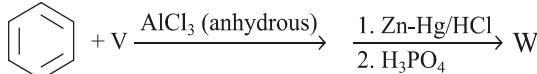
(2012)

**Passage-5**

P and Q are isomers of dicarboxylic acid  $C_4H_4O_4$ . Both decolorized  $Br_2/H_2O$ . On heating, P forms the cyclic anhydride. Upon treatment with dilute alkaline  $KMnO_4$ , P as well as Q could produce one or more than one from S, T and U.



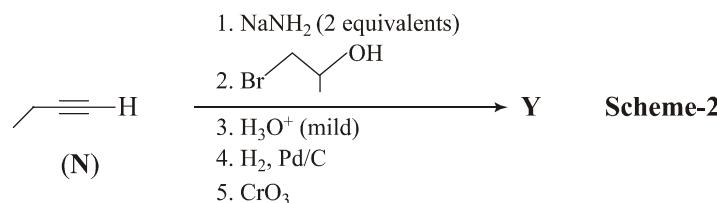
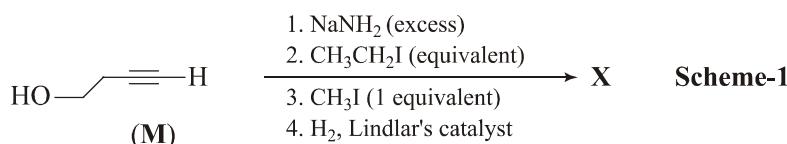
1. Compounds formed from P and Q, respectively, are
  - (a) Optically active S and optically active pair (T, U)
  - (b) Optically inactive S and optically inactive pair (T, U)
  - (c) Optically active pair (T, U) and optically active S
  - (d) Optically inactive pair (T, U) and optically inactive S
2. In the following reaction sequences V and W are, respectively



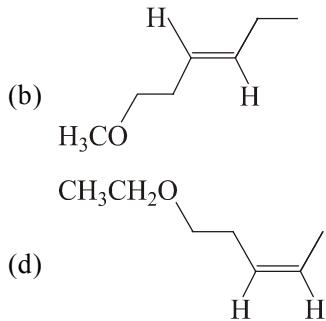
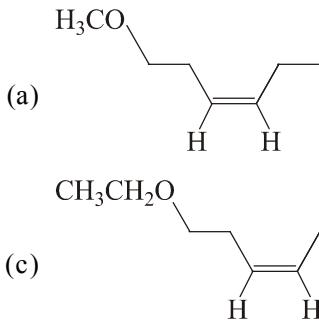
(2013)

**Passage 6**

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the **major products** formed in each step for both the schemes.



1. The product **X** is



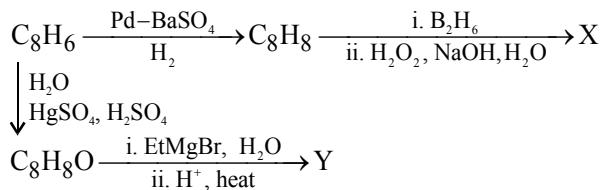
2. The correct statement with respect to product **Y** is:

- (a) It gives a positive Tollens test and is a functional isomer of **X**
- (b) It gives a positive Tollens test and is a geometrical isomer of **X**
- (c) It gives a positive iodoform test and is a functional isomer of **X**
- (d) It gives a positive iodoform test and is a geometrical isomer of **X**

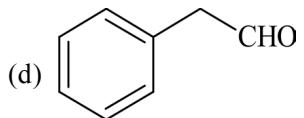
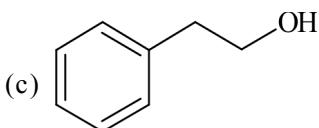
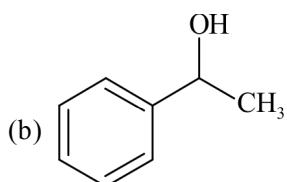
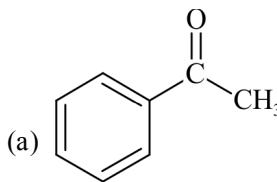
(2014)

#### Passage-7

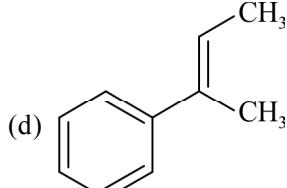
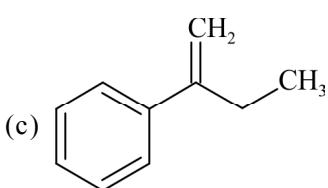
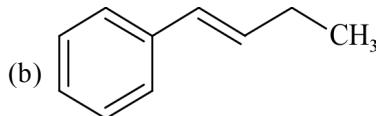
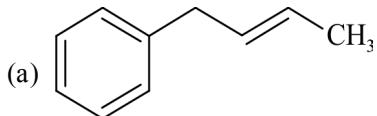
In the following reaction



1. Compound **X** is



2. The major compound **Y** is



(2015)

**Matching Type**

1. (a) Cyclopropane, Chlorine and light  
 (b) Propanone and sodium bisulphite  
 (c) Ethanal and Methanal  
 (d) Benzene, nitric acid and sulphuric acid  
 (e) Propene, hydrogen bromide and a peroxide catalyst  
 (p) Electrophilic substitution  
 (q) Homologous pair  
 (r) Homolytic addition  
 (s) Free radical substitution  
 (t) Nucleophilic addition (1981)
2. (a) Pyrolysis of alkanes  
 (b) Benzene + chloroethane (+ anhydrous  $\text{AlCl}_3$ )  
 (c)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH}$   
 (d) Preparation of alkanes  
 (e) Phenol +  $\text{CHCl}_3(\text{NaOH})$   
 (f)  $\text{C}_2\text{H}_5\text{Br} + \text{alc KOH}$   
 (p) Elimination reaction  
 (q) Saponification  
 (r) Wurtz reaction  
 (s) Friedel-Crafts reaction  
 (t) Reimer-Tiemann reaction  
 (u) Cracking (1982)
3. (a) Decarboxylation  
 (b) Ozonolysis  
 (c) Williamson's synthesis  
 (d) Dichloroethylene  
 (p) Addition reaction  
 (q) Soda lime  
 (r) Structure of alkene  
 (s) Ether (1983)
4. (a) Lucas test  
 (b) Neutral  $\text{FeCl}_3$   
 (c) Dye test  
 (d) Tollens test  
 (p) Phenol  
 (q) Glucose  
 (r) Tertiary alcohol  
 (s) Aniline (1983)
5. Friedel-Crafts      Oil      alkenes  
 Fermentation      Lewis acid      soap  
 Dehydrohalogenation      cuprous chloride      anhydrous  $\text{AlCl}_3$   
 Sandmeyer      yeast      chlorobenzene  
 Saponification      alcoholic alkali      ethanol (1988)

6. Match the compounds/ions in Column I with their properties/reactions in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

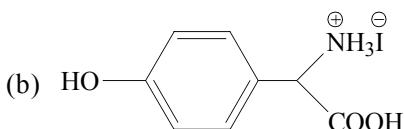
**Column I****Column II**

- |  |   |
|--|---|
| (a) $\text{C}_6\text{H}_5\text{CHO}$     | (p) gives precipitate with 2,4-dinitrophenylhydrazine |
| (b) $\text{CH}_3\text{C}\equiv\text{CH}$ | (q) gives precipitate with $\text{AgNO}_3$            |
| (c) $\text{CN}^-$                        | (r) is a nucleophile                                  |
| (d) $\text{I}^-$                         | (s) is involved in cyanohydrin formation (2007)       |

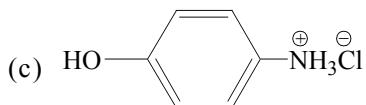
7. Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

**Column I****Column II**

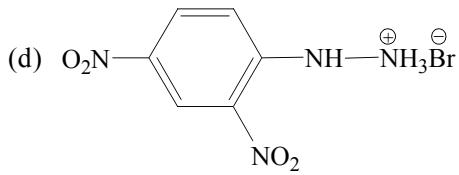
- |   |   |
|---|---|
| (a) $\text{H}_2\text{N}-\overset{\oplus}{\text{NH}_3}\text{Cl}$ | (p) sodium fusion extract of the compound gives prussian blue colour with $\text{FeSO}_4$ |
|---|---|



- (q) gives positive  $\text{FeCl}_3$  test



(r) gives white precipitate with  $\text{AgNO}_3$



(s) reacts with aldehydes to form the corresponding hydrazone derivative

(2008)

**8.** Match each of the compounds in Column I with its characteristic reaction(s) in Column II.

**Column I**

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$
- (b)  $\text{CH}_3\text{CH}_2\text{OCOCH}_3$
- (c)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{OH}$
- (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

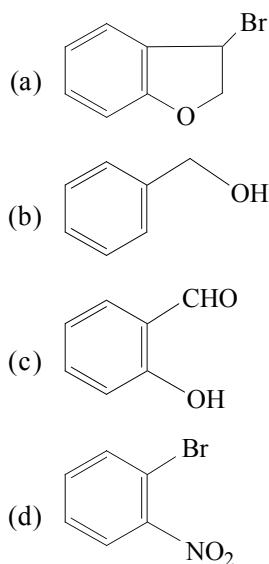
**Column II**

- (p) Reduction with  $\text{Pd-C}/\text{H}_2$
- (q) Reduction with  $\text{SnCl}_2/\text{HCl}$
- (r) Development of foul smell on treatment with chloroform and alcoholic KOH
- (s) Reduction with diisobutyl aluminium hydride (DIBAL-H)
- (t) Alkaline hydrolysis

(2009)

**9.** Match each of the compounds given in **Column I** with the reaction(s) that they can undergo given in **Column II**.

**Column I**

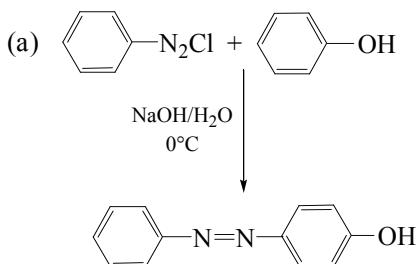


**Column II**

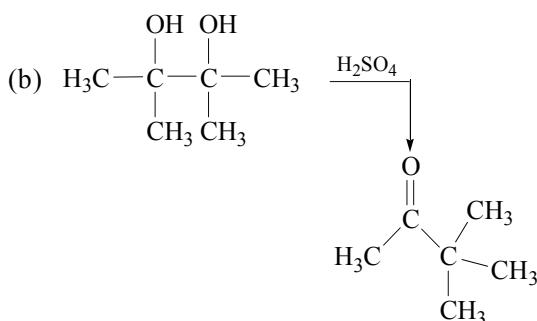
- (p) Nucleophilic substitution
- (q) Elimination
- (r) Nucleophilic addition
- (s) Esterification with acetic anhydride
- (t) Dehydrogenation

(2009)

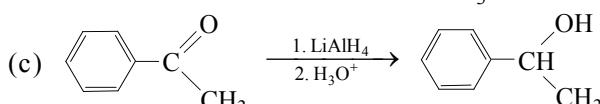
**10.** Match the reactions in **Column I** with appropriate options in **Column II**.

**Column I****Column II**

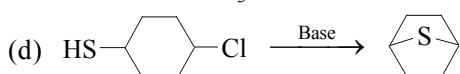
(p) Racemic mixture



(q) Addition reaction



(r) Substitution reaction

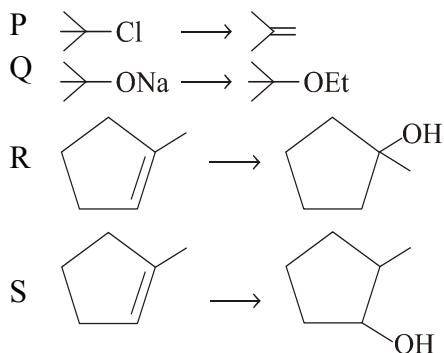


(s) Coupling reaction

(t) Carbocation intermediate

(2010)

**11.** Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the Lists.

**List I****List II**

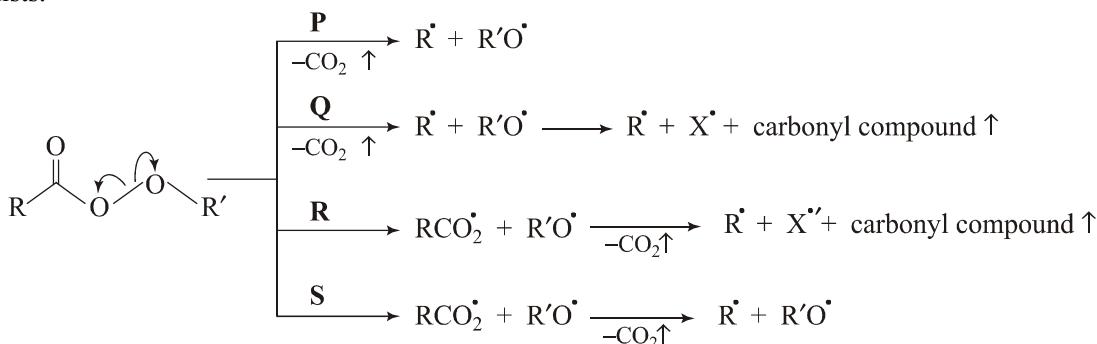
- 1 (i)  $\text{Hg}(\text{OAc})_2$ ; (ii)  $\text{NaBH}_4$
- 2  $\text{NaOEt}$
- 3  $\text{Et}-\text{Br}$
- 4 (i)  $\text{BH}_3$ ; (ii)  $\text{H}_2\text{O}_2/\text{NaOH}$

**Codes**

	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

(2013)

12. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List-I** with an appropriate structure from **List-II** and select the correct answer using the code given below the lists.



**List-I**

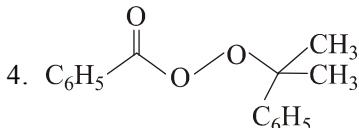
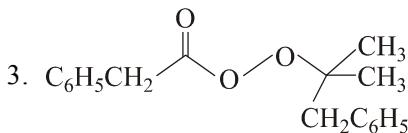
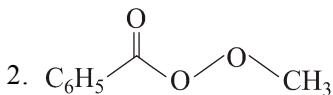
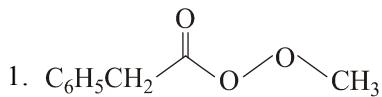
P. Pathway **P**

Q. Pathway **Q**

R. Pathway **R**

S. Pathway **S**

**List-II**



**Code:**

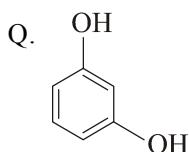
	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	3	1
(c)	4	1	2	3
(d)	3	2	1	4

(2014)

13. Match the four starting materials (**P, Q, R, S**) given in **List-I** with the corresponding reaction schemes (I, II, III, IV) provided in **List-II** and select the correct answer using the code given below the lists.

**List-I**

P. H#CH



**List-II**

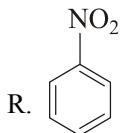
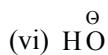
1. **Scheme I**

- (i) KMnO4, H2O, heat
- (ii) H+, H2O
- (iii) SOCl2, (iv) NH3

?  $\xrightarrow{\quad}$  C7H6N2O3

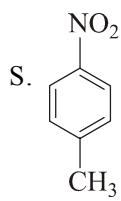
2. **Scheme II**

- (i) Sn/HCl (ii) CH3COCl
- (iii) conc. H2SO4, (iv) HNO3
- (v) dil. H2SO4, heat



## 3. Scheme III

- (i) red hot iron, 873 K
- (ii) fuming  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , heat
- (iii)  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , (iv)  $\text{NaNO}_2$ ,  $\text{H}_2\text{SO}_4$
- (v) hydrolysis



## 4. Scheme IV

- (i) conc.  $\text{H}_2\text{SO}_4$ , 60 °C
- (ii) conc.  $\text{HNO}_3$ , conc.  $\text{H}_2\text{SO}_4$
- (iii) dil.  $\text{H}_2\text{SO}_4$ , heat

**Code:**

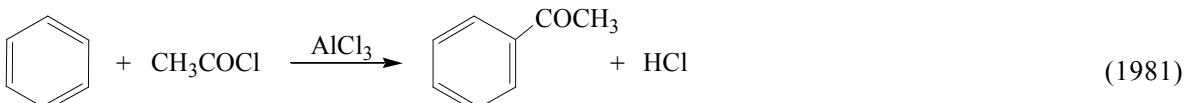
	P	Q	R	S
(a)	1	4	2	3
(b)	3	1	4	2
(c)	3	4	2	1
(d)	4	1	3	2

(2014)

**Short Answer Type****I. Descriptive**

1. Give the major product (with formula) formed by the action of:
  - (i) Alkaline  $\text{KMnO}_4$  on ethylene
  - (ii) Dilute  $\text{HCl}$  on methane
  - (iii)  $\text{HOCl}$  on ethylene
  - (iv) Ammoniacal cuprous chloride on acetylene
  - (v)  $\text{Cl}_2$  on  $\text{CS}_2$  in presence of anhydrous  $\text{AlCl}_3$
  - (vi)  $\text{AgNO}_3$  solution on carbon tetrachloride
2. Give one characteristic test which would distinguish
  - (i)  $\text{CH}_4$  from  $\text{C}_2\text{H}_2$
  - (ii)  $\text{C}_2\text{H}_5\text{OH}$  from  $\text{CHCl}_3$
3. (i) Write the chemical equation to show what happens when ethyl acetate is treated with sodium ethoxide in ethanol, and the reaction mixture acidified with acetic acid.
  - (ii) Outline the reaction sequence for the conversion of methanol to ethanol. (The number of steps should not be more than three.)
  - (iii) Outline the reaction sequence for the conversion of ethane to ethyne. (The number of steps should not be more than two.)

- (iv) Outline the accepted mechanism of the following reaction. Show the various steps including the charged intermediate.



4. Write the structural formula of the main organic product formed when:
- (i) The compound obtained by the hydration of ethyne is treated with dilute alkali
  - (ii) Chloroform reacts with aniline in the presence of excess alkali
  - (iii) Methanal reacts with ammonia
  - (iv) Bromomethane reacts with one-half of the molar quantity of silver carbonate
  - (v) Ethyl acetate is treated with double the molar quantity of ethyl magnesium bromide, and the reaction mixture is poured into water
  - (vi) Ethene mixed with air is passed under pressure over a silver catalyst at 27 °C
5. Sodium metal can be used for drying diethyl ether but not ethanol.
6. Carry out the following conversions.
- (i) 1 propanol from 2-propanol (in three steps)
  - (ii) *n*-propylamine from ethyl chloride (in two steps)
  - (iii) Chlorobenzene from aniline (in two steps)
7. Give reasons for the following in one or two sentences.
- (i) Acetic acid can be halogenated in the presence of red P and Cl<sub>2</sub> but formic acid cannot be halogenated in the same way.
  - (ii) Methane does not react with chlorine in the dark
  - (iii) Propene reacts with HBr to give isopropyl bromide but does not give *n*- propyl bromide.
  - (iv) Although benzene is highly unsaturated, normally it does not undergo addition reaction
8. State the conditions under which following preparations are carried out. Give the necessary equations which need not be balanced.
- |                                       |                           |
|---------------------------------------|---------------------------|
| (i) Ethanol from acetylene            | (ii) Aniline from benzene |
| (iii) Acetic acid from methyl iodide. |                           |
9. Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water.
10. A compound of molecular formula C<sub>7</sub>H<sub>8</sub>O is insoluble in water and dilute sodium bicarbonates but dissolves in dilute aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of C<sub>7</sub>H<sub>5</sub>OBr<sub>3</sub>. Write down the structural formula of the compound.
11. Give a chemical test to distinguish between the following pairs of compounds.
- |                           |                           |
|---------------------------|---------------------------|
| (i) 2-Butyne and 1-Butyne | (ii) Methanol and ethanol |
|---------------------------|---------------------------|
12. Write the structural formula of all possible isomers of dichloroethene. Which of them will have zero dipole moment?
13. Give complete reaction when acetamide is reacted with bromine in the presence of potassium hydroxide.
14. Answer the following with suitable equations wherever necessary:-
- (i) How can you prepare benzene from lime ?
  - (ii) How will you convert toluene to *m*-nitrobenzoic acid ?
  - (iii) Suggest a reagent to distinguish acetaldehyde from acetone.
  - (iv) What happens when excess chlorine is passed through boiling toluene in the presence of sunlight ?
  - (v) What effect should the following resonance of vinylchloride have on its dipole moment?



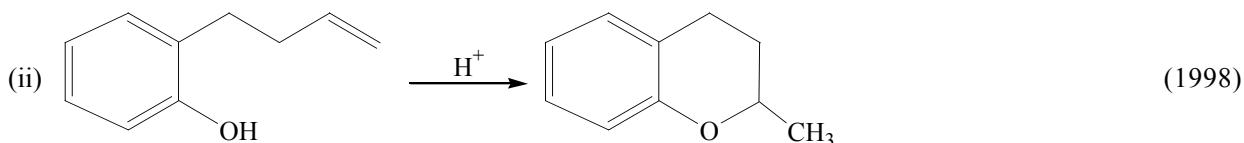
15. Carbon oxygen bond lengths in formic acid are 123 pm and 136 pm and both the carbon oxygen bonds in sodium formate have the same value of 127 pm. Explain (1988)

16. Give a chemical test and the reagents used to distinguish between the following pairs of compounds:

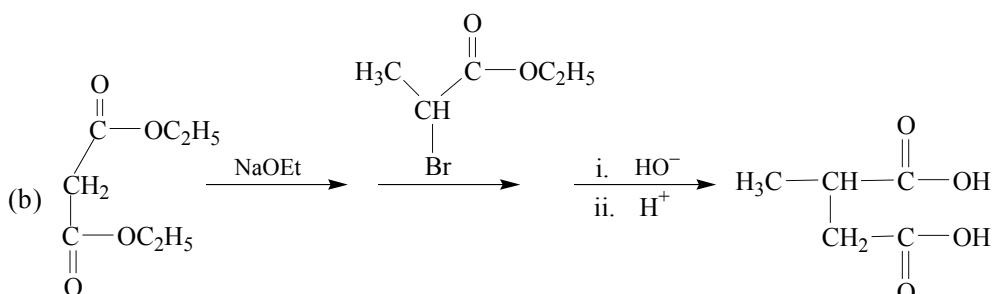
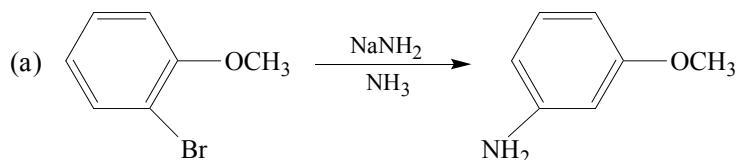
  - (i) Cyclohexane and cyclohexene (ii) Ethylamine and diethylamine. (1988)

17. 2,2-Dimethyloxirane can be cleaved by acid ( $H^+$ ). Write mechanism. (1997)

18. Write the intermediate steps for each of the following reactions.



- 19.** Explain briefly the formation of the products giving the structure of the intermediates.

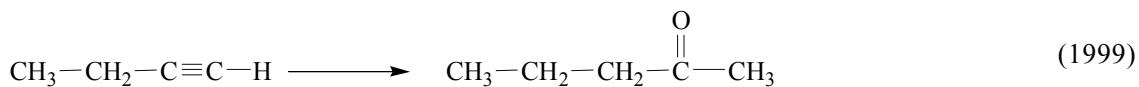


20. There is a solution of *p*-hydroxybenzoic acid and *p*-aminobenzoic acid. Discuss one method by which we can separate them and also write down the confirmatory tests of the functional groups. (2003)

## II. Organic Conversions

1. Aniline to Chlorobenzene (1985)
  2. Acetylene to acetone (1985)
  3. Benzaldehyde to cyanobenzene (1986)
  4. Ethyl alcohol to vinyl acetate (1986)
  5. How will you bring about the following conversions?
    - (i) 4-Nitroaniline to 1,2,3-tribromobenzene.
    - (ii) Ethanal to 2-hydroxy-3-butenoic acid.
    - (iii) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.
  6. Outline a synthesis of *p*-bromonitrobenzene from benzene in two steps. (1990)
  7. How will you bring about the following conversions?
    - (i) 4-Nitrobenzaldehyde from benzene      (ii) Benzamide from nitrobenzene
  8. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)? (1996)
  9. Show the steps to carry out the following transformations.
    - (i) Ethylbenzene → benzene
    - (ii) Ethylbenzene → 2-phenylpropionic acid. (1998)

10. Carry out the following transformation in not more than three steps.

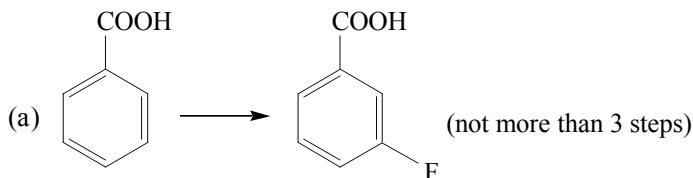


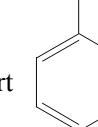
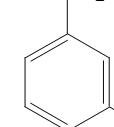
11. How would you bring about the following conversion (in 3 steps)?



12. How would you synthesise 4-methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme. (2001)

13. Convert



14. Convert   $\longrightarrow$   in not more than 4 steps mentioning the reagents, reaction conditions and intermediates in the above conversion. (2004)

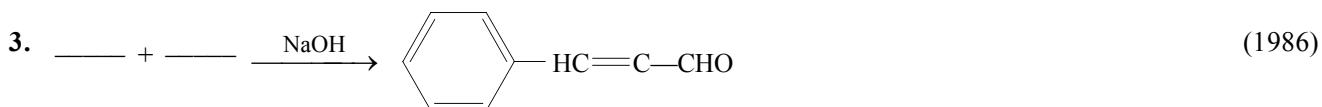
15. Write down the reactions involved in the preparation of the following using the reagents indicated against each in parenthesis

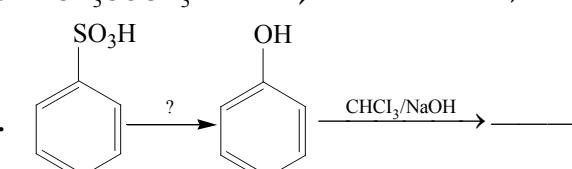
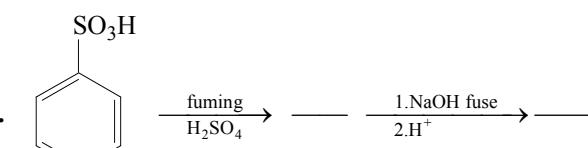
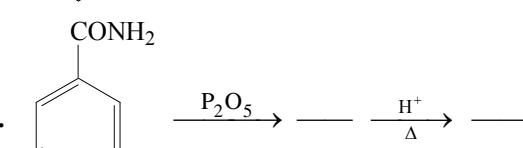
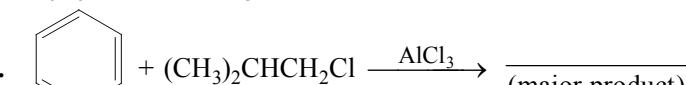
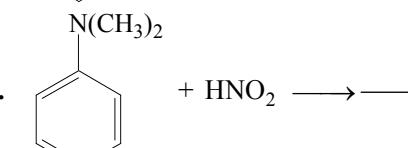
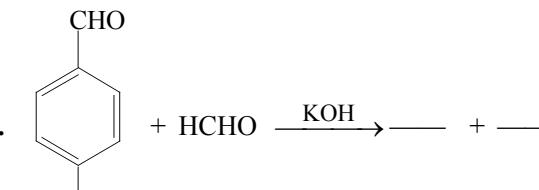
(i) Ethylbenzene from benzene [ $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{PCl}_5$ , anhydrous  $\text{AlCl}_3$ ]

(ii) Propanoic anhydride from propanal [ $\text{AgNO}_3/\text{NH}_4\text{OH}$ ,  $\text{P}_2\text{O}_5$ ]

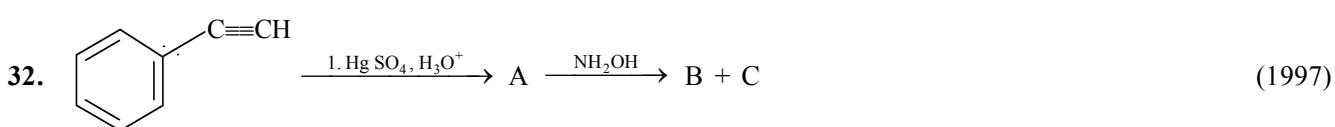
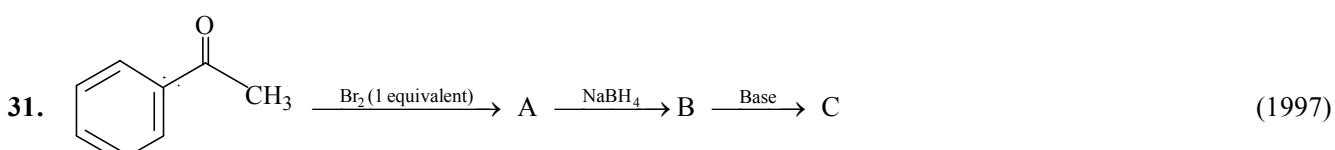
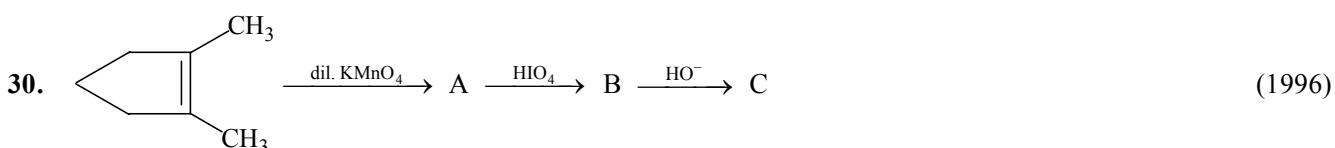
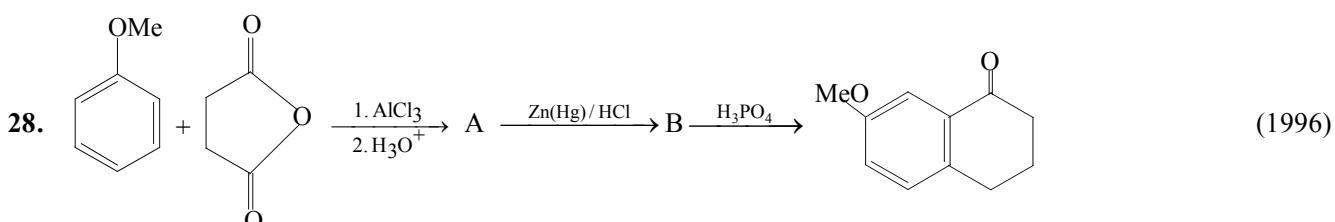
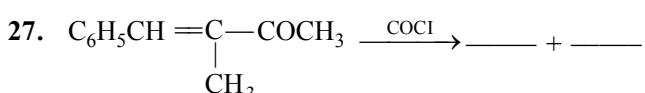
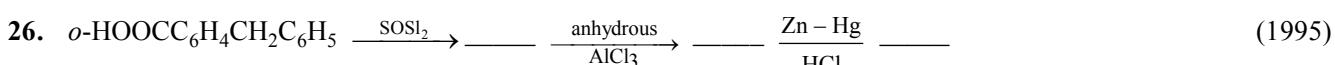
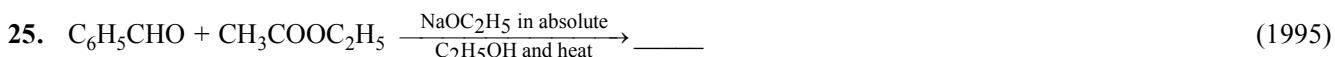
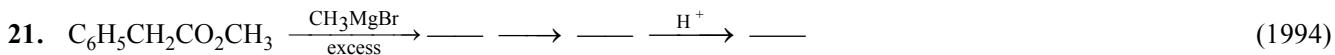
(iii) Acetoxime from acetaldehyde [ $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ,  $\text{Ca(OH)}_2$  and  $\text{NH}_2\text{OH.HCl}$ ] (1984)

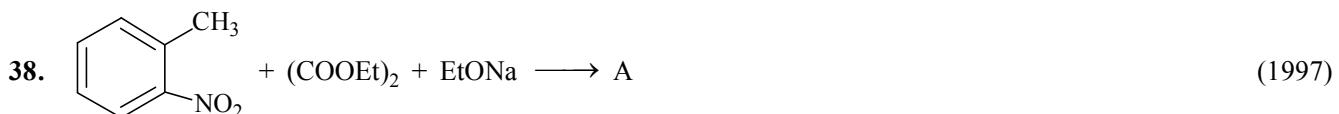
### III. Complete the reactions

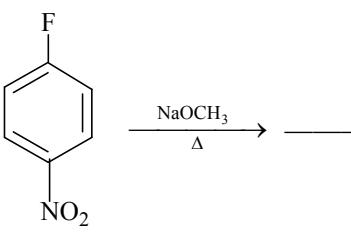
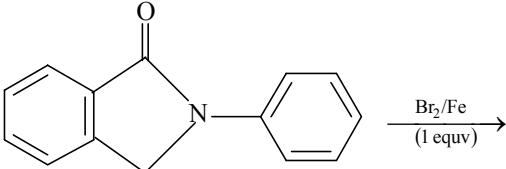
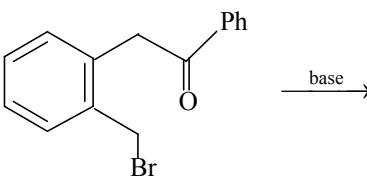
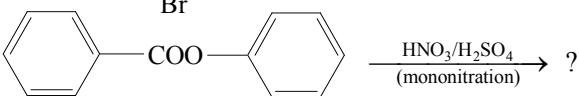
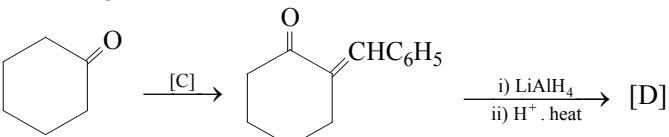
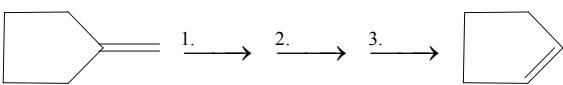
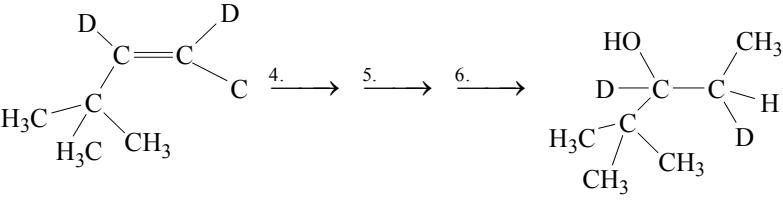
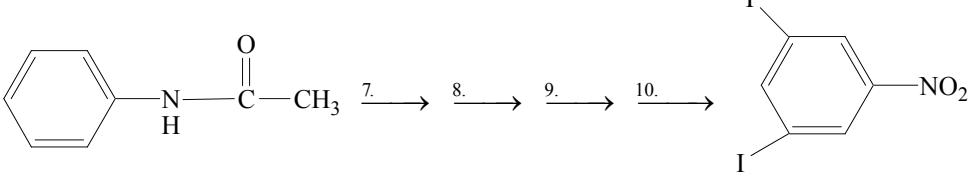


5.  $\text{H}_3\text{CCHO} \xrightarrow{\text{CH}_3\text{MgBr}} ? \xrightarrow{?} \text{H}_3\text{C}-\begin{array}{c} \text{OH} \\ | \\ \text{C}-\text{CH}_3 \\ | \\ \text{H} \end{array}$  (1988)
6.  $\text{CH}_3\text{COOH} \xrightarrow{?} \text{ClCH}_2\text{COH} \xrightarrow[\text{excess}]{\text{NH}_3} ?$  (1988)
7.  $2 \text{CH}_3\text{COCH}_3 \xrightarrow{\text{base}} ? \xrightarrow{\text{acid}} ?$  (1988)
8.  (1988)
9.  $\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{PCl}_5} ? \xrightarrow{\text{NH}_3} ? \xrightarrow{\text{P}_2\text{O}_5} ? \xrightarrow{\text{H}_2/\text{Ni}} ?$  (1991)
10.  $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CHO} \xrightarrow{\text{NaBH}_4} ? \xrightarrow[\text{ZnCl}_2]{\text{HCl}} ? \xrightarrow[\text{H}^+]{\text{KCN}} ?$  (1991)
11.  (1992)
12.  (1992)
13.  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Br})\text{CH}_3 \xrightarrow[\Delta]{\text{KOH (alc)}} ? \xrightarrow{\text{(major product)}} ? \xrightarrow{\text{HBr}} ?$  (1992)
14.  $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5 \xrightarrow[\text{mononitration}]{\text{HNO}_3 / \text{H}_2\text{SO}_4} ?$  (1993)
15.  $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \longrightarrow ? + ?$  (1992)
16.  (1992)
17.  (1992)
18.  (1992)
19.  $(\text{CH}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{CH}_3 \xrightarrow{\text{KOH (alc)}} ?$  (1992)

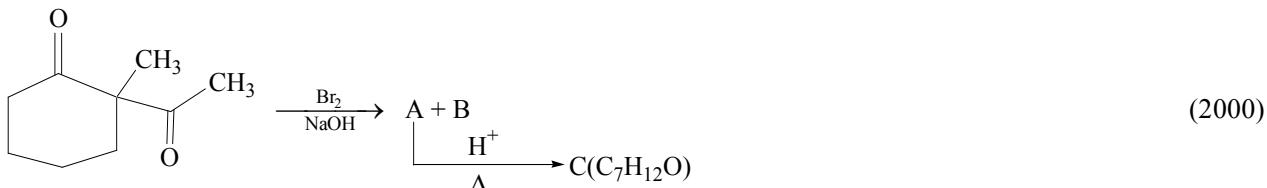
**34.18** IIT Chemistry: Topic-wise Solved Questions



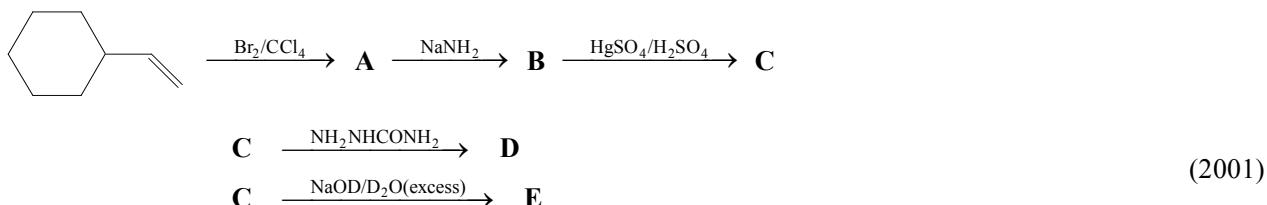


52.  (2000)
53.  (2000)
54.  (2000)
55.  $(CH_3CO)_2O + C_6H_5OH \xrightarrow{\text{base}} \text{?} + \text{?}$  (1982)
56.  $C_6H_5-CH_2-\underset{\substack{| \\ \text{Br}}}{\text{CH}}-\text{CH}_3 \xrightarrow[\text{KOH, } \Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$  (1993)
57.  (1993)
58.  $C_6H_5COOH + CH_3MgI \rightarrow ? + ?$  (1993)
59.  $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} ?$  (1994)
60.  $R-C\begin{array}{c} \diagup \\ \equiv \\ \diagdown \end{array}C-R + HClO_4 \xrightarrow{\text{G}} \text{---}$  (1997)  
 [R = n-Pr]
61.  (1998)
62. 
63. 
64.  (1999)

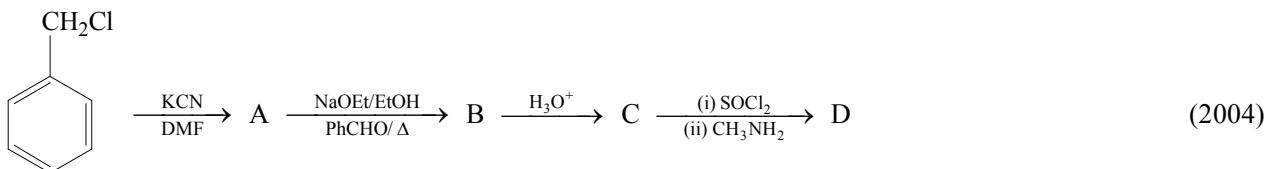
65. Identify A, B and C, and give their structures.



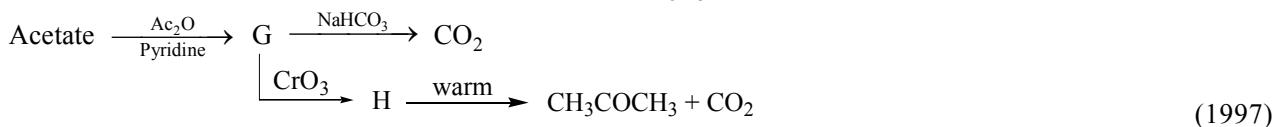
66. Identify **A**, **B**, **C**, **D**, and **E** in the following schemes and write their structures:



67. Identify the compounds A to D in the following reactions.



68. Write down the structure of G and H where G is  $C_4H_8O_3$ .



#### IV. Increasing / Decreasing Characteristics

- Increasing reactivity towards HCN:  $CH_3CHO$ ,  $CH_3COCH_3$ ,  $HCHO$ ,  $C_2H_5COCH_3$  (1985)
- Increasing basicity: *p*-toluidine, *N,N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline. (1986)
- Increasing ease of hydrolysis:  $CH_3COOC_2H_5$ ,  $CH_3COCl$ ,  $(CH_3CO)_2O$ ,  $CH_3CONH_2$  (1986)
- Increasing order of acid strength: (1991)



- Increasing reactivity in nucleophilic substitution reactions:



- Increasing order of expected enol content:  
 $CH_3COCH_2CHO$ ,  $CH_3COCH_3$ ,  $CH_3CHO$ ,  $CH_3COCH_2COCH_3$  (1992)
- Increasing order of boiling point: *n*-butane, *n*-butanol, *n*-butyl chloride, isobutane (1988)
- Increasing order of reactivity towards sulphonation with fuming sulphuric acid:  
benzene, toluene, methoxybenzene, chlorobenzene (1988)
- Increasing order of base strength: methylamine, dimethylamine, aniline, *N*-methylaniline (1988)

#### Subjective Type

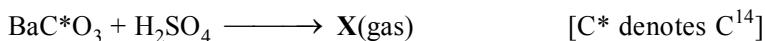
- A sample of gaseous hydrocarbon occupying 1.12 L at STP when completely burnt in air produced 2.2 g of  $CO_2$  and 1.8 g of  $H_2O$ . Calculate the mass of the compound taken and the volume of  $O_2$  at STP required for the burning. Also determine the molecular formula of the hydrocarbon. (1978)

2. A sample of a volatile compound, of 0.220 g, containing carbon, hydrogen and chlorine only, yielded on combustion in oxygen, 0.195 g  $\text{CO}_2$  and 0.0804 g  $\text{H}_2\text{O}$ ; 0.120 g of the compound occupied a volume of 37.24 mL at 105 °C and 768 mmHg pressure. Calculate the molecular formula of the compound. (1978)
3. 5 mL of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 mL) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to STP. Calculate the molecular formula of the hydrogen gas. (1979)
4. An organic liquid (A) containing C, H and O with boiling point 78 °C and possessing a rather pleasant odour, on heating with concentrated sulphuric acid, gives a gaseous product (B) with the empirical formula,  $\text{CH}_2$ . B decolourises bromine water as well as alkaline  $\text{KMnO}_4$  solution and taken up one mole of  $\text{H}_2$  (per mole of B) in the presence of finely divided nickel at high temperature. Identify the substances A and B. (1979)
5. A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. 1 Liter of the vapour of the hydrocarbon, at 127 °C and 1 atm pressure, weighs 2.8 g. Find the molecular formula. (1980)
6. A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, X yields only one organic product Y. On hydrolysis Y yields a new compound Z which can be converted to Y by reaction with red phosphorus and iodine. The compound Z on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds X, Y and Z? Write chemical equations leading to the conversion of X to Y. (1981)
7. One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound  $\text{C}_5\text{H}_{10}\text{Br}_2$ . Substance A on treatment with cold, dilute alkaline potassium permanganate solution forms a compound  $\text{C}_5\text{H}_{12}\text{O}_2$ . On ozonolysis, A gives equimolar quantities of propanone and ethanal. Deduce the structure formula of A. (1981)
8. An alkaline A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid B. When B is treated with bromine in presence of phosphorus, it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D. (1982)
9. An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molar mass is  $121 \text{ g mol}^{-1}$ . Draw two possible structures for this compound. (1982)
10. An organic compound  $\text{C}_x\text{H}_{2y}\text{O}_y$  was burnt with twice the amount of oxygen needed for complete combustion to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983)
11. An alcohol A, when heated with concentrated  $\text{H}_2\text{SO}_4$  gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute  $\text{H}_2\text{SO}_4$  in presence of  $\text{HgSO}_4$ . D can also be obtained either by oxidising A with  $\text{KMnO}_4$  or from acetic acid through its calcium salt. Identify A, B, C and D. (1983)
12. A certain hydrocarbon A was found to contain 85.7% carbon and 14.3% hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.0 g of hydrocarbon A just decolourised 38.05 g of a 5 per cent solution (by mass) of  $\text{Br}_2$  in  $\text{CCl}_4$ . Compound A, on oxidation with concentrated  $\text{KMnO}_4$ , gave compound C (molecular formula  $\text{C}_4\text{H}_8\text{O}$ ) and compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of A and deduce the structures A, B and C. (1984)

13. A white precipitate was formed slowly when silver nitrate was added to compound A with molecular formula  $C_6H_{13}Cl$ . Compound A on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes B and C, having formula  $C_6H_{12}$ . The mixture of B and C on ozonolysis, furnished four compounds: (i)  $CH_3CHO$ , (ii)  $C_2H_5CHO$ , (iii)  $CH_3COCH_3$  and (iv)  $H_3C—CH—CHO$ . What are the structures of A, B and C?
- $\begin{array}{c} | \\ CH_3 \end{array}$  (1986)
14. A liquid X, having a molecular formula  $C_6H_{12}O_2$  is hydrolysed with water in the presence of an acid to give a carboxylic acid, Y, and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z? (1986)
15. An unknown compound of carbon, hydrogen, and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molar mass of  $86\text{ g mol}^{-1}$ . It does not reduce Fehling's solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures? (1987)
16. An organic compound A on treatment with acetic acid in presence of sulphuric acid produces an ester B. The compound A on mild oxidation gives C. The compound C with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates A and D. The compound D with phosphorus pentachloride followed by reaction with ammonia gives E. The compound E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E. (1987)
17. An organic compound A, containing C, H, N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. A on boiling with NaOH gives off  $NH_3$  and a salt which on acidification gives a monobasic nitrogen free acid B. The silver salt of B contains 59.67% silver. Deduce the structures of A and B. (1988)
18. A hydrocarbon A (molecular formula  $C_5H_{10}$ ) yields 2-methylbutane on catalytic hydrogenation. A adds HBr (in accordance with Markovnikov's rule) to form a compound B which on reaction with silver hydroxide forms an alcohol,  $C_5H_{12}O$ . Alcohol C on oxidation gives a ketone D. Deduce the structures A, B, C and D and show the reactions involved. (1988)
19. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. The compound Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound, while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z. (1989)
20. *n*-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at STP required to produce 55 g *n*-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. (1989)
21. A ketone A which undergoes a haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms mono-ozonide D. The compound D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B and C. Write down the reactions involved. (1989)
22. The sodium salt of a carboxylic acid, A, was produced by passing a gas, B, into an aqueous solution of caustic alkali at an elevated temperature and pressure. A, on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, C. A sample of 0.4 g of acid C, on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B and C. (1990)
23. Compound A ( $C_6H_{12}O_2$ ) on reduction with  $LiAlH_4$  yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. The latter on catalytic hydrogenation gave C. The compound D was oxidised further to give F which was found to be a monobasic acid (molar mass :  $60.0\text{ g mol}^{-1}$ ). Deduce the structures of A, B, C, D and E. (1990)
24. A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C ( $C_7H_5N$ ) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula  $C_7H_6O_2$ . Identify the compounds A, B, C, D, and E and write their structures. (1990)

25. An organic compound containing C, H and O exists in two isomeric forms A and B. A mass of 0.108 g of one of the isomers gives on combustion 0.308 g of  $\text{CO}_2$  and 0.072 g of  $\text{H}_2\text{O}$ . A is insoluble in NaOH and  $\text{NaHCO}_3$  while B is soluble in NaOH. A reacts with concentrated HI to give compounds C and D. C can be separated from D by the ethanolic  $\text{AgNO}_3$  solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula,  $\text{C}_7\text{H}_5\text{OBr}_3$ . Identify A, B, C, D and E with justification and give their structures. (1991)
26. An organic compound A on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with  $\text{KMnO}_4$  also gives B. The compound B on heating with  $\text{Ca}(\text{OH})_2$  gives E (molecular formula  $\text{C}_3\text{H}_6\text{O}$ ). E does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Identify A, B, C, D and E. (1992)
27. Compound X ( $\text{C}_5\text{H}_8\text{O}$ ) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess  $\text{CH}_3\text{MgBr}$ , 0.42 g of X gives 22.4 mL of  $\text{CH}_4$  at STP. Treatment of X and  $\text{H}_2$  in presence of Pt catalyst followed by boiling with excess HI gives *n*-pentane. Suggest structure of X and write the equations involved. (1992)
28. A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aqueous HCl, and treated with  $\text{NaNO}_2$  solution at 0 °C liberated a colourless, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule. (1993)
29. An organic compound A,  $\text{C}_8\text{H}_6$ , on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A. (1994)
30. An organic compound E ( $\text{C}_5\text{H}_8$ ) on hydrogenation gives compound F( $\text{C}_5\text{H}_{12}$ ). Compound E on ozonolysis gives formaldehyde and 2-keto-propanal. Deduce the structure of compound E. (1995)
31. An organic compound A( $\text{C}_6\text{H}_{10}$ ) on reduction first gives B( $\text{C}_6\text{H}_{12}$ ) and finally C( $\text{C}_6\text{H}_{14}$ ). Compound A on ozonolysis followed by hydrolysis gives two aldehydes D( $\text{C}_2\text{H}_4\text{O}$ ) and E( $\text{C}_2\text{H}_2\text{O}_2$ ). Oxidation of B with acidified  $\text{KMnO}_4$  gives the acid F( $\text{C}_4\text{H}_8\text{O}_2$ ). Determine the structures of the compounds A to F with proper reasoning. (1993)
32. A hydrocarbon A, of the formula  $\text{C}_8\text{H}_{10}$ , on ozonolysis gives compound B( $\text{C}_4\text{H}_6\text{O}_2$ ) only. The compound B can also be obtained from the alkyl bromide, C( $\text{C}_3\text{H}_5\text{Br}$ ) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and also give equations for the reactions. (1996)
33. A compound D( $\text{C}_8\text{H}_{10}\text{O}$ ) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E( $\text{C}_7\text{H}_6\text{O}_2$ ). Write the structures of D, E and explain the formation of E. (1996)
34. An optically active alcohol A( $\text{C}_6\text{H}_{10}\text{O}$ ) absorbs two moles of hydrogen per mole of A upon catalytic hydrogenation and gives a product B. The compound B is resistant to oxidation by  $\text{CrO}_3$  and does not show any optical activity. Deduce the structures of A and B. (1996)
35. One mole of the compound A (molecular formula  $\text{C}_8\text{H}_{12}$ ), incapable of showing stereoisomerism, reacts with only one mole of  $\text{H}_2$  on hydrogenation over Pd. A undergoes ozonolysis to give symmetrical diketone B( $\text{C}_8\text{H}_{12}\text{O}_2$ ). What are the structures of A and B? (1997)
36. A hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When A is oxidised vigorously with  $\text{KMnO}_4$ , a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. (1997)
37. An ester A( $\text{C}_4\text{H}_8\text{O}_2$ ), on treatment with excess methyl magnesium chloride followed by acidification, gives an alcohol B as the sole organic product. Alcohol B, on oxidation with  $\text{NaOCl}$  followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved. (1998)

38. An aldehyde A( $C_{11}H_8O$ ), which does not undergo self aldol condensation, gives benzaldehyde and two moles of B on ozonolysis. Compound B, on oxidation with silver ion gives oxalic acid. Identify the compounds A and B. (1998)
39. Compound A( $C_8H_8O$ ) on treatment with  $NH_2OH \cdot HCl$  gives B and C. B and C rearrange to give D and E, respectively, on treatment with acid. The compounds B, C, D and E are all isomers of molecular formula ( $C_8H_9NO$ ). When D is boiled with alcoholic KOH, an oil F ( $C_6H_7N$ ) separates out. The compound F reacts rapidly with  $CH_3COCl$  to give back D. On the other hand, E on boiling with alkali followed by acidification gives a white solid G( $C_7H_6O_2$ ). Identify A—G. (1999)
40. An organic compound A,  $C_6H_{10}O$ , on reaction with  $CH_3MgBr$  followed by acid treatment gives compound B. The compound B on ozonolysis gives compound C, which in presence of a base gives 1-acetylcyclopentene D. The compound B on reaction with HBr gives compound E. Write the structures of A, B, C and E. Show how D is formed from C. (2000)
41. An organic compound A,  $C_8H_4O_3$ , in dry benzene in the presence of anhydrous  $AlCl_3$  gives compound B. The compound B on treatment with  $PCl_5$  followed by reaction with  $H_2/Pd(BaSO_4)$  gives compound C, which on reaction with hydrazine gives a cyclised compound D( $C_{14}H_{10}N_2$ ). Identify A, B, C and D. Explain the formation of D from C. (2000)
42. Compound ‘X’ containing chlorine, on treatment with strong ammonia gives a solid ‘Y’ which is free from chlorine. ‘Y’ analysed as: C = 49.31%, H = 9.59% and N = 19.18% and reacts with  $Br_2$  and caustic soda to give a basic compound ‘Z’, ‘Z’ reacts with  $HNO_2$  to give ethanol. Suggest structure for ‘X’, ‘Y’ and ‘Z’. (1992)
43. 1,4-Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound X which upon reaction with excess of Mg in dry ether forms Y. Identify the structure of compounds X and Y. (1995)
44. An alkylhalide, X, of formula  $C_6H_{13}Cl$  on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z ( $C_6H_{12}$ ). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. (1996)
45. A hydrocarbon A of the formula  $C_7H_{12}$  on ozonolysis gives a compound B which undergoes aldol condensation giving 1-acetylcyclopentene. Identify A and B. (1997)
46. Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The major product consists of carbon: 42.86%, hydrogen: 2.40%, nitrogen: 16.67% and oxygen: 38.07%. (i) Calculate the empirical formula of the minor product. (ii) When 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84 °C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula.  
(Molal boiling point elevation constant of benzene is  $2.53\text{ K kg mol}^{-1}$ ). (1999)
47. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reacts with ethanol to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of A, B and explain how C is obtained from B. (2001)
48. An alkene A ( $C_{16}H_{16}$ ) on ozonolysis gives only one product B ( $C_8H_8O$ ). Compound B on reaction with  $NaOH/I_2$  yields sodium benzoate. Compound B reacts with  $KOH/NH_2NH_2$  yielding a hydrocarbon C ( $C_8H_{10}$ ). Write the structures of compound B and C. Based on this information two isomeric structures can be proposed for alkene A. Write their structures and identify the isomer which on catalytic hydrogenation ( $H_2/Pd-C$ ) gives a racemic mixture. (2001)
49. Identify X, Y, and Z in the following synthetic scheme and write their structures. Explain the formation of labeled formaldehyde ( $H_2C^*O$ ) as one of the products when compound Z is treated with HBr and subsequently ozonolysis. **Mark the C\* carbon in the entire scheme.**



50. Five isomeric *para*-disubstituted aromatic compounds **A** to **E** with molecular formula  $\text{C}_8\text{H}_8\text{O}_2$  were given for identification. Based on the following observations, give structures of the compounds.

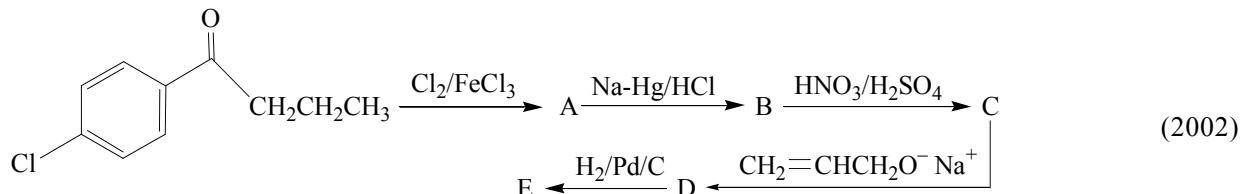
- (i) Both **A** and **B** from a silver mirror with Tollens reagent: also, **B** gives a positive test with  $\text{FeCl}_3$  solution.
- (ii) **C** gives positive iodoform test.
- (iii) **D** is readily extracted in aqueous  $\text{NaHCO}_3$  solution.
- (iv) **E** on acid hydrolysis gives 1,4-dihydroxybenzene. (2002)

51. Identify **X**, **Y** and **Z** in the following synthetic scheme and write their structures.



Is the compound **Z** optically active? Justify your answer. (2002)

52. Write structure of the products **A**, **B**, **C**, **D** and **E** in the following scheme.

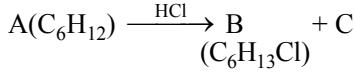


53. A biologically active compound, Bombykol ( $\text{C}_{16}\text{H}_{30}\text{O}$ ) is obtained from a natural source. The structure of the compound is determined by the following reactions.

- (a) On hydrogenation, Bombykol gives a compound **A**,  $\text{C}_{16}\text{H}_{34}\text{O}$ , which reacts with acetic anhydride to give an ester;
- (b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis ( $\text{O}_3/\text{H}_2\text{O}_2$ ) gives a mixture of butanoic acid, oxalic acid and 10-acetoxydecanoic acid.

Determine the number of double bonds in Bombykol. Write the structure of compound **A** and Bombykol. How many geometrical isomers are possible for Bombykol? (2002)

54. In the following reactions, identify the compounds **A** to **G**.



55. (a) An organic compound (**A**),  $\text{C}_5\text{H}_{10}\text{O}$  reacts with dilute  $\text{H}_2\text{SO}_4$  to give the compounds **B** and **C**. Both **B** and **C** give positive iodoform test. The reactivity of organic compound **A** is  $10^{15}$  times more than ethylene with respect to dilute  $\text{H}_2\text{SO}_4$ . (a) Identify the compounds **A**, **B** and **C**.

- (b) Why is the compound **A** much more reactive than ethylene? (2004)

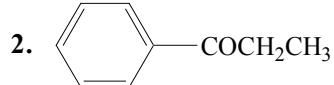
**ANSWERS****Straight Objective Type**

1. (b)      2. (e)      3. (c)      4. (b)      5. (a)      6. (d)  
 7. (a)      8. (a)      9. (a)      10. (a)      11. (a)

**Multiple Correct-Choice Type**

1. (b), (c)

**Fill-in-the-Blanks Type**

1. Aniline                          2.   
 3.  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$                           4.  $\text{CHI}_3$   
 5. Peroxides                                  6. Dipolar ionic or zwitterion

**Integer Answer Type**

1. 4                          2. 4

**Linked-Comprehension Type****Passage 1**

1. (d)      2. (a)      3. (c)

**Passage 2**

1. (b)      2. (a)      3. (d)

**Passage 3**

1. (d)      2. (b)

**Passage 4**

1. (c)      2. (a)

**Passage 5**

1. (b)      2. (a)

**Passage 6**

1. (a)      2. (c)

**Passage 7**

1. (c)      2. (d)

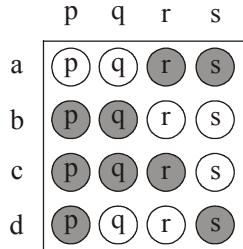
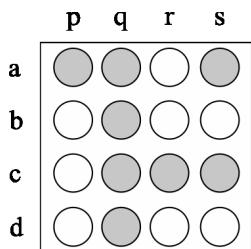
**Matching Type**

1. (a)-(s);      (b)-(t);      (c)-(q);      (d)-(p);      (e)-(r)  
 2. (a)-(u);      (b)-(s);      (c)-(q);      (d)-(r);      (e)-(t);      (f)-(p)  
 3. (a)-(q);      (b)-(r);      (c)-(s);      (d)-(p)  
 4. (a)-(r);      (b)-(p);      (c)-(s);      (d)-(q)

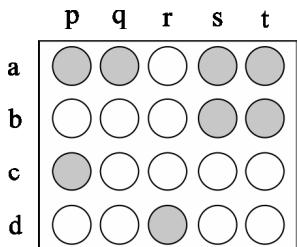
5. Friedel-Crafts; Lewis acid; anhydrous AlCl<sub>3</sub>; Fermentation; yeast; ethanol  
Dehydrohalogenation; alcoholic alkali; alkenes  
Sandmeyer; cuprous chloride; chlorobenzene  
Saponification; oil; soap

6.

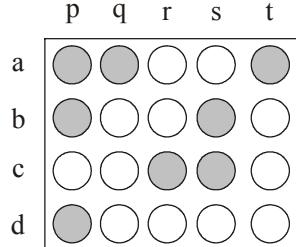
7. The correct-bubbled diagram is as follows.



8. The correct-bubbled diagram is



9. The correct-bubbled diagram is



10. (a) (r), (s); (b) (t); (c) (p), (q); (d) (r)

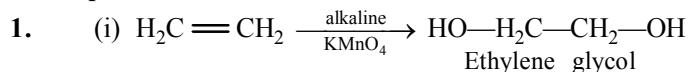
11. (a)

12. (a)

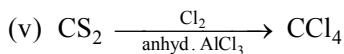
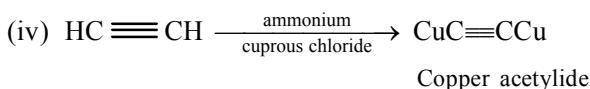
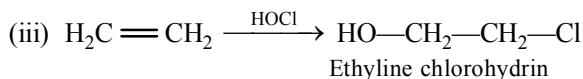
13. (c)

### Short Answer Type

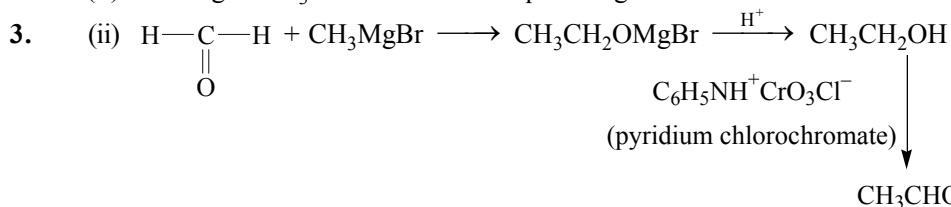
#### I. Descriptive

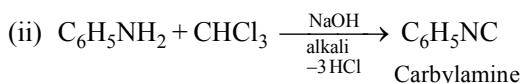
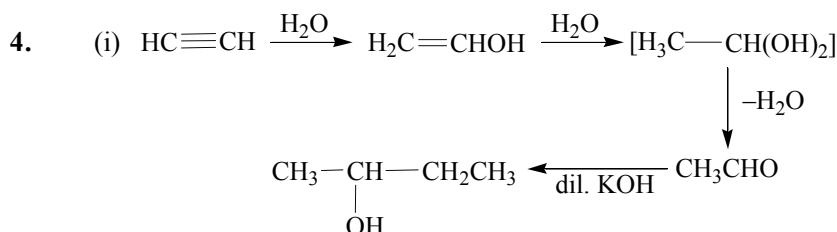
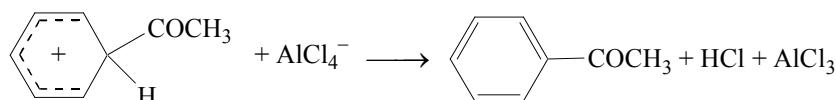
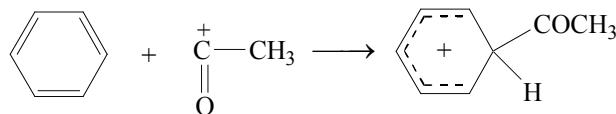
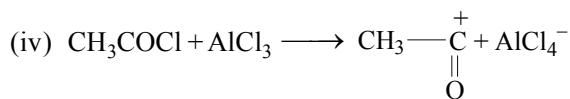


(ii) No reaction

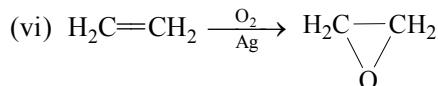
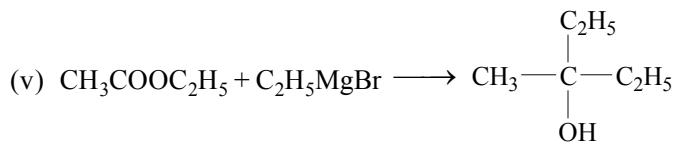
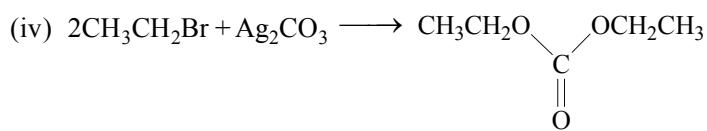
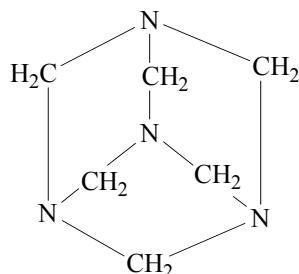


(vi) No reaction

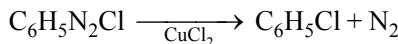
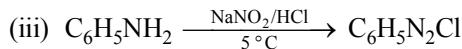
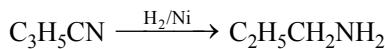
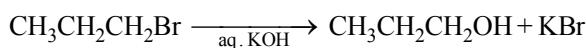
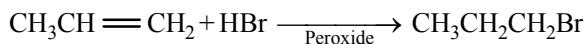
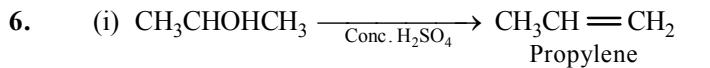
2. (i) Bromine water gets decolourised by C<sub>2</sub>H<sub>2</sub> and not by CH<sub>4</sub>(ii) Heating CHCl<sub>3</sub> with aniline and aq. KOH gives an offensive smell. No such smell is shown by C<sub>2</sub>H<sub>5</sub>OH.



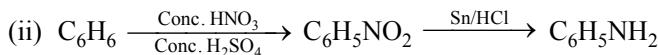
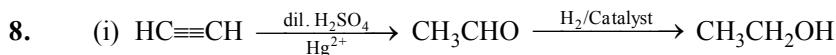
(iii) The main product is urotropine



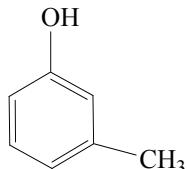
5. Ethanol reacts with sodium

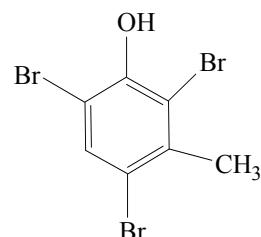


7. (i) Acetic acid has an  $\alpha$ -hydrogen atom while formic acid does not possess  $\alpha$ -hydrogen atom.  
(ii) Chlorination of methane proceeds via free radical mechanism. In the dark, no free radicals from  $\text{Cl}_2$  are obtained.  
(iii) The reaction proceeds via Markownikoff's rule. Because secondary carbonium ion is more stable than the primary carbonium ion.  
(iv) Benzene is resonance stabilized.



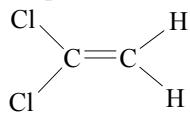
9. Because of hydrogen bondings in butanol, it has much higher boiling point as compared to butanal.

10. The compound is  . On bromination, it gives

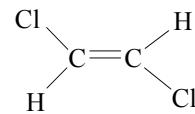


11. (i) 1-Butyne has acidic hydrogen. It reacts with ammoniacal solution of  $\text{AgNO}_3$  to form acetylides. No such hydrogen is present in 2-butyne.  
(ii) Ethanol will give iodoform test while methanol will not show iodoform test.

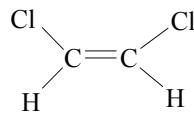
12. The possible isomers



1,1-dichloroethene

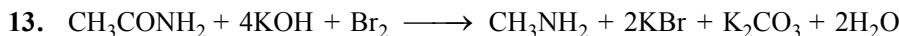


trans-dichloroethene

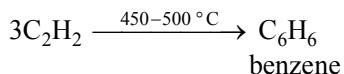
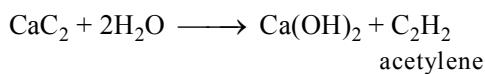
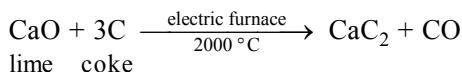


cis-dichloroethene

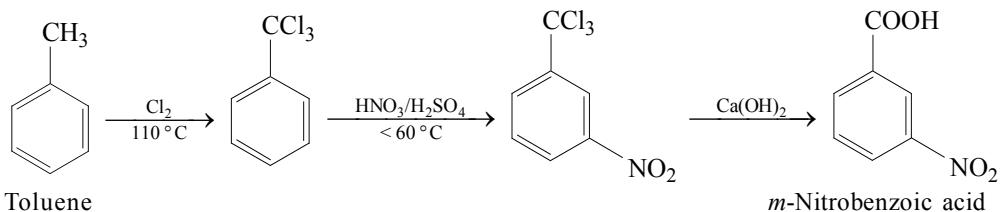
Only trans- dichloroethene will have zero dipole moment.



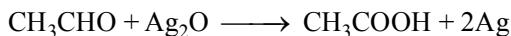
14. (i) Benzene from lime



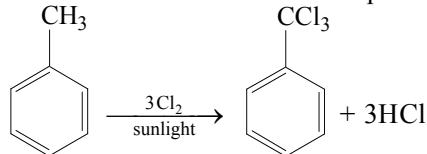
(ii) Toluene to *m*-nitrobenzoic acid



(iii) Tollens reagent (ammoniacal silver nitrate solution) may be used to distinguish acetaldehyde from acetone. Acetaldehyde is oxidised to acetic acid while there is no effect on acetone

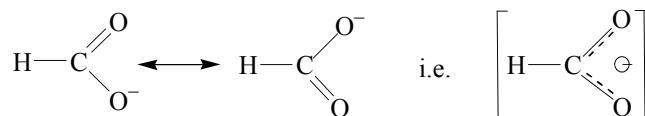


(iv) Benzotrichloride is obtained when chlorine is passed through boiling toluene in the presence of light.



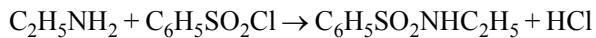
(v) The resonating structure will cause an increase in dipole moment.

15. Unlike formic acid, formate ion involves resonance

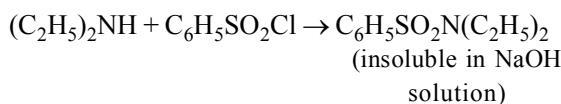


The resonance makes both the C—O bonds in formate of equal length.

16. (i) Cyclohexene contains a double bond whereas cyclohexane is a saturated hydrocarbon. Thus, cyclohexene will decolourise bromine water or Baeyer reagent (alkaline  $\text{KMnO}_4$  solution).
- (ii) Ethylamine is a primary amine whereas diethylamine is a secondary amine. The Hinsberg reagent (benzenesulphonyl chloride) can be used to distinguish these two.



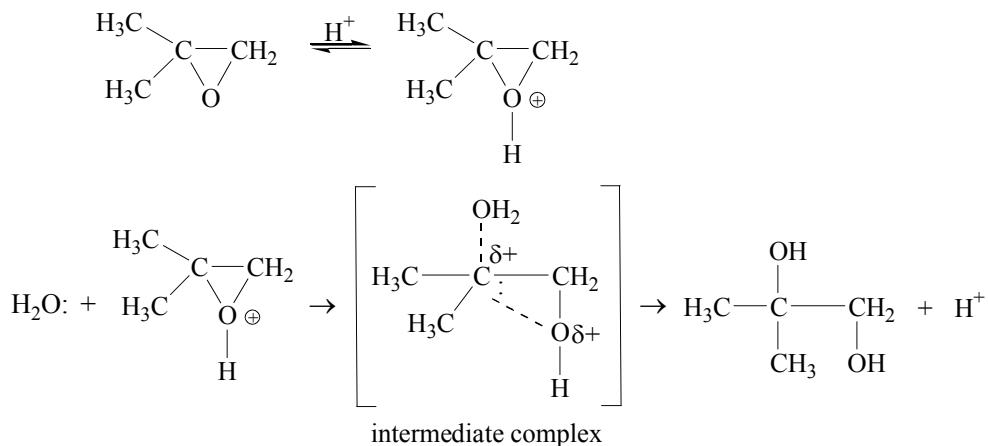
N-ethylbenzene-  
 sulphonamide  
 $\downarrow \text{NaOH}$   
 $\text{C}_6\text{H}_5\text{SO}_2\text{NC}_2\text{H}_5\text{Na}$   
 (water soluble)



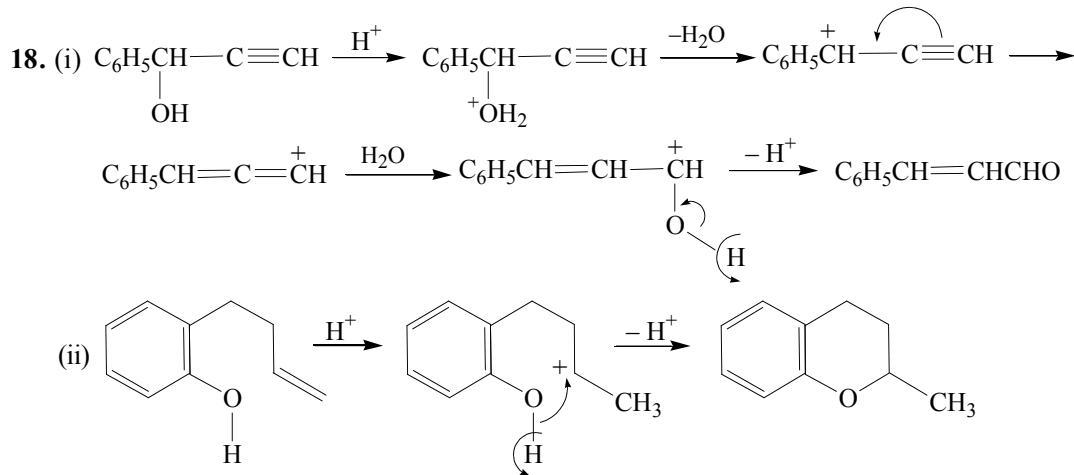
Thus ethylamine forms a complex which is soluble in NaOH solution whereas the complex of diethylamine is insoluble in sodium hydroxide solution.

(Alternatively,  $\text{HNO}_2$  may be used. Ethylamine gives  $\text{N}_2$  gas whereas diethylamine gives yellow insoluble oil.)

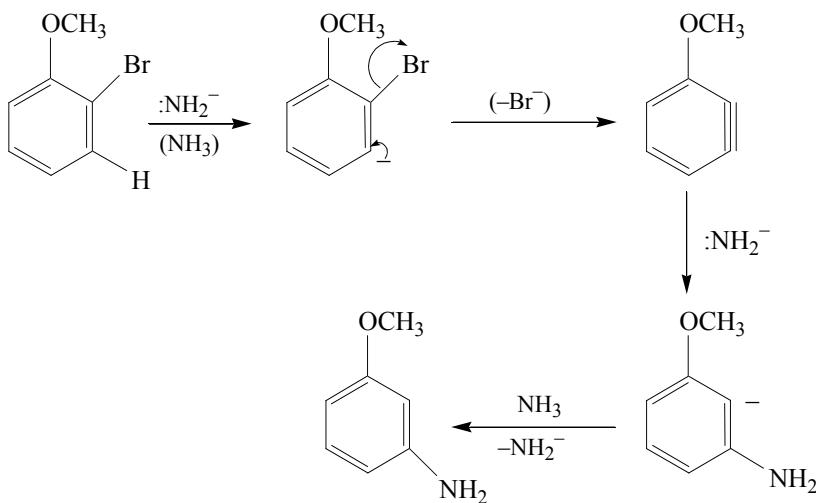
17. The oxirane ring is cleaved via  $S_N2$  mechanism



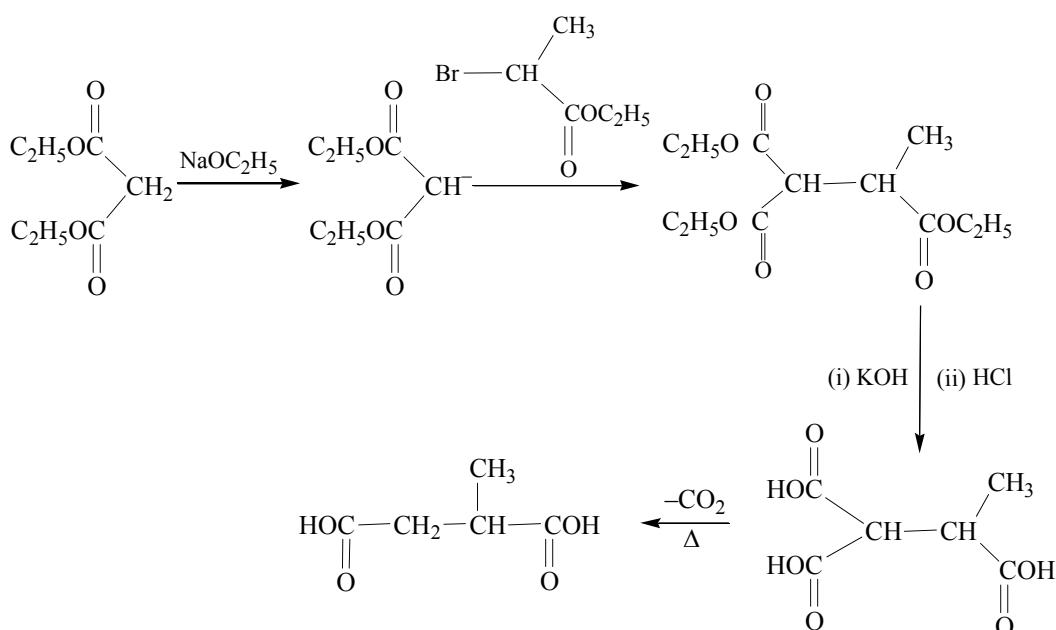
In the transition state, the bond breaking proceeds more than bond making. This is due to the weak carbon-oxygen bond because of the angle strain of the three-membered ring. This bond is further weakened due to the protonation of oxygen. The bond breaking involves the removal of good leaving weakly basic alcoholic hydroxyl group. The nucleophile  $H_2O$  is a poor one and thus bond making which occurs at the position remote from the  $^+OH$  proceeds to the lesser extent. The leaving group and nucleophile being far apart, it is the electronic factor and not the steric factor which decides the position of nucleophilic attack. The carbon which can best accommodate the positive charge becomes the position of attack by the nucleophile.



19. (a) The reaction proceeds via benzyne formation.



(b)

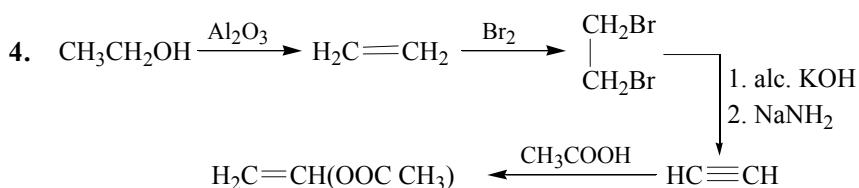
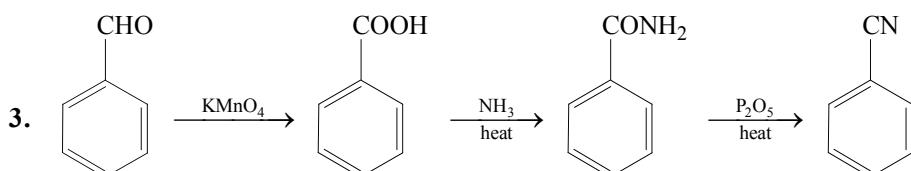
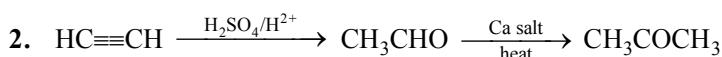
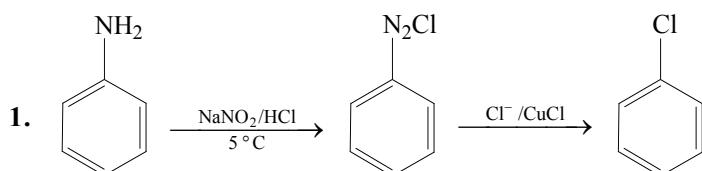


20. The treatment of the solution with hydrochloric acid causes *p*-aminobenzoic acid to dissolve in it while *p*-hydrobenzoic acid remains undissolved. Treating the acid solution with alkali will cause the recovery of *p*-aminobenzoic acid.

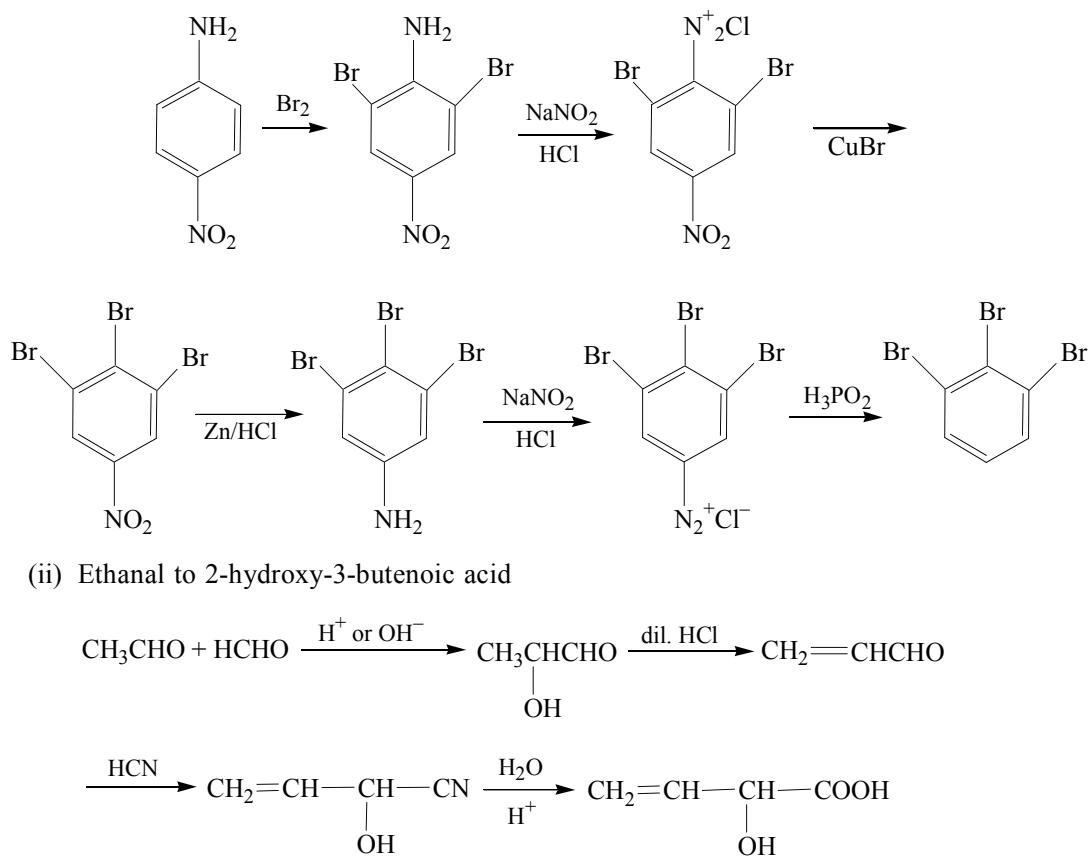
Both the compounds give effervescence with NaHCO<sub>3</sub> indicating the presence of —COOH group. The group —NH<sub>2</sub> can be confirmed by carrying out the azo-dye test or the carbylamine test.

The phenolic —OH group can be confirmed by the FeCl<sub>3</sub> test which gives violet colour.

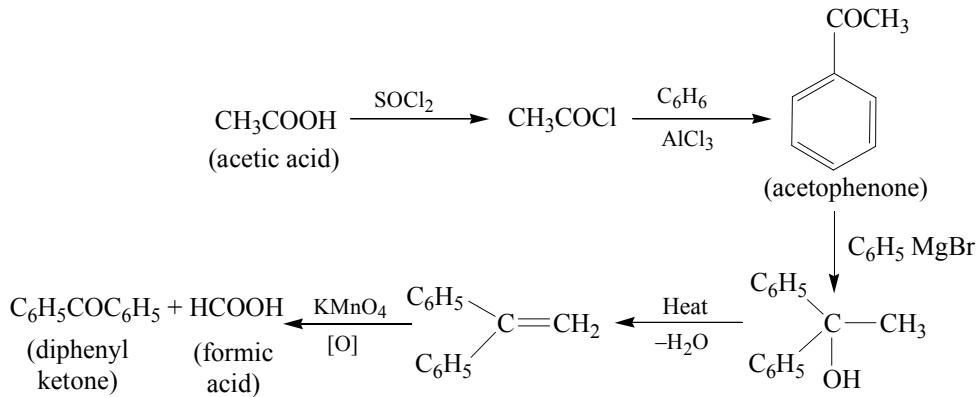
## II. Organic Conversions



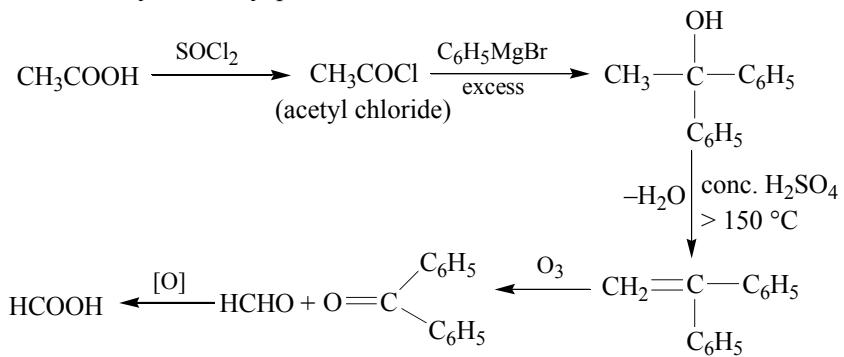
5. (i) 4- Nitroaniline to 1,2,3-tribromobenzene

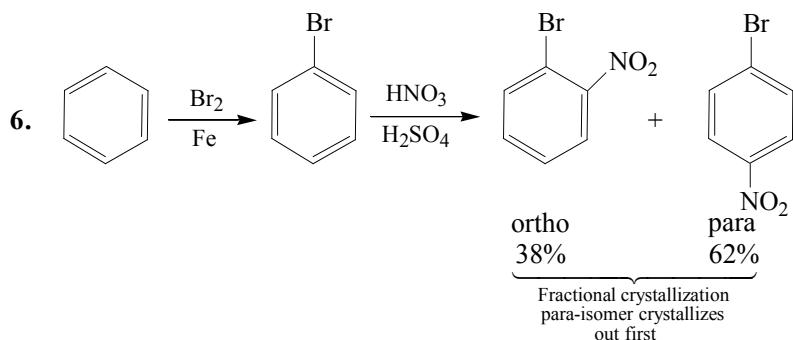


(iii) Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

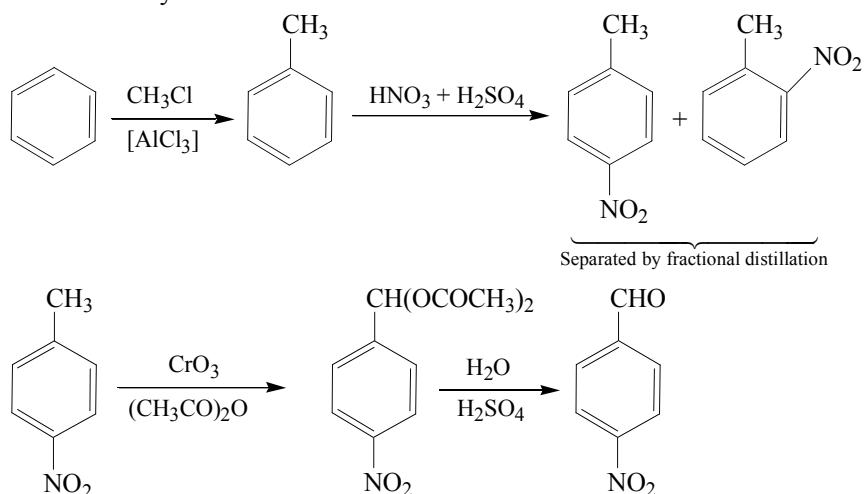


Alternatively, we may proceed as follows.

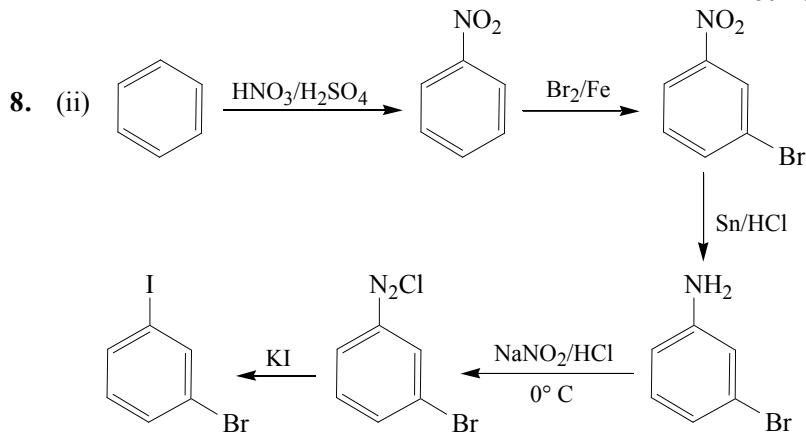
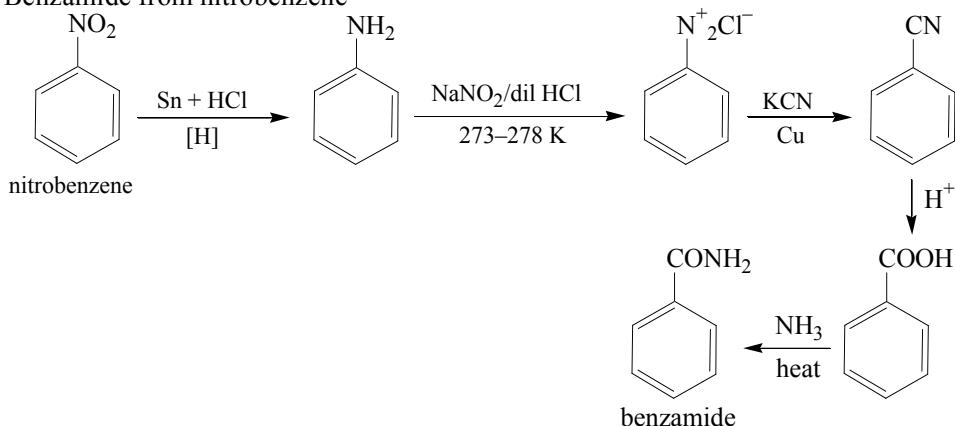




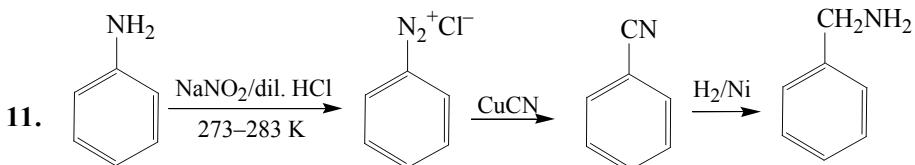
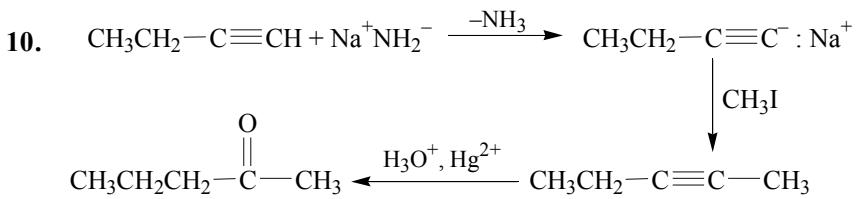
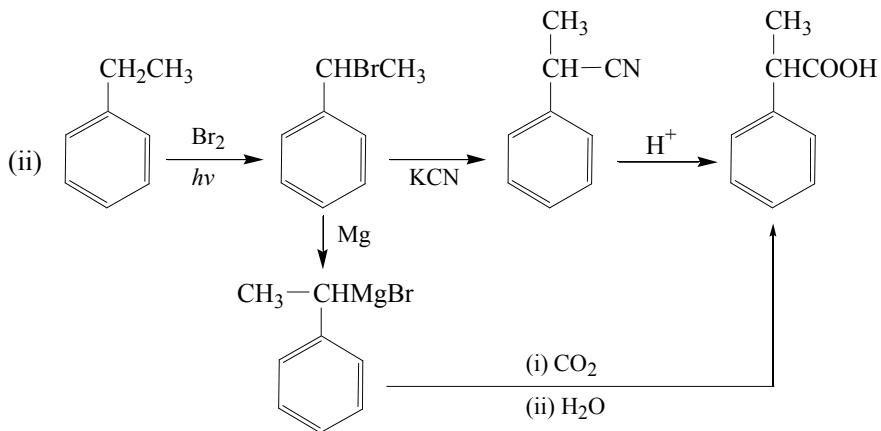
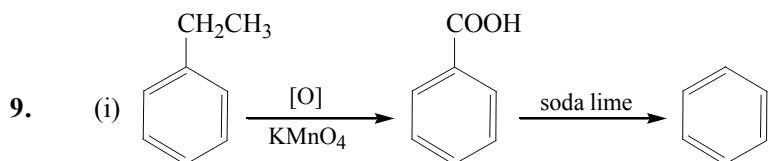
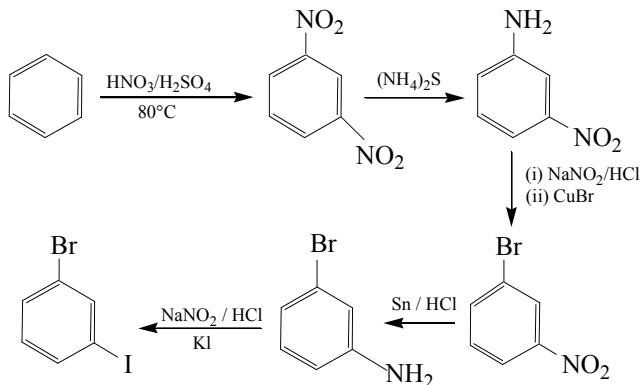
7. (i) 4-Nitrobenzaldehyde from benzene

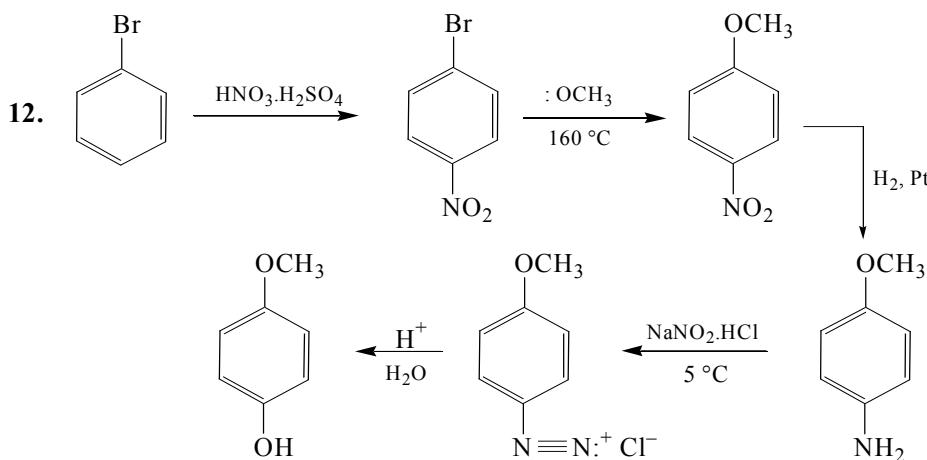


(ii) Benzamide from nitrobenzene

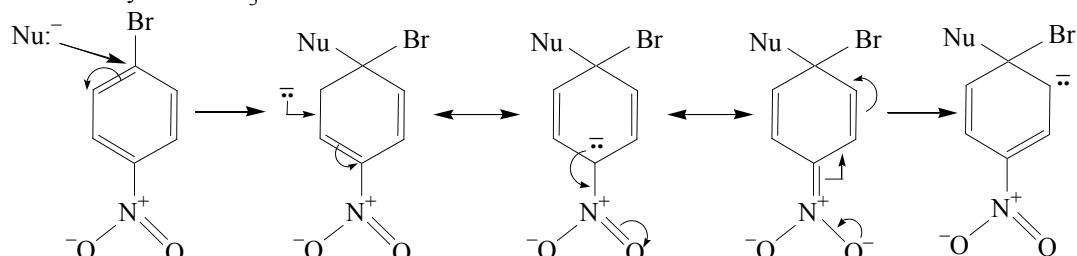


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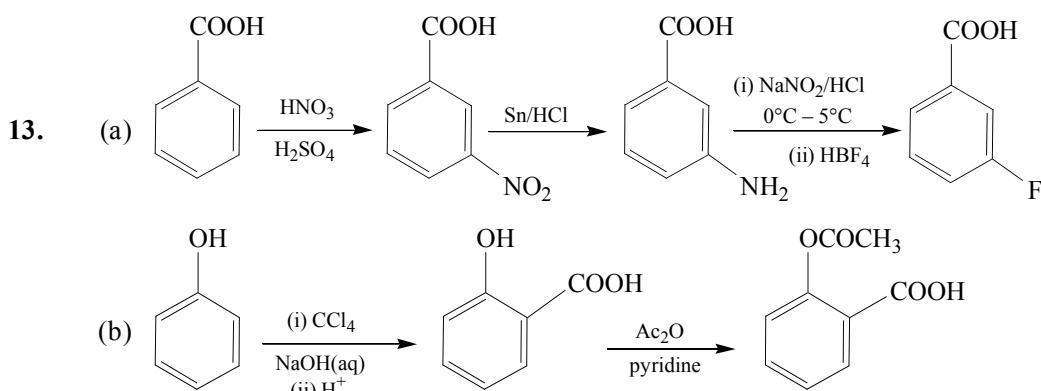




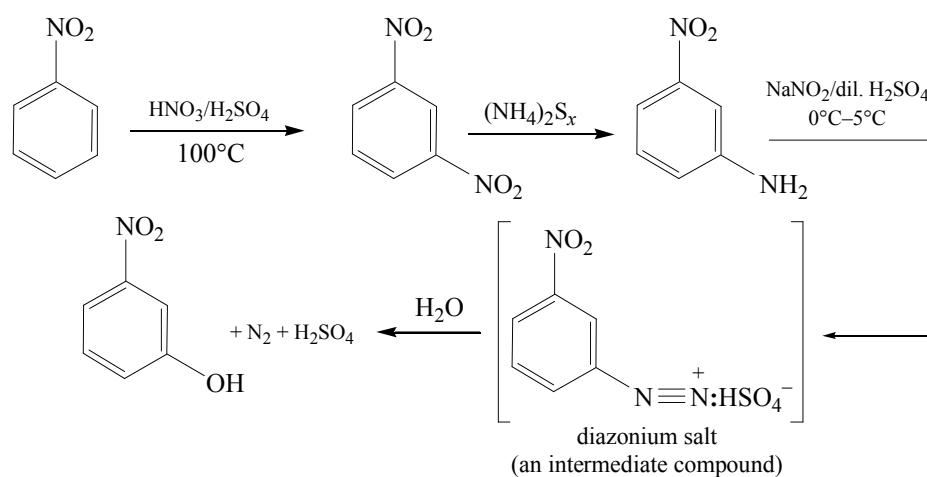
The introduction of  $\text{—NO}_2$  group at *para* position in bromobenzene facilitates the nucleophilic replacement of  $\text{—Br}$  by  $\text{—OCH}_3$ .

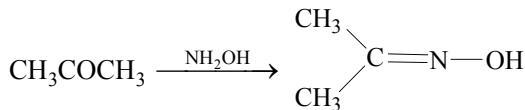
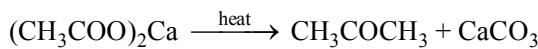
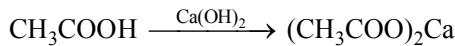
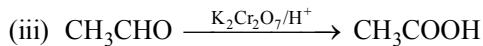
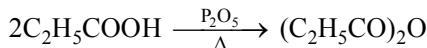
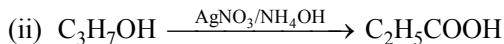
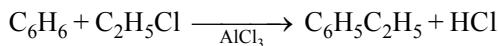


The negative charge is strongly stabilised by resonance involving *para*-nitro group.

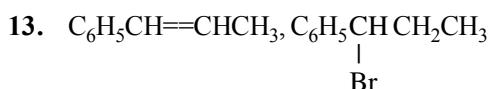
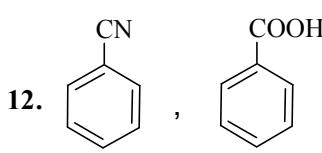
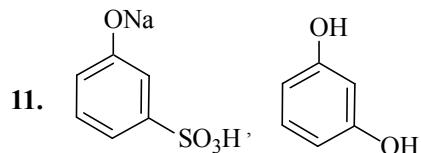
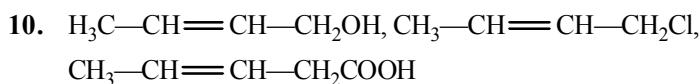
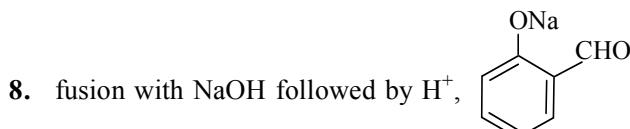
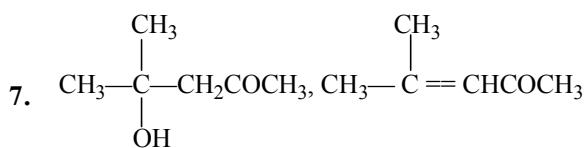
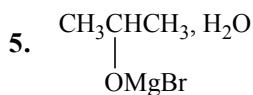
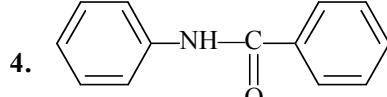
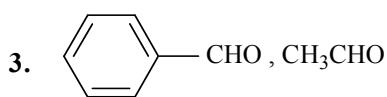
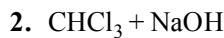


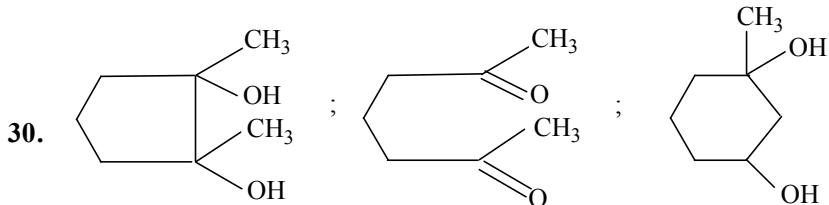
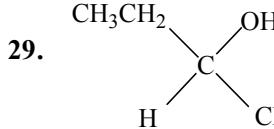
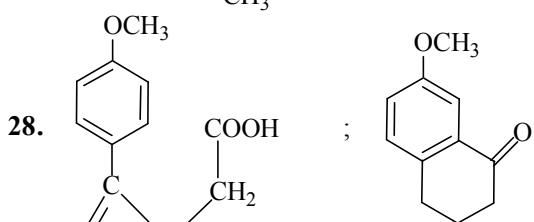
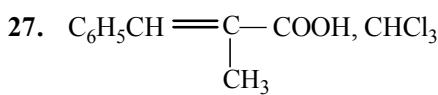
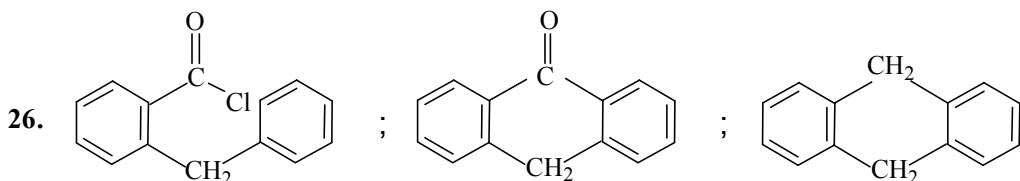
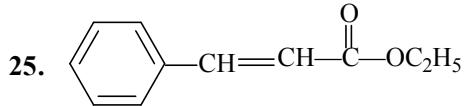
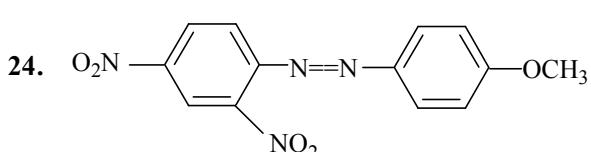
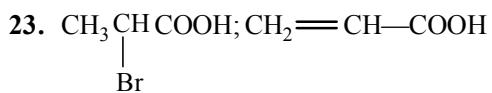
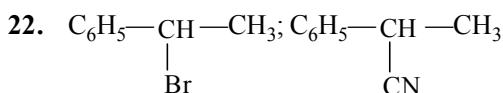
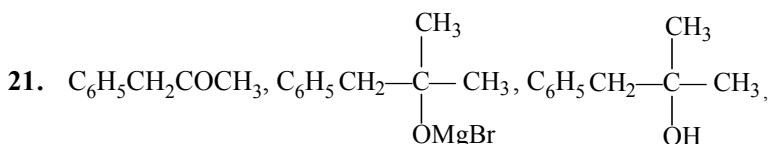
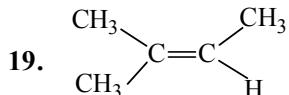
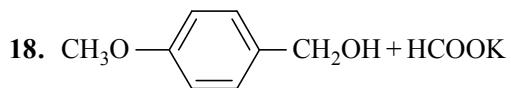
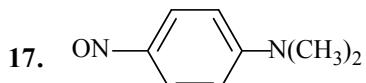
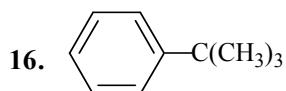
14. The given conversion can be carried out as follows.

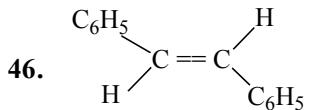
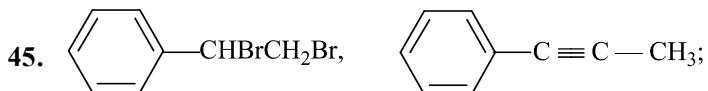
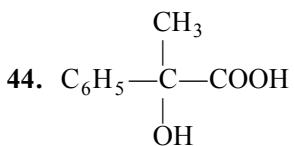
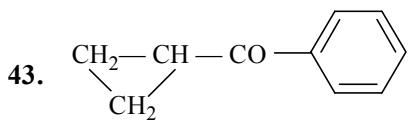
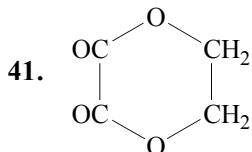
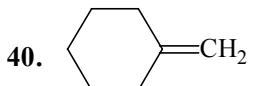
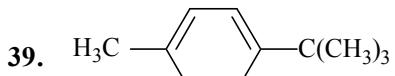
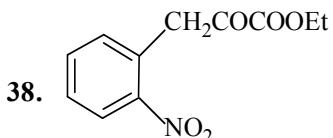
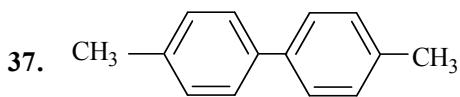
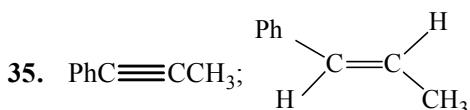
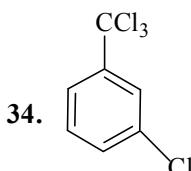
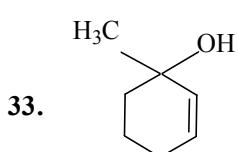
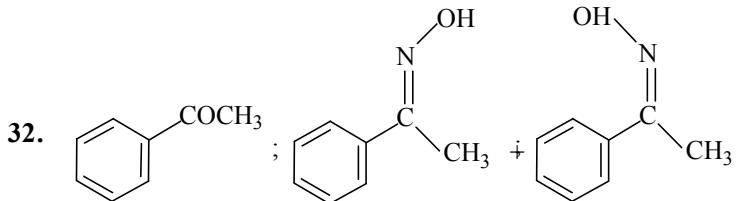
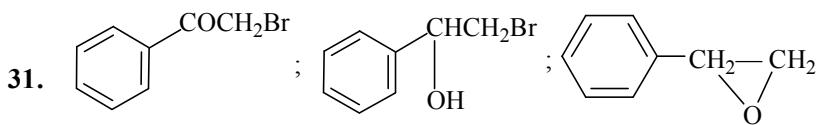


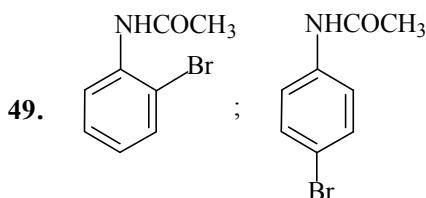


### III. Completing the reactions

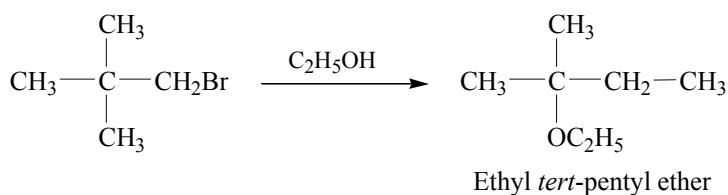




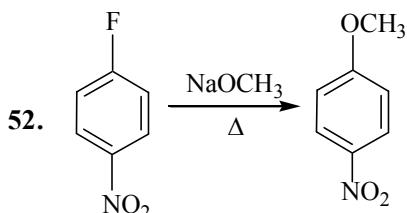
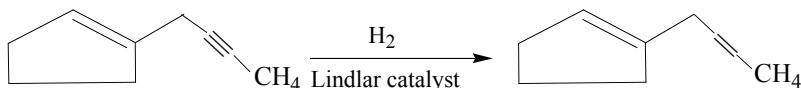




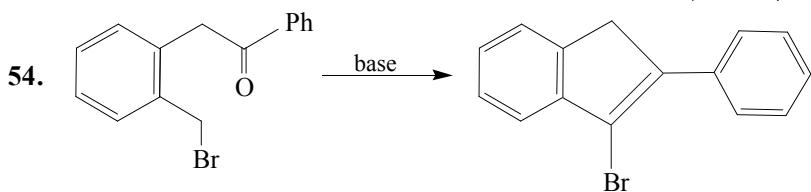
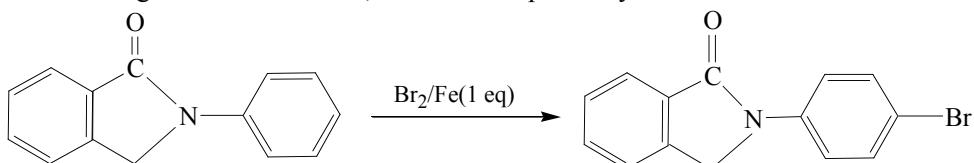
50. The reaction proceeds via S<sub>N</sub>1 mechanism with rearrangement of neopentyl carbocation to *tert*-pentyl carbocation.



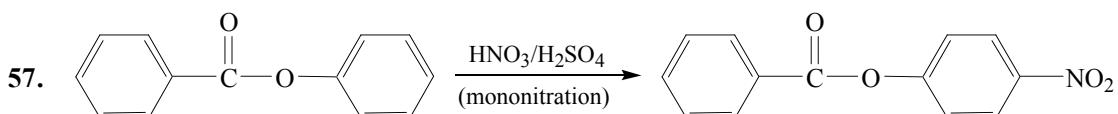
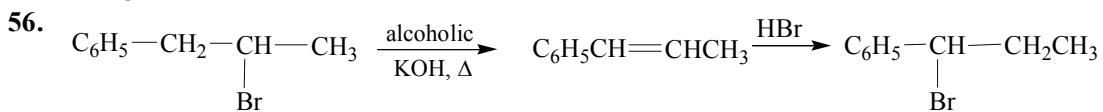
51. In the presence of Lindlar's catalyst (Pd on solid CaCO<sub>3</sub> or BaSO<sub>4</sub>, deactivated with quinoline), a triple bond is reduced to a double bond only.



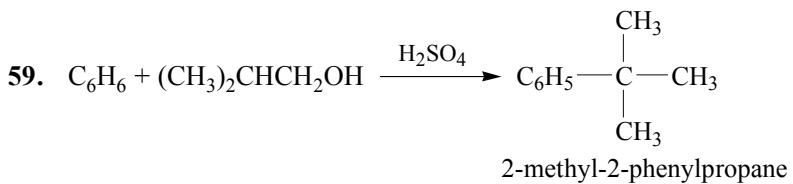
53. The carbonyl group attached to benzene ring deactivates it while the substituted amine group attached to benzene ring activates it. Thus, substitution primarily occurs in the latter benzene ring.



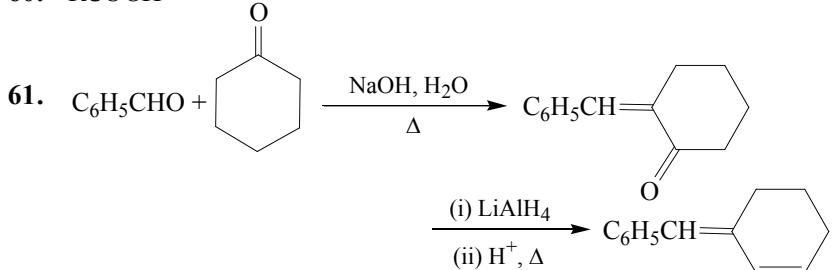
55.  $\text{CH}_3\text{COC}_6\text{H}_5$ ;  $\text{CH}_3\text{COOH}$



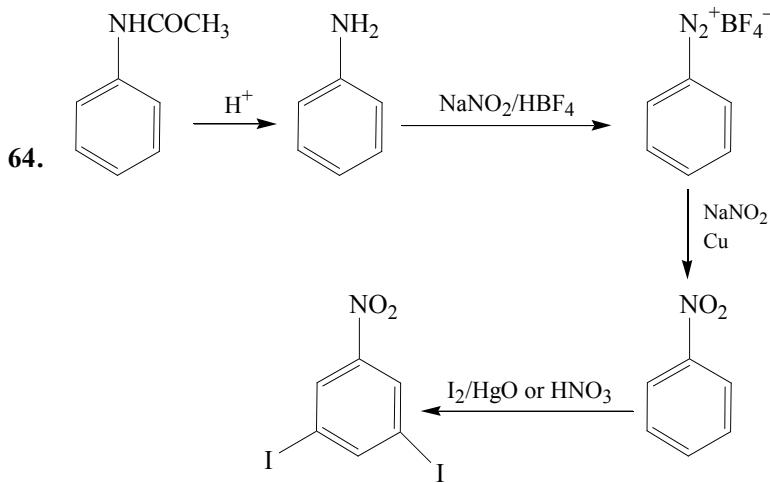
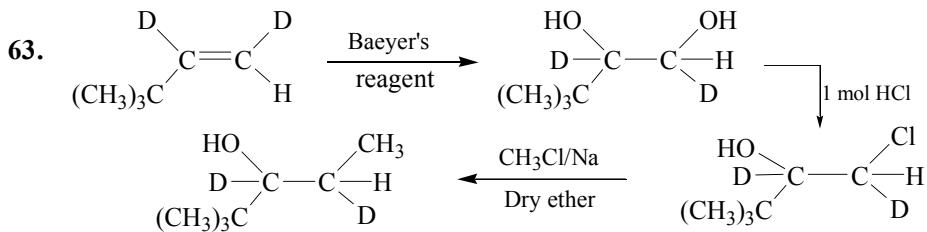
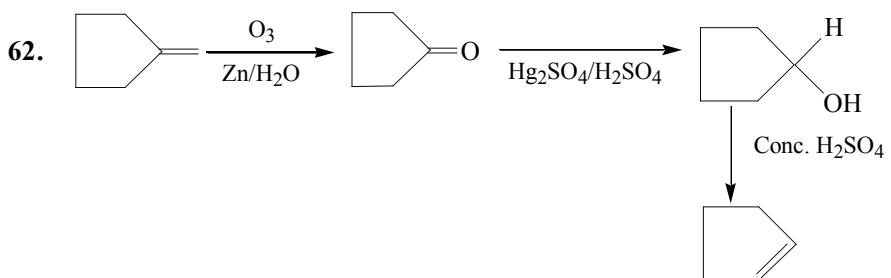
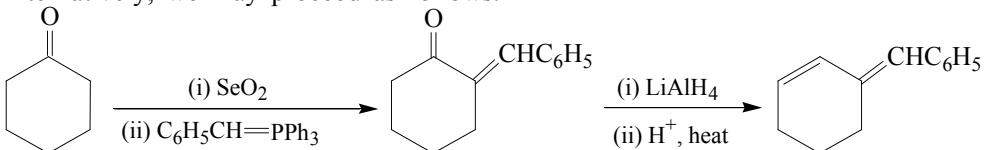
58.  $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \rightarrow \text{CH}_4 + \text{C}_6\text{H}_5\text{COOMgBr}$

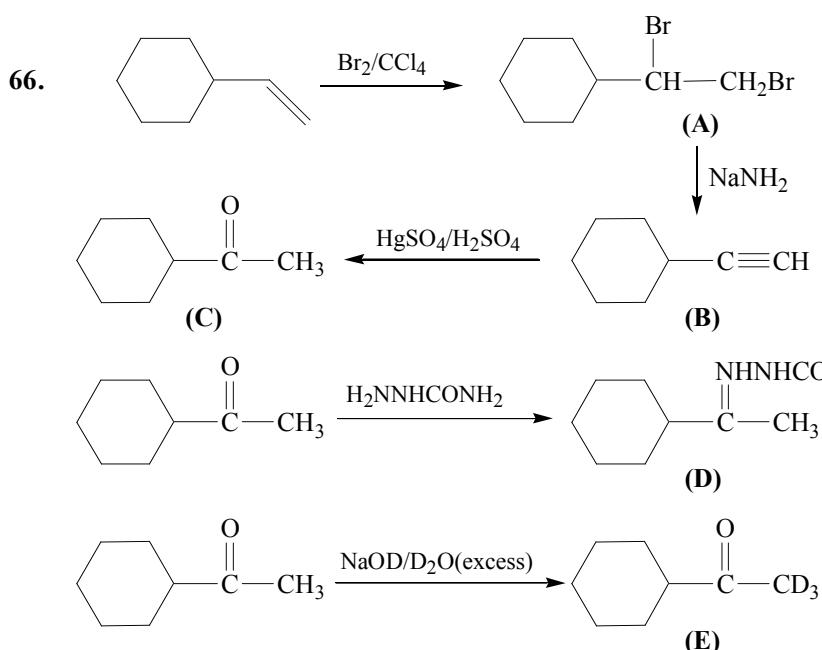
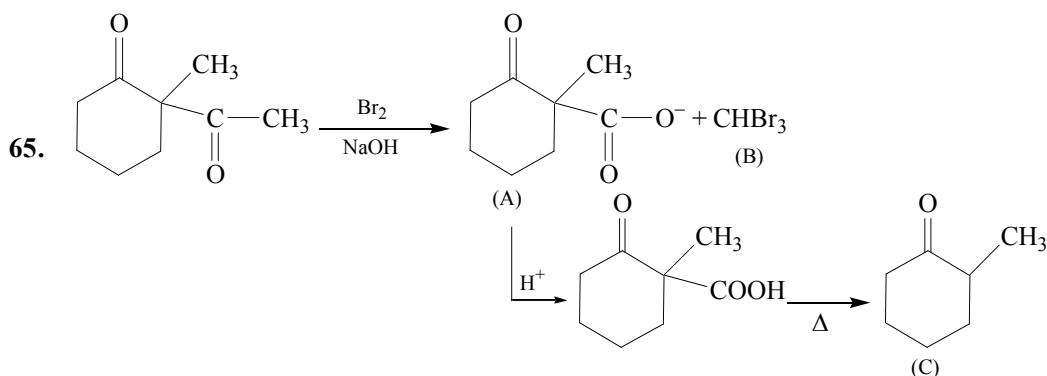


60. RCOOH

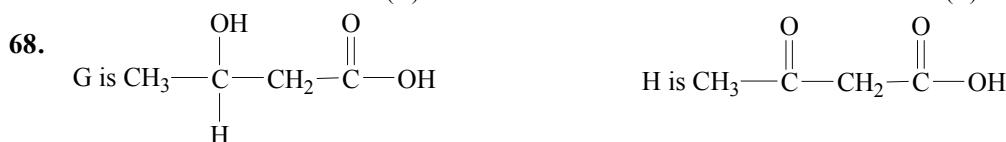
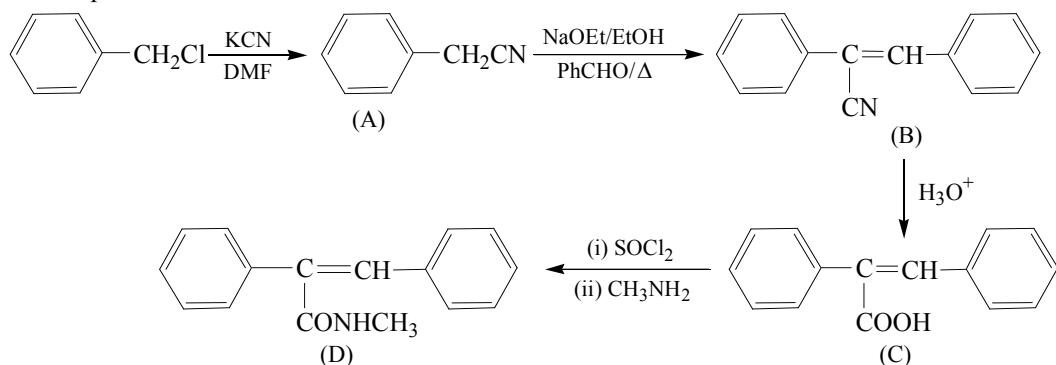


Alternatively, we may proceed as follows.





67. The sequence of reactions is follows.



#### IV. Increasing/Decreasing Characteristics

- $\text{C}_2\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}$

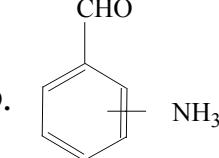
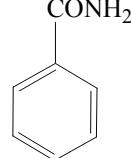
The nucleophilic addition of HCN across carbonyl group is mainly governed by steric factors. Aldehydes generally undergo nucleophilic addition more readily than ketones because alkyl or aryl group causes more crowding in the transition state. Also, an alkyl group releases electrons causing destabilization of the transition state.

2.  $p$ -nitroaniline < aniline <  $p$ -toluidine <  $N, N$ -dimethyl- $p$ -toluidine.

Electron-releasing group enhances the availability of a pair of electrons on nitrogen while electron withdrawing group lowers the availability.

3.  $\text{CH}_3\text{CONH}_2 < \text{CH}_3\text{COOC}_2\text{H}_5 < (\text{CH}_3\text{CO})_2\text{O} < \text{CH}_3\text{COCl}$
4.  $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}_2\text{COOH} < \text{ClCH}_2\text{CH}_2\text{COOH} < \text{CH}_3\text{COOH} < \text{ClCH}_2\text{COOH}$
5.  $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$
6.  $\text{CH}_3\text{CHO} < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{COCH}_3$
7. isobutane < *n*-butane < *n*-butyl chloride < *n*-butanol
8. chlorobenzene < benzene < toluene < methoxybenzene
9. aniline < *N*-methylaniline < methylamine < dimethylamine

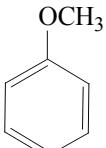
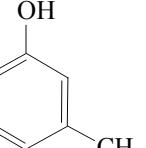
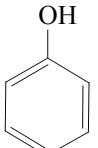
### Subjective Type

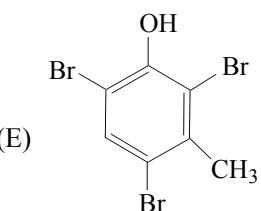
1.  $\text{CH}_4$
2.  $\text{C}_2\text{H}_4\text{Cl}_2$
3.  $\text{C}_2\text{H}_4$
4. (A)  $\text{C}_2\text{H}_5\text{OH}$ ; (B)  $\text{H}_2\text{C}=\text{CH}_2$
5.  $\text{C}_7\text{H}_8$
6. (X)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ ; (Y)  $\text{CH}_3\text{CH}_2\text{I}$ ; (Z)  $\text{CH}_3\text{CH}_2\text{OH}$
7.  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{H}$
8. (A)  $\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}—\text{CH}(\text{CH}_3)—\text{CH}_3$   
 (B)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$   
 (C)  $\text{CH}_3\text{CBr}(\text{CH}_3)\text{COOH}$   
 (D)  $\text{CH}_3\text{COH}(\text{CH}_3)\text{COOH}$
9.  and 
10.  $\text{C}_5\text{H}_{10}\text{O}_5$
11. (A)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ;  
 (B)  $\text{CH}_3\text{CH}=\text{CH}_2$ ;  
 (C)  $\text{CH}_3\text{C}\equiv\text{CH}$ ;  
 (D)  $\text{CH}_3\text{COCH}_3$
12. (A)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$ ;  
 (B)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ ;  
 (C)  $\text{CH}_3\text{COCH}_2\text{CH}_3$
13. (A)  $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}(\text{CH}_3)_2$ ;  
 (B)  $\text{CH}_3\text{CH}=\text{CHCH}(\text{CH}_3)_2$ ;  
 (C)  $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$
14. (X)  $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$ ;  
 (Y)  $\text{CH}_3\text{CH}_2\text{COOH}$ ;  
 (Z)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
15.  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$   
 or  
 $\text{CH}_3\text{COCH}(\text{CH}_3)_2$
16. (A)  $\text{CH}_3\text{OH}$ ;  
 (B)  $\text{CH}_3\text{COOCH}_3$ ;  
 (C)  $\text{HCHO}$ ;  
 (D)  $\text{HCOOH}$ ;  
 (E)  $\text{HCONH}_2$
17. (A)  $\text{CH}_3\text{CH}_2\text{NH}_2$ ;  
 (B)  $\text{C}_2\text{H}_5\text{COOH}$
18. (A)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$ ;  
 (B)  $(\text{CH}_3)_2\text{CHCH}(\text{Br})\text{CH}_3$ ;  
 (C)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})\text{CH}_3$ ;  
 (D)  $(\text{CH}_3)_2\text{CHCOCH}_3$
19. (X)  $\text{C}_2\text{H}_4\text{Cl}_2$ ;  
 (Y)  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ;  
 (Z)  $\text{CH}_3\text{CHCl}_2$
20. 55.54 L

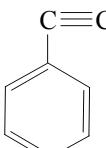
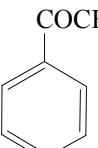
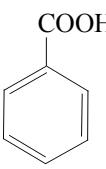
21. (A)  $\text{CH}_3\text{COCH}_2\text{CH}_3$ ;  
 (B)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ ;  
 (C)  $\text{CH}_3\text{CH}=\text{CHCH}_3$

23. (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$ ;

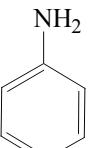
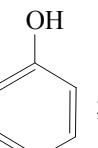
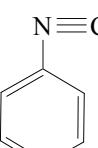
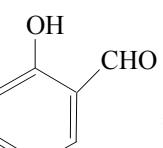
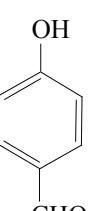
- (B)  $\text{CH}_3\text{CH}_2\text{OH}$ ;  
 (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ;  
 (D)  $\text{CH}_3\text{CHO}$ ;  
 (E)  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

25. (A)  ; (B)  ;  
 (C)  $\text{CH}_3\text{I}$  ; (D)  ;

27. (X)  $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 (E) 

29. (A)  ; (B)  ;  
 (C)  ; (D)  $\text{CHI}_3$

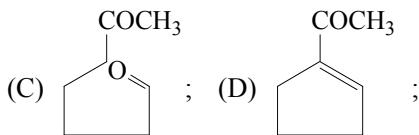
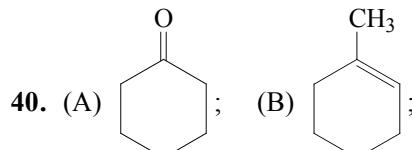
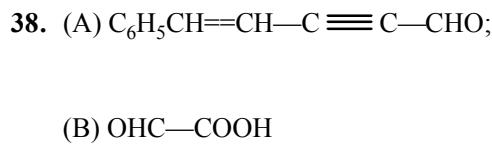
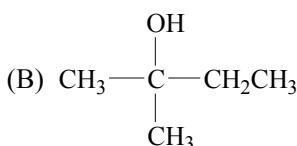
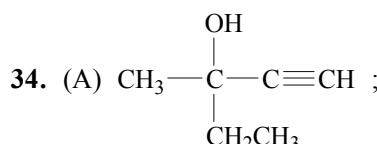
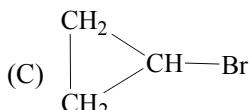
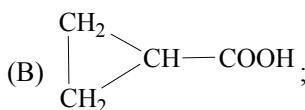
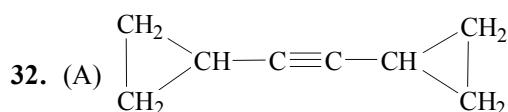
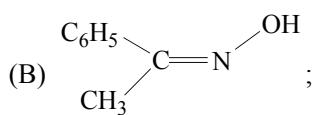
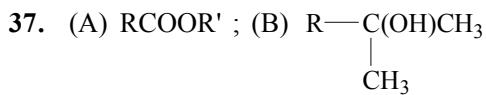
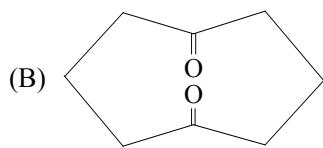
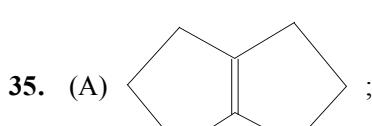
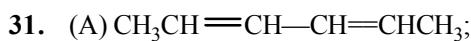
22. (A)  $\text{HCOOH}$ ;  
 (B)  $\text{CO}$ ;  
 (C)  $(\text{COOH})_2$

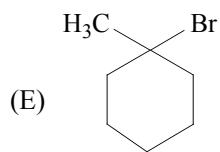
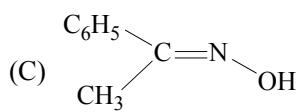
24. (A)  ; (B)  ;  
 (C)  ; (D)  ;  
 (E) 

26. (A)  $(\text{CH}_3\text{CO})_2\text{O}$ ; (B)  $\text{CH}_3\text{COOH}$ ;  
 (C)  $\text{CH}_3\text{COOC}_2\text{H}_5$ ; (D)  $\text{C}_2\text{H}_5\text{OH}$ ;  
 (E)  $\text{CH}_3\text{COCH}_3$

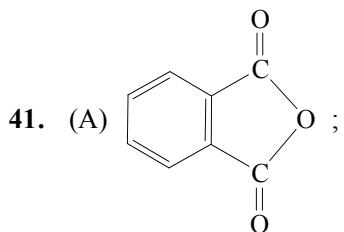
28.  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_3$

30. 2-methyl-1, 3-butadiene

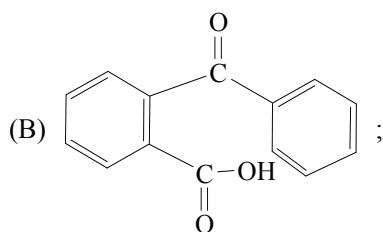




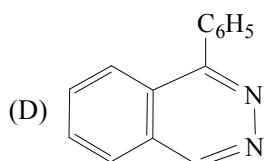
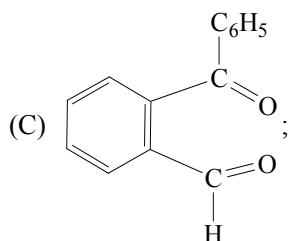
- (D)  $\text{CH}_3\text{CONHC}_6\text{H}_5$ ;  
 (E)  $\text{C}_6\text{H}_5\text{CONHCH}_3$ ;  
 (F)  $\text{C}_6\text{H}_5\text{NH}_2$  ;  
 (G)  $\text{C}_6\text{H}_5\text{COOH}$



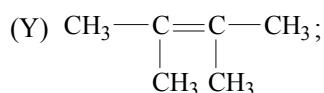
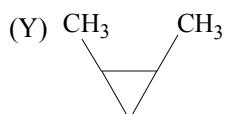
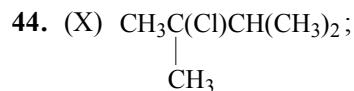
42. (X)  $\text{C}_2\text{H}_5\text{COCl}$ ; (Y)  $\text{C}_2\text{H}_5\text{CONH}_2$ ;



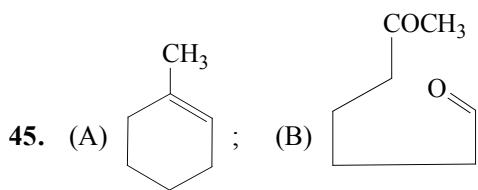
- (Z)  $\text{C}_2\text{H}_5\text{NH}_2$



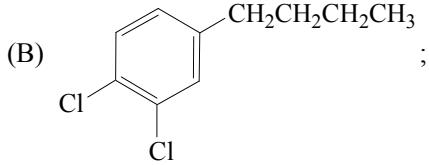
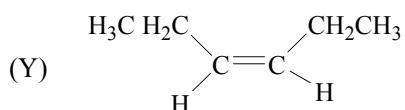
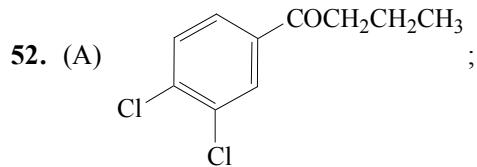
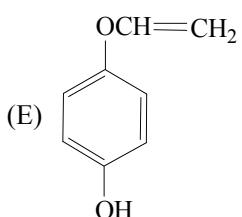
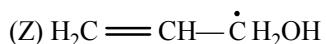
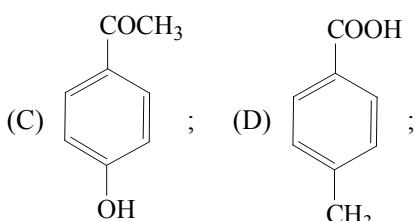
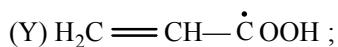
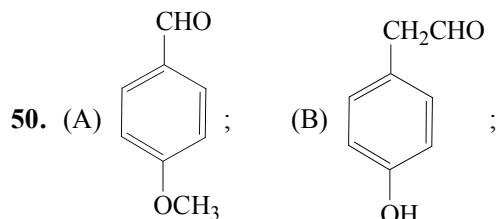
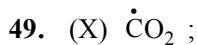
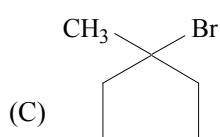
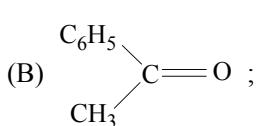
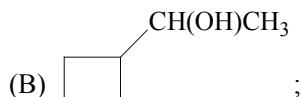
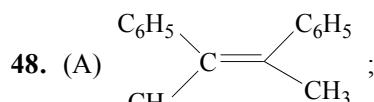
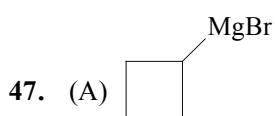
43. (X)  $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ ;

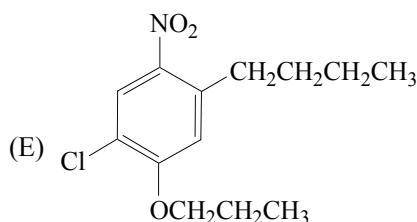
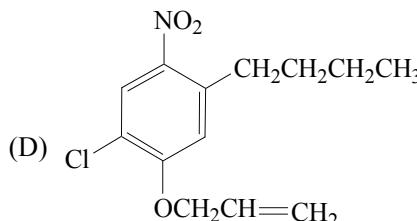
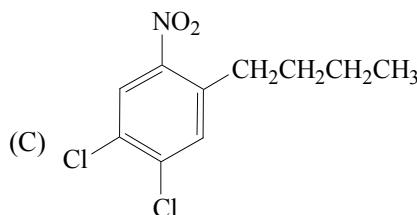
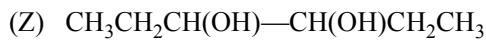


- (Z)  $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$

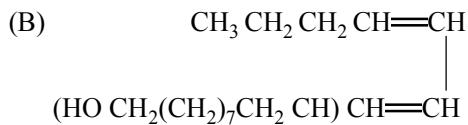


46. 168 g mol<sup>-1</sup>; C<sub>6</sub>H<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>; *m*-dinitrobenzene





53. (A)  $\text{CH}_3\text{CH}_2(\text{CH}_2)_{13}\text{CH}_2\text{OH}$



55. (A)  $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)=\text{CH}_2$ ;

(B)  $\text{CH}_3\text{CH}_2\text{OH}$ ;

(C)  $\text{CH}_3\text{COCH}_3$

54. (A)  $(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$ ;

(B)  $(\text{CH}_3)_3\text{CCH}(\text{CH}_3)_2$

(C)  $(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl}$ ;

(D)  $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$

(E)  $\text{CH}_3\text{COCH}_3$ ;

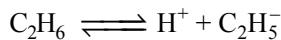
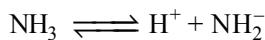
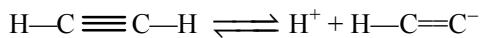
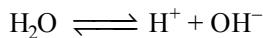
(F)  $(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{CHO}$ ;

(G)  $\text{HCHO}$

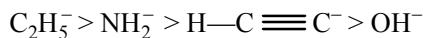
## HINTS AND SOLUTIONS

### Straight Objective Type

5. The decreasing trends of ionization of the species are as follows.

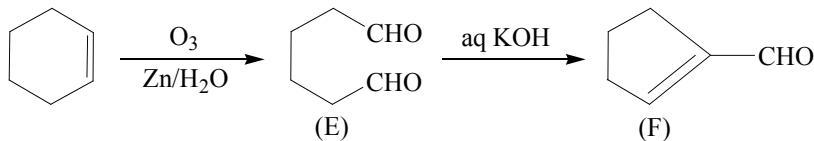


Hence, the conjugate bases follow the reverse order. Thus, the decreasing order of strength of the bases is



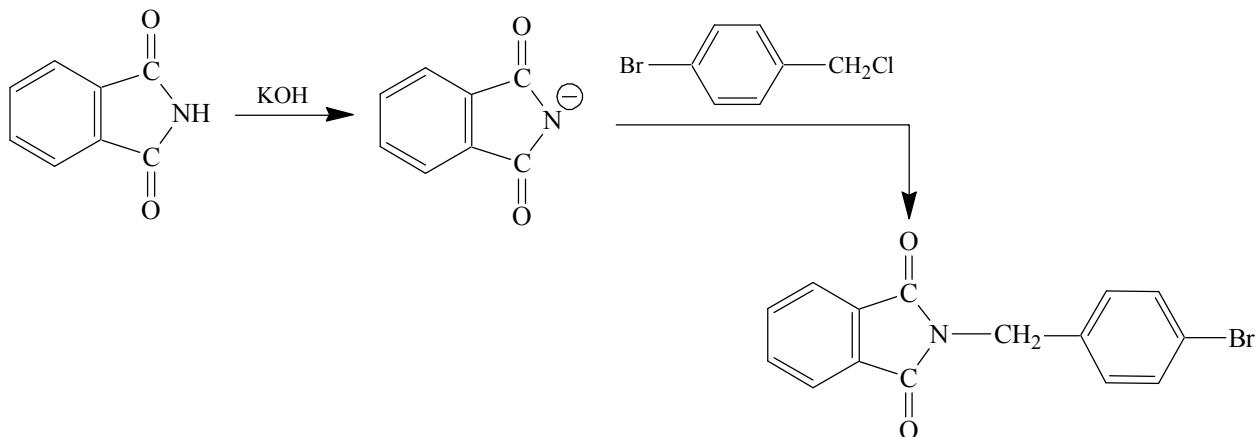
6. In organometallic compounds, a metal is directly attached to carbon.

- 2 mol of  $\text{NaNH}_2$  will be able to abstract two moles of most acidic hydrogens from the molecule. These are from  $-\text{COOH}$  group and  $-\text{OH}$  group from the benzene ring containing  $-\text{NO}_2$  group.
  - The involved reactions are as follows.

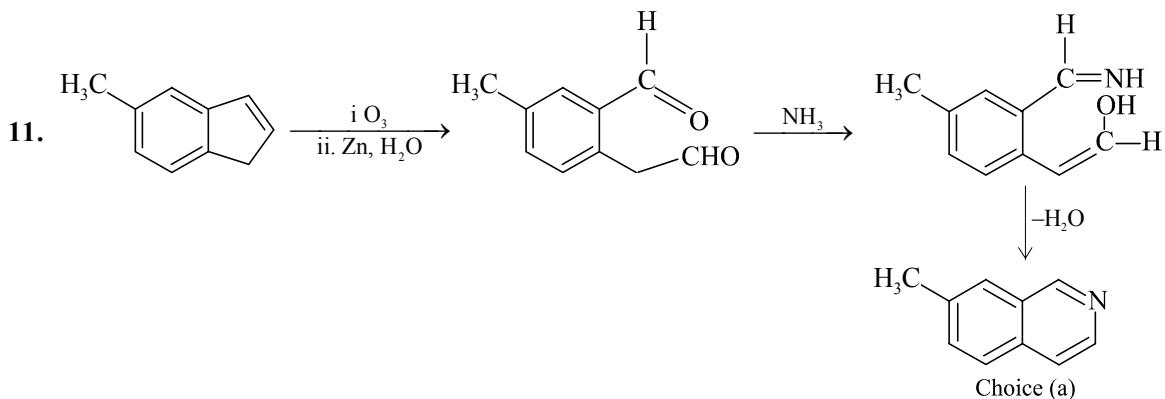


The reaction  $E \rightarrow F$  involves intramolecular aldol condensation followed by dehydration to give  $\alpha$ - $\beta$ -unsaturated aldehyde.

9. The reactions are



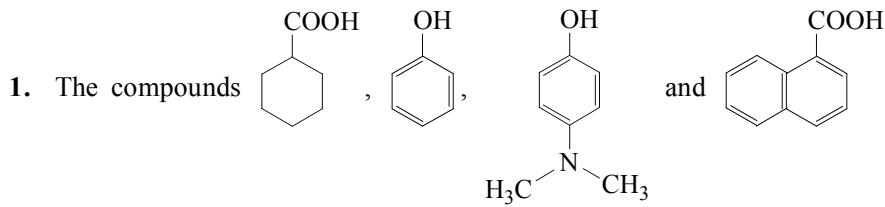
- 10.** Only the group —CH<sub>2</sub>NH<sub>2</sub> is acetylated.



## **Multiple Correct-Choice Type**

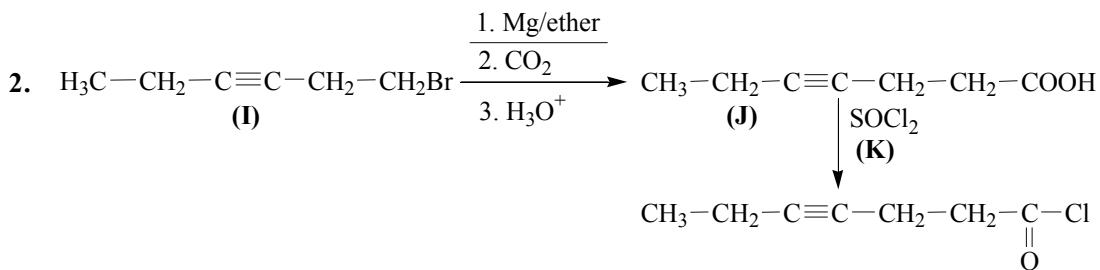
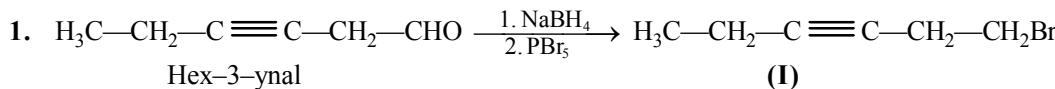
1. Cyclobutadiene (choice b) is an unstable due to much strain in the ring because of the shorter double-bond length and larger deviation from the stable bond angles. This molecule has not been isolated and has only a lifetime shorter than 5s in the free state. Cyclopentadienone (choice c) is also very reactive and has not been isolated. Its life time is about 15s. The cyclopentadiene ring with the formaion of the carbocation at the carbonyl carbon in its resonance structure has an anti-aromatic character due to which it is destabilised. Cycloheptatrienone (choice d) is quite stable due to the aromatic character of the ring with the formation of carbocation at the carbonyl carbon in its resonance structure.

Therefore the **choices (b) and (c)** are correct.

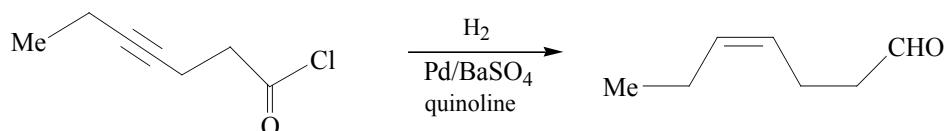
**Integer Answer Type**

are soluble in aqueous NaOH as these carry either phenolic —OH or —COOH group

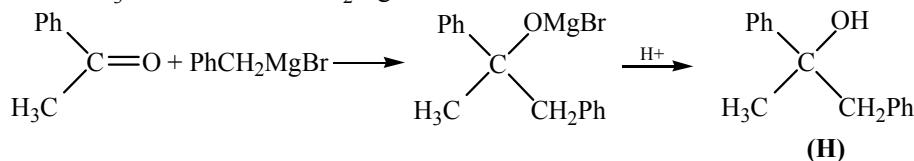
2. In all the **four** reactions, benzaldehyde is produced..

**Linked-Comprehension Type****Passage-1**

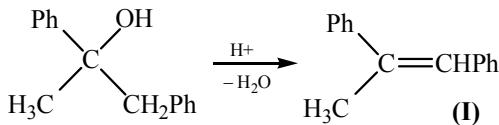
3. The use of Lindlar catalyst leads to *syn* addition. This causes the formation *cis* isomer. Besides this, —COCl is reduced to CHO.

**Passage-2**

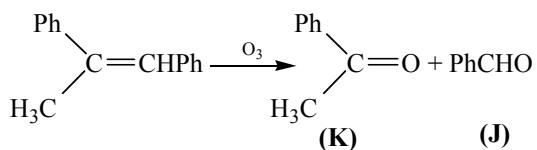
1. A tertiary alcohol (**H**) which can undergo acid catalysed dehydration will be formed when the ketone  $\text{PhCOCH}_3$  reacts with  $\text{PhCH}_2\text{MgBr}$ . The reaction is



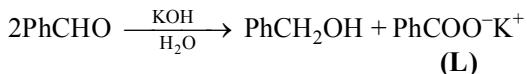
2. The acid catalysed debyration reaction is.



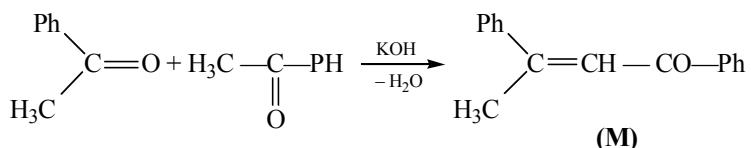
3. The ozonolysis of the compound I is as follows.



The compound J is PhCHO. It undergoes Cannizzaro reaction.

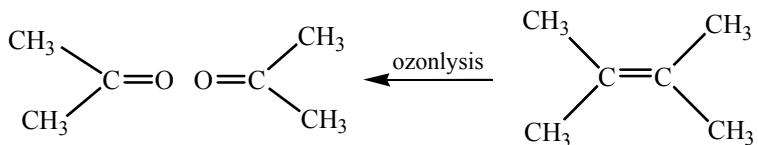


The compound K undergoes aldol condensation.



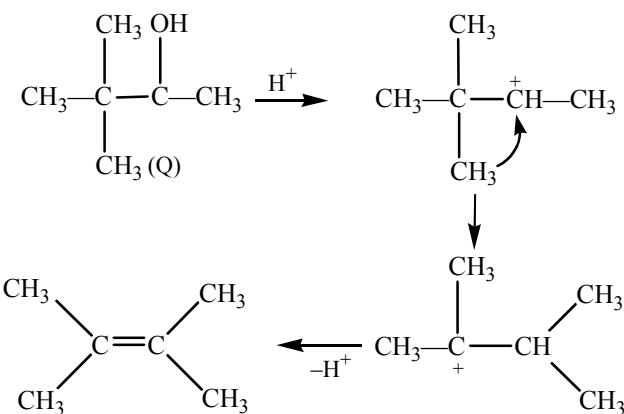
### Passage-3

1. 2. Working the given reactions from the final product, we must have

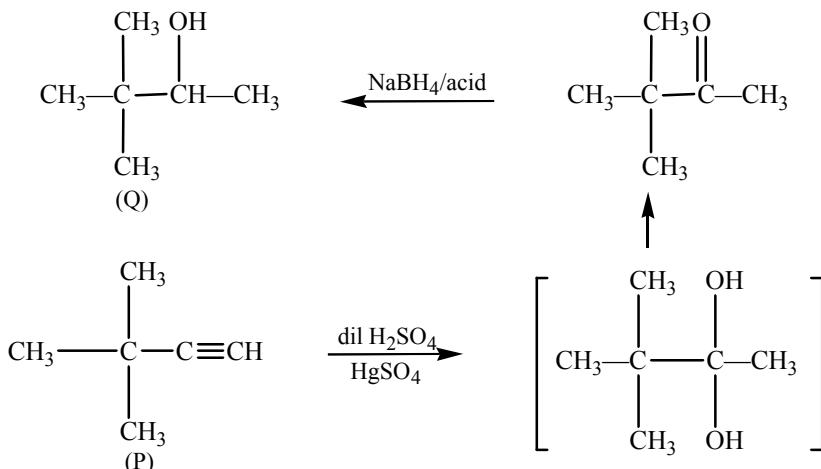


The double bond in  $\begin{array}{c} \text{CH}_3 \text{---} \text{C}=\text{C} \text{---} \text{CH}_3 \\ | \qquad \quad | \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$  is formed by the dehydration of the intermediate product Q

with the use of calculated amount of  $\text{H}_2\text{SO}_4$ . The compound Q must be a hydroxy compound. Since the reaction proceeds via the formation of carbocation due to the removal of  $-\text{OH}$  by  $\text{H}^+$  ion, this reaction involves rearrangement as shown in the following.



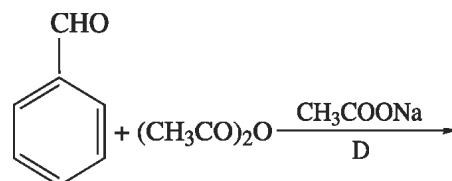
The formation of Q from P involves the addition of water molecule followed by reduction. Thus, we must have



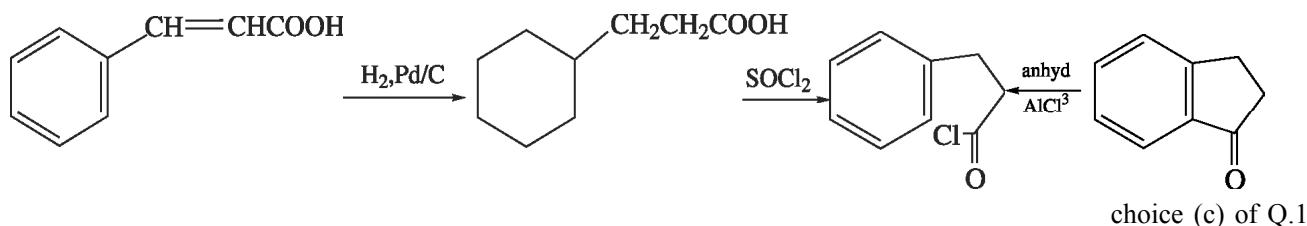
Hence, the **choice (d) of Q.1** and the **choice (b) of Q.2** are correct.

#### Passage-4

- 1. 2.** The compound J must contain a —COOH group as it gives effervescence with  $\text{NaHCO}_3$ . Also, it is an unsaturated compound as it gives positive Baeyer's test (decolourization of pink colour of alkaline  $\text{KMnO}_4$ ). Since the compound J is obtained by treating the compound I with  $(\text{CH}_3\text{CO})_2\text{O}$  and  $\text{CH}_3\text{COONa}$ , and more over the compound J seems to be aromatic (high carbon content), the compound I amongst the choices given in Q.2 seems to be benzaldehyde as it shows Perkin condensation shown in the following



The conversion J to K is as follows.

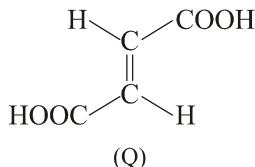
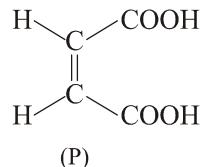


Hence, we have

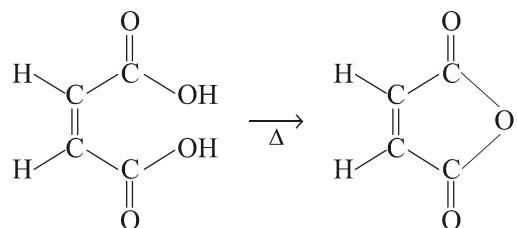
- 1. The choice (c) is correct.**
- 2. The choice (a) is correct.**

#### Passage-5

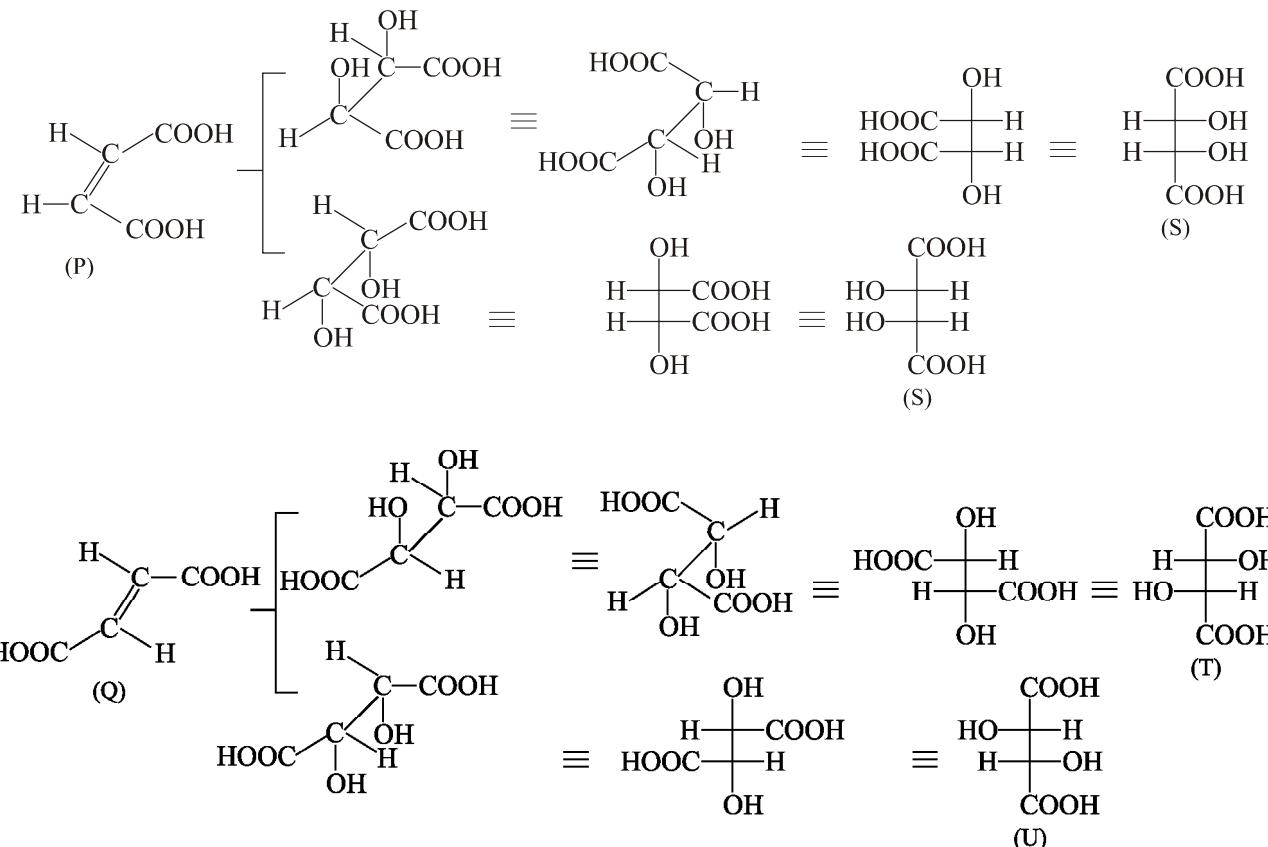
- The compounds P and Q are



The compound P forms cyclic anhydride



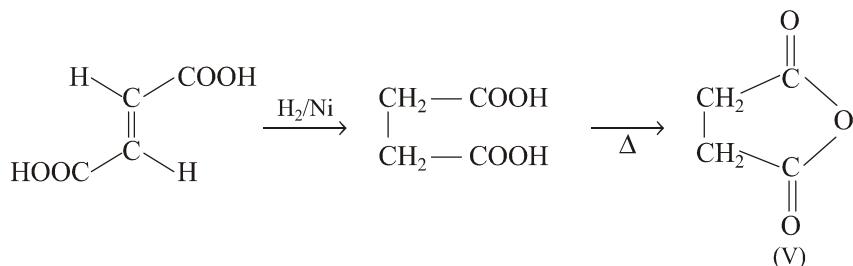
The treatment of P and Q with alkaline  $\text{KMnO}_4$ , causes hydroxylation across the double bond via syn mode.

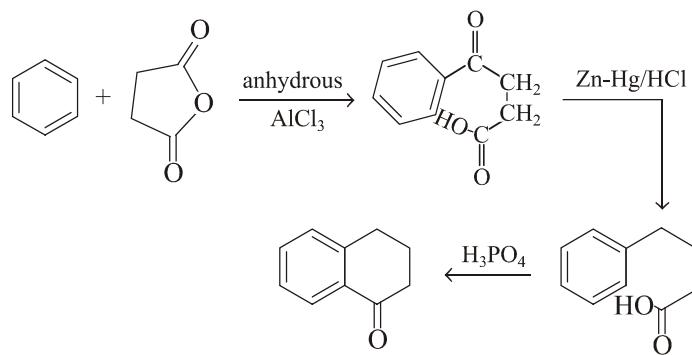


Hydroxylation P gives rise to optically inactive *meso* compound S while that of Q produces optically inactive pair (T, U) of racemic mixture.

Therefore, the **choice (b)** of Q.1 is correct.

- 2** The reactions involved in Q.2 are as follows.





Therefore, the choice (a) of Q. 2 is correct.

### Passage 6

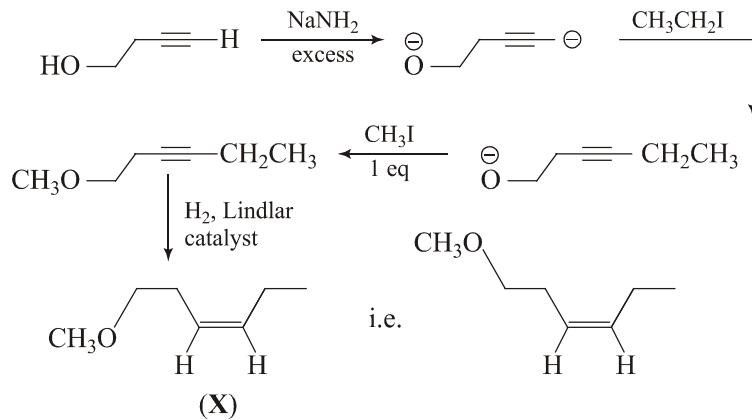
- $\text{NaNH}_2$  (excess) removes acetylinic hydrogen and hydroxyl hydrogen.

$\text{CH}_3\text{CH}_2\text{I}$  causes substitution of  $\text{CH}_3\text{CH}_2-$  towards acetylinic end.

$\text{CH}_3\text{I}$  causes the formation of ether.

$\text{H}_2$ , Lindlar's catalyst causes *syn* addition of hydrogen in the triple bond.

The reactions are



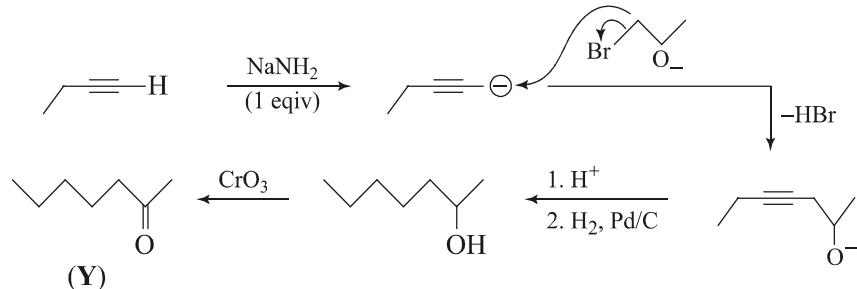
- $\text{NaNH}_2$  (1 equiv.) removes acetylinic hydrogen

$\text{Br}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2$  forms  $\text{Br}-\text{CH}_2-\text{CH}(\text{O}^-)-\text{CH}_2$  in the presence of  $\text{NaNH}_2$  and adds up towards acetylinic end with the elimination of  $\text{Br}^-$ .

The treatment of the resultant compound with  $\text{H}_3\text{O}^+$  converts it into alcohol.

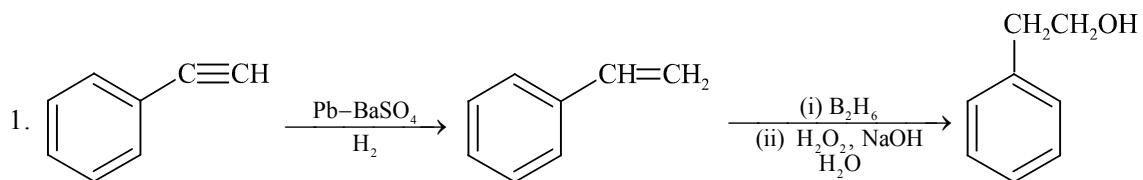
$\text{H}_2$ ,  $\text{Pd/C}$  causes hydrogenation of triple bond upto the fully saturation.

$\text{CrO}_3$  causes oxidation of hydroxyl group. The reactions are as follows.

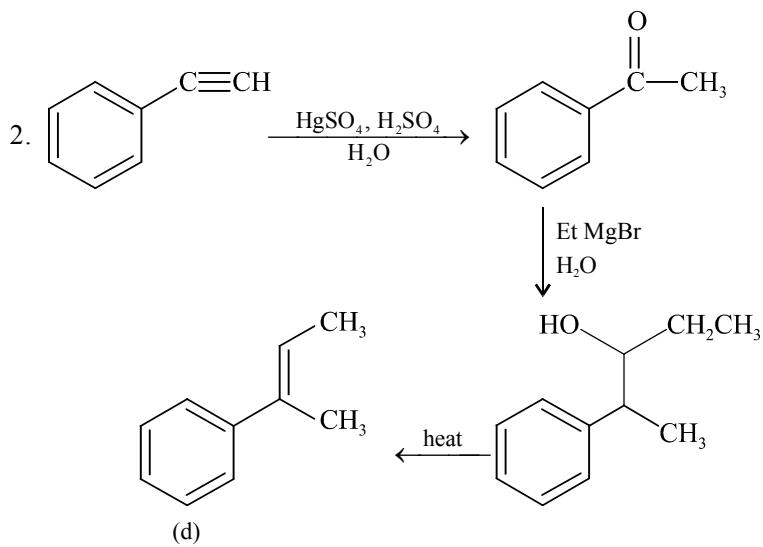


The compound Y will show iodoform test as this contains  $\text{CH}_3\text{CO}-$  group.

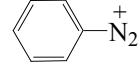
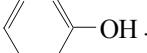
The compound Y is a functional isomer of X, same molecular formula (X contains ether group and Y contains keto group).

**Passage-7**

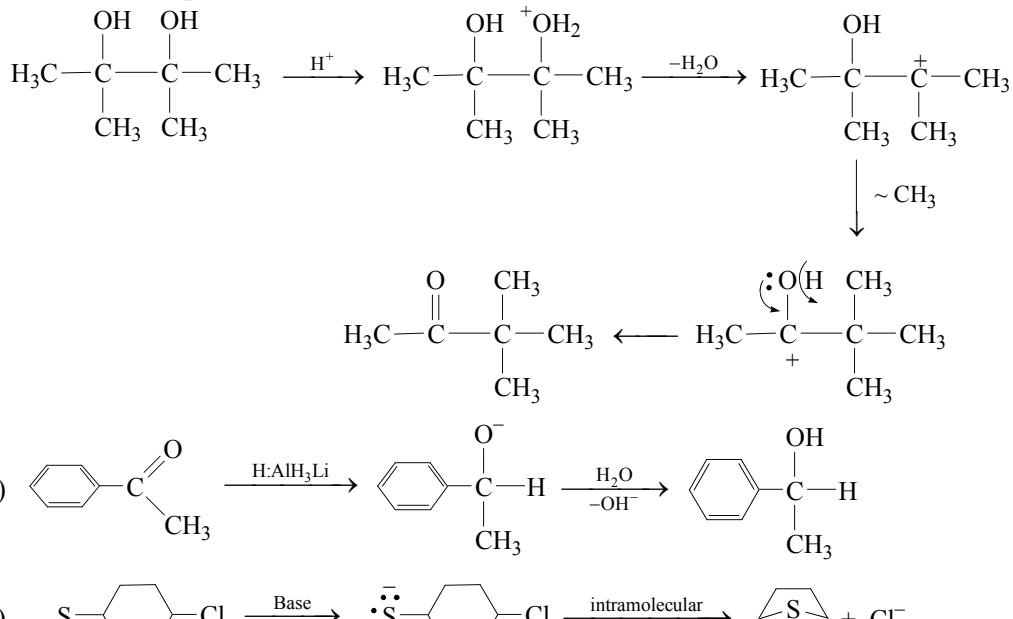
The first step is partial hydrogenation and the second step is hydroboration–oxidation process where  $\text{H}_2\text{O}$  is added to double bond in accordance with anti-Markovnikov's rule.

**Matching Type**

6. (a)  $\text{C}_6\text{H}_5\text{CHO}$  (i) gives precipitate with 2,4-dinitrophenylhydrazine (choice p), (ii) gives precipitate with  $\text{AgNO}_3$  provided it is ammoniacal (choice q), and (iii) is involved in cyanohydrine formation (choice s).  
 (b)  $\text{CH}_3\text{C}\equiv\text{CH}$  gives precipitate with  $\text{AgNO}_3$  (choice q)  
 (c)  $\text{CN}^-$  (i) gives precipitate with  $\text{AgNO}_3$  (choice q), (ii) is a nucleophile (choice r), and (iii) is involved in cyanohydrine formation (choice s)  
 (d)  $\text{I}^-$  gives precipitate with  $\text{AgNO}_3$  (choice q)
7. (a) No test of N as there is no carbon. It will show the test of  $\text{Cl}^-$  (choice r) and also reacts with aldehydes (choice s)  
 (b) This compound will give the test of the extra element N (choice p) and test of phenolic OH group (choice q)  
 (c) This compound will give the test of the extra element N (choice p), test of  $\text{Cl}^-$  ion (choice r) and the test of phenolic—OH group (choice q).  
 (d) This compound will give the test of the extra element N (choice p) and the reaction with aldehyde (choice s)
8. The matching goes as follows
- |                |          |       |       |
|----------------|----------|-------|-------|
| (a) p, q, s, t | (b) s, t | (c) p | (d) r |
|----------------|----------|-------|-------|
9. The correct matching are
- |                      |                 |
|----------------------|-----------------|
| (a)—(p), (q) and (t) | (b)—(p) and (s) |
| (c)—(r) and (s)      | (d)—(p)         |

10. (a) The reaction is a coupling reaction. It is also electrophilic substitution where electrophile is  and substitution occurs in .

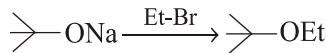
(b) The reaction proceeds as follows.



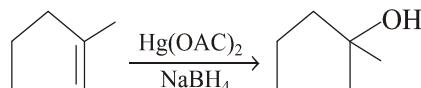
11. For the choice P in List I, a strong base such as  $\text{RO}^-$  is required. This is given by the choice 2 in List II. Hence



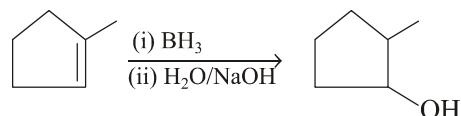
For the reaction Q, the reagent Et-Br (choice 3 of List II) can be used.



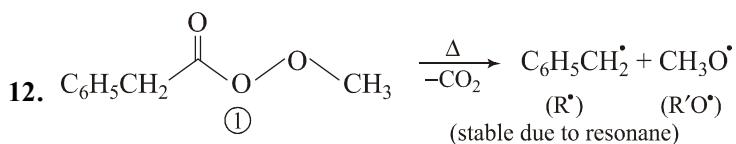
For the choice R in List I, it may be achieved by oxymercuration – demercuration process. The reagent used in this process is mercury acetate in water followed by reduction with sodium borohydride. The net result is the addition of  $\text{H}_2\text{O}$  across the double bond in accordance with Markovnikov's rule ( $-\text{OH}$  is attached to the more substituted carbon). The choice 1 of List II provides these reagents



For the choice S in List I, it may be achieved by hydroboration-oxidation process. The reagent used in this process is diborane followed by oxidation with alkaline  $\text{H}_2\text{O}_2$ . The net result is the addition of  $\text{H}_2\text{O}$  across the double bond in accordance with anti-Markovnikov's rule ( $-\text{OH}$  is attached to the less substituted carbon). The choice 4 of List II provides these reagents.



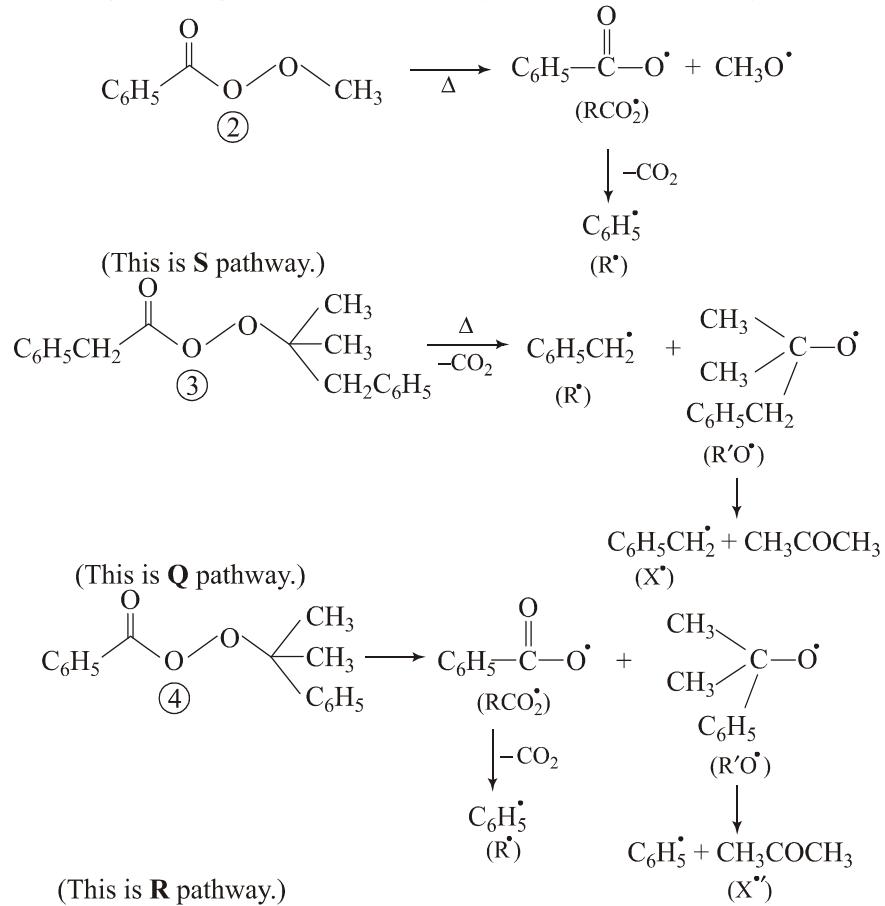
Therefore, the **choice (a)** of the given codes is the correct answer.



(This is **P** pathway.)

This fixing of pathway P for the compound (1) indicates the **choice (a)** of the given code is correct. This follows from the fact that the choices (b), (c) and (d) do not involve the structure (1) with the pathway P.

However, the remaining matchings in the **choice (a)** may be carried out to verify the correctness of choice (a)



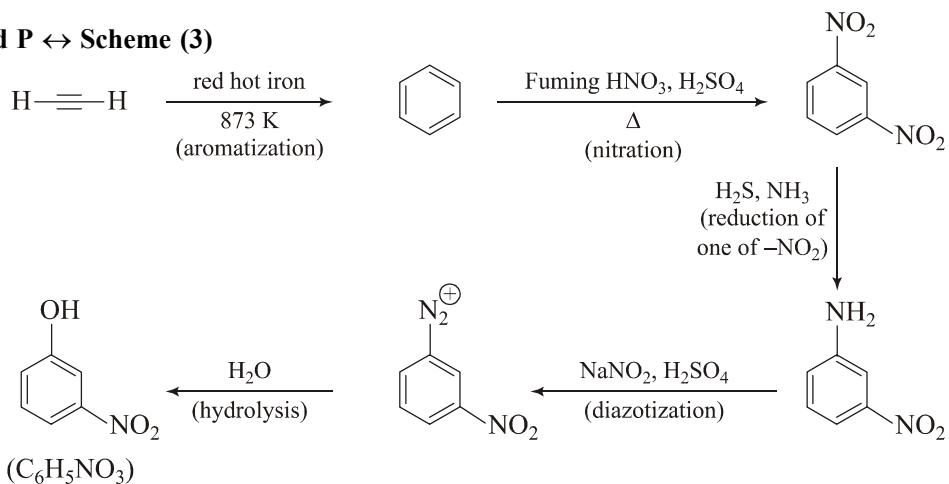
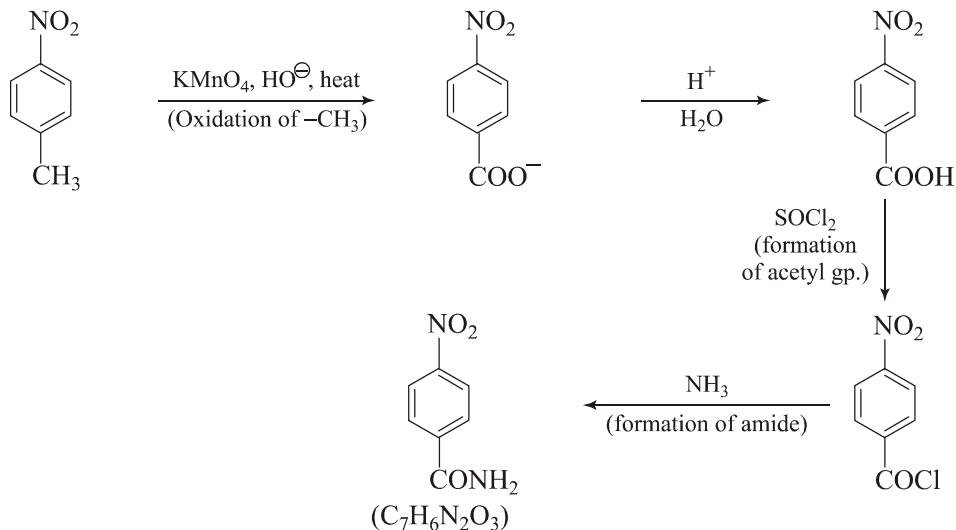
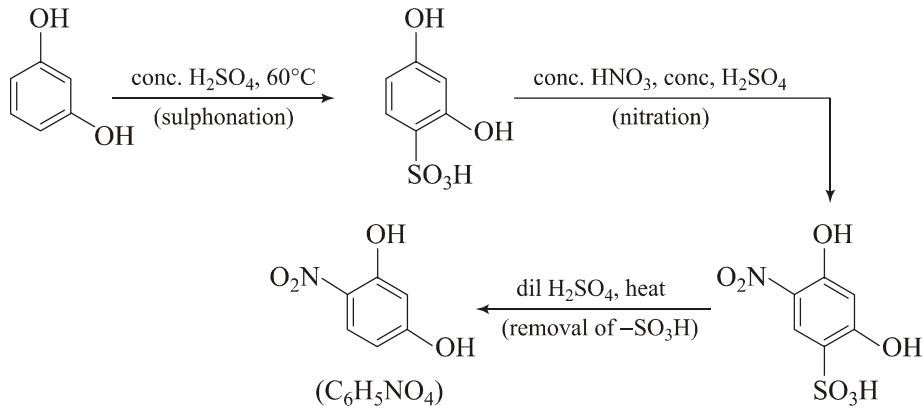
13. This question deals with the organic conversions of a compound into another compound via series of steps.

The correct answer, however, can be arrived at by the following observations.

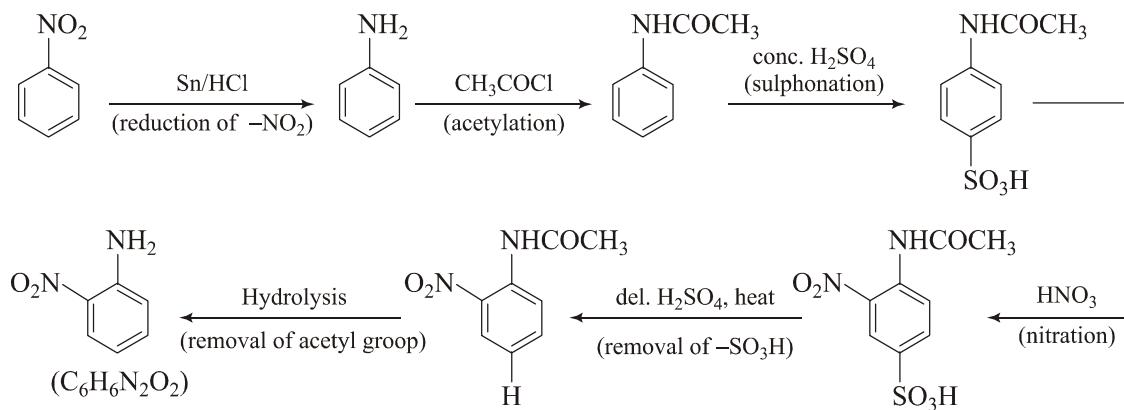
- (1) All the products given in the schemes 1, 2, 3 and 4 are probably aromatic. Only the compound P is aliphatic which can be converted into aromatic by the use of red hot iron at 873 K, which is given as the first step in Scheme III. Thus, the compound **P** is fixed with the Scheme III.
- (2) The first step in Scheme I uses Baeyer's reagent (alkaline KMnO<sub>4</sub>) This will oxidize the side group—CH<sub>3</sub> of the compound S into—COOH group. Thus, the compound **S** is fixed with the Scheme I.

Based on the above informations, the **choice (c)** of the given code seems to be the correct choice. This choice, fixes the compound **R** with the scheme (2) and **Q** with the scheme (4).

The correctness of the choice (c) may be ascertained by carrying out the actual conversions, which are given in the following.

**Compound P  $\leftrightarrow$  Scheme (3)****Compound S  $\leftrightarrow$  Scheme (1)****Compound Q  $\leftrightarrow$  Scheme (4)**

**Compound R  $\leftrightarrow$  Scheme (2)**



**Subjective Type**

1. Mass of C in 2.2 g of  $\text{CO}_2$  is

$$m_{\text{C}} = \left( \frac{M_{\text{C}}}{M_{\text{CO}_2}} \right) m_{\text{CO}_2} = \left( \frac{12}{44} \right) (2.2 \text{ g}) = 0.6 \text{ g}$$

Mass of H in 1.8 g of  $\text{H}_2\text{O}$  is

$$m_{\text{H}} = \left( \frac{2M_{\text{H}}}{M_{\text{H}_2\text{O}}} \right) m_{\text{H}_2\text{O}} = \left( \frac{2}{18} \right) (1.8 \text{ g}) = 0.2 \text{ g}.$$

Ratio of relative atomic masses of C and H is

$$\text{C : H} :: \frac{0.6}{12} : \frac{0.2}{1} \Rightarrow \text{C : H} :: 1 : 4$$

Empirical formula of hydrocarbon :  $\text{CH}_4$

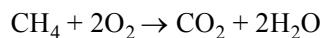
Mass of hydrocarbon =  $m_{\text{C}} + m_{\text{H}} = 0.6 \text{ g} + 0.2 \text{ g} = 0.8 \text{ g}$

This mass of hydrocarbon occupies 1.12 L at STP.

Therefore, the molar mass of hydrocarbon is

$$M = (0.8 \text{ g}) \left( \frac{22.414 \text{ L mol}^{-1}}{1.12 \text{ L}} \right) = 16.01 \text{ g mol}^{-1}$$

Hence, molecular formula of hydrocarbon is also  $\text{CH}_4$ . Its combustion reaction is



1.12 L of  $\text{CH}_4$  will require 2.24 L of  $\text{O}_2$  at STP.

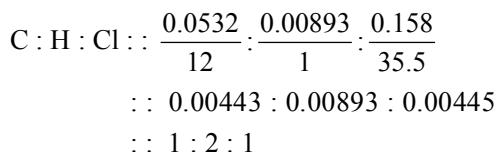
2. We have

$$m_{\text{C}} = \left( \frac{M_{\text{C}}}{M_{\text{CO}_2}} \right) m_{\text{CO}_2} = \left( \frac{12}{44} \right) (0.195 \text{ g}) = 0.0532 \text{ g}$$

$$m_{\text{H}} = \left( \frac{2M_{\text{H}}}{M_{\text{H}_2\text{O}}} \right) m_{\text{H}_2\text{O}} = \left( \frac{2}{18} \right) (0.0804 \text{ g}) = 0.00893 \text{ g}$$

$$m_{\text{Cl}} = 0.220 \text{ g} - m_{\text{C}} - m_{\text{H}} = 0.220 \text{ g} - 0.0532 \text{ g} - 0.00893 \text{ g} = 0.158 \text{ g}$$

Ratio of relative atomic masses of C, H and Cl is



Empirical formula of the compound:  $\text{CH}_2\text{Cl}$

The molar mass of the compound can be computed from the ideal gas law:

$$pV = nRT = \left(\frac{m}{M}\right)RT \quad \Rightarrow \quad M = \frac{mRT}{pV}$$

Substituting the given data, we get

$$M = \frac{(0.120 \text{ g})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(378.15 \text{ K})}{(768 \text{ atm}/760)(37.24 \times 10^{-3} \text{ L})}$$

$$= 98.9 \text{ g mol}^{-1}$$

Ratio of molar mass and empirical molar mass is

$$n = \frac{98.9 \text{ g mol}^{-1}}{(12 + 2 + 35.5) \text{ g mol}^{-1}} \approx 2$$

Hence, molecular formula is  $C_2H_4Cl_2$

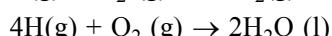
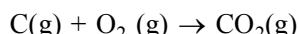
3. In 25 mL of mixed gases after the explosion, we have

Partial volume of  $\text{CO}_2$  = 10 mL

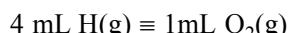
Partial volume of  $O_2 = 15 \text{ mL}$

Hence, Partial volume of O<sub>2</sub> used in combustion = (30 – 15) mL = 15 mL

From the combustion reactions.



we conclude that



Let the formula of the gas is  $C_xH_y$ . 5 mL of this gas will produce (5 mL) $x$  of C(g) and (5 mL) $y$  of H(g). Since 10 mL of CO<sub>2</sub> is produced, we must have

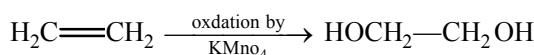
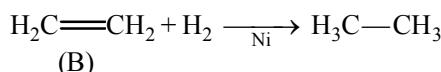
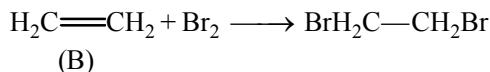
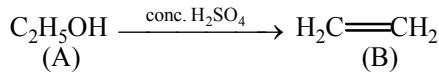
$$(5 \text{ mL})x = 10 \text{ mL} \quad \Rightarrow \quad x = 2$$

Partial volume of O<sub>2</sub> used in the combustion of H = (15 – 10) mL = 5 mL  
 Hence, we have

$$(5 \text{ mL}) y = 4 \times 5 \text{ mL} \quad \Rightarrow \quad y = 4$$

Hence, the formula of the gas is  $\text{C}_2\text{H}_4$ .

4. The compound A is  $C_2H_5OH$ . The given reactions are as follows.



5. Molar mass of hydrocarbon

$$M = \frac{mRT}{pV} = \frac{(2.8 \text{ g})(0.082 \text{ L atm K}^{-1} \text{ mol}^{-1})(400 \text{ K})}{(1 \text{ atm})(1 \text{ L})}$$

$$= 91.84 \text{ g mol}^{-1}$$

Relative ratio of C and H in the hydrocarbon is

$$\text{C : H} :: \frac{10.5}{12} : 1 \Rightarrow \text{C : H} :: 0.875 : 1$$

$$:: 7 : 8$$

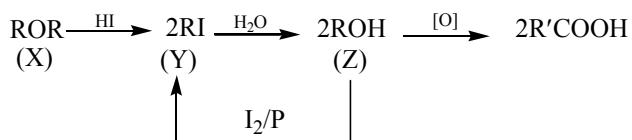
Empirical formula of the hydrocarbon:  $\text{C}_7\text{H}_8$

Molar empirical mass =  $(7 \times 12 + 8) \text{ g mol}^{-1} = 92 \text{ g mol}^{-1}$

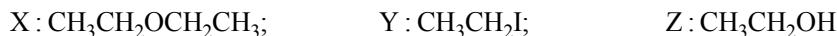
This is equal to the molar mass. Hence,

Molecular formula:  $\text{C}_7\text{H}_8$

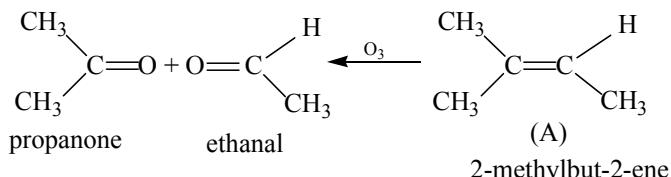
6. Since the compound is unreactive towards sodium, it is neither alcohol (including phenol) nor carboxylic acid. It is also not an aldehyde. It may be a symmetrical ether because on refluxing with excess of HI, it gives only one product. Thus, we have



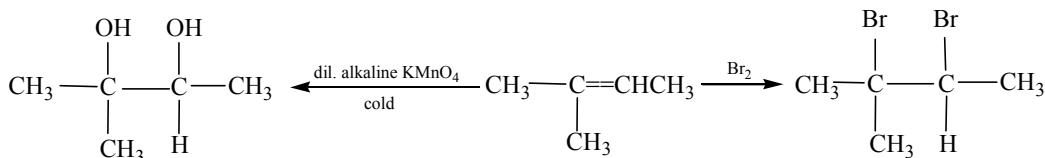
Now the equivalent weight of  $\text{R}'\text{COOH}$  is 60. From this, it follows that  $\text{R}'$  is  $-\text{CH}_3$  group and hence R is  $-\text{CH}_2\text{CH}_3$  group. Thus, the compounds X, Y and Z are



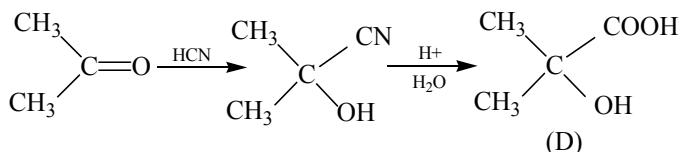
7. From the products of ozonolysis, we conclude that



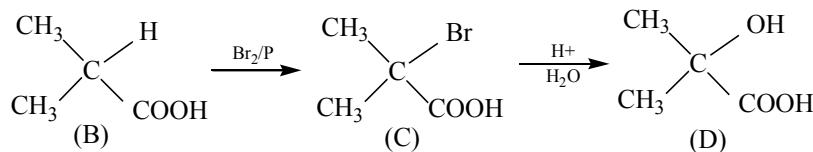
The compound A contains a double bond. This is also confirmed from the fact that the compound A reacts with one mole of bromine. Thus, the given reactions are



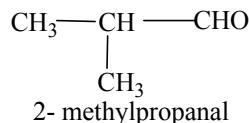
8. The structure of compound D is easily deduced from the fact that it is obtained by the combination of acetone with hydrogen cyanide followed by hydrolysis.



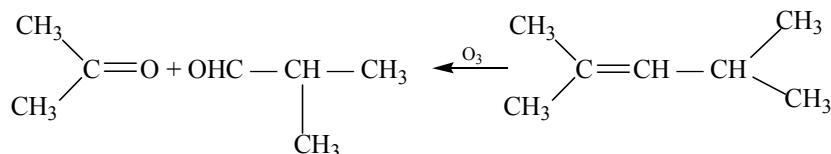
The conversion B to C and then C to D indicates that the reaction B to C is Hell-Volhard-Zelinsky reaction. Thus, we have



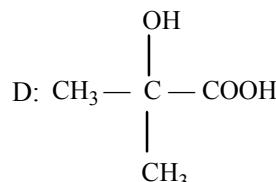
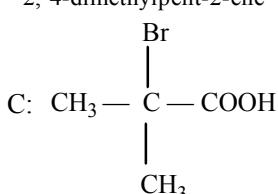
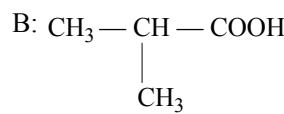
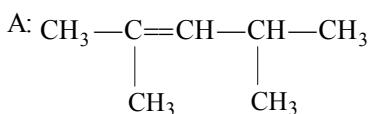
Hence, we conclude that the aldehyde from which compound B is obtained by oxidation has the structure



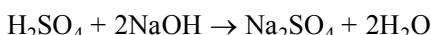
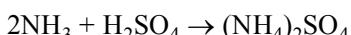
Now, the ozonolysis of the compound A gives acetone and 2-methyl-propanal, i.e.



Hence, the compound A, B, C and D are



#### 9. The reactions involved are



Amount of sodium hydroxide to neutralise excess of sulphuric acid

$$= (25 \text{ mL}) \left( \frac{0.1 \text{ mol}}{1000 \text{ mL}} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Amount of sulphuric acid neutralised with sodium hydroxide} = \frac{1}{2} \left( \frac{1}{400} \text{ mol} \right) = \frac{1}{800} \text{ mol}$$

$$\text{Amount of sulphuric acid taken to start with} = (50 \text{ mL}) \left( \frac{0.05 \text{ mol}}{1000 \text{ mL}} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Amount of sulphuric acid neutralised by ammonia} = \left( \frac{1}{400} - \frac{1}{800} \right) \text{ mol} = \frac{1}{800} \text{ mol}$$

$$\text{Amount of ammonia evolved} = 2 \left( \frac{1}{800} \text{ mol} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Mass of nitrogen in the evolved ammonia} = \left( \frac{1}{400} \text{ mol} \right) (14 \text{ g mol}^{-1}) = \frac{7}{200} \text{ g}$$

$$\text{Per cent of nitrogen in the given aromatic compound} = \frac{(7/200) \text{ g}}{0.303 \text{ g}} \times 100 = 11.6$$

Per cent of oxygen in the given aromatic compound =  $100 - (69.4 + 5.8 + 11.6) = 13.2$   
The ratios of atoms present in the given compound are

$$\text{C : H : N : O} :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.6}{14} : \frac{13.2}{16} :: 5.8 : 5.8 : 0.83 : 0.83 :: 7 : 7 : 1 : 1$$

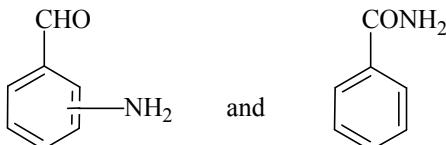
Hence, for the given compound, we have

$$\text{Empirical formula} = \text{C}_7\text{H}_7\text{NO} \quad \text{Empirical molar mass} = 121 \text{ g mol}^{-1}$$

It is given that  $121 \text{ g mol}^{-1}$  is also the molar mass. Hence,

$$\text{Molecular formula} = \text{C}_7\text{H}_7\text{NO}$$

Since, the given compound is aromatic, the two possible structures are



10. The combustion reaction is  $\text{C}_x\text{H}_{2y}\text{O}_y + x \text{ O}_2 \rightarrow x \text{ CO}_2 + y \text{ H}_2\text{O}$

To start with, the amount of  $\text{O}_2$  taken is  $2x$ . Hence, after the combustion reaction, we will be left with the following amounts.

$$\text{Amount of oxygen left unreacted} = x$$

$$\text{Amount of carbon dioxide} = x$$

$$\text{Amount of water} = y$$

When this mixture is cooled to  $0^\circ\text{C}$  and 1 atm, we will be left with oxygen and carbon dioxide. Hence, the amount  $2x$  occupies the given volume of 2.24 L at STP. Hence,

$$\text{Amount } x = \frac{(2.24/2) \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.05 \text{ mol}$$

$$\text{Now, Mass of water collected} = 0.9 \text{ g}$$

$$\text{Amount of water collected, } y = \frac{0.9 \text{ g}}{18 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

Thus, the empirical formula of the compound is  $\text{C}_{0.05}\text{H}_{2\times 0.05}\text{O}_{0.05}$ , i.e.  $\text{CH}_2\text{O}$ . Now, according to Raoult's law

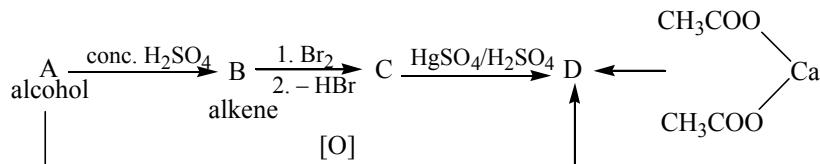
$$-\frac{\Delta p}{p^*} = x_2 \quad \text{i.e.} \quad \frac{0.104 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{(50 \text{ g}/M)}{(50 \text{ g}/M) + (1000 \text{ g}/18 \text{ g mol}^{-1})}$$

$$\text{Solving for } M, \text{ we get} \quad M = 150.5 \text{ g mol}^{-1}$$

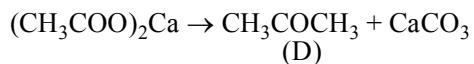
$$\text{Number of repeating units of CH}_2\text{O in the molecular formula} = \frac{150.5}{12 + 2 + 16} \approx 5$$

Hence, Molecular formula of the compound is  $\text{C}_5\text{H}_{10}\text{O}_5$ .

11. The given reactions are as follows.



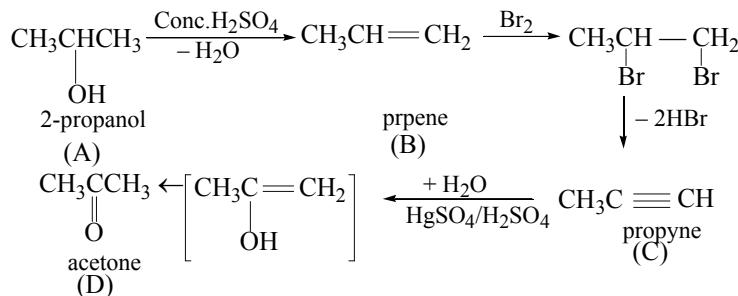
The reaction of obtaining D from calcium acetate is



Hence, D is acetone. Since the latter is also obtained from the oxidation of alcohol A, compound A will be



Hence, the reactions depicted above are as follows.



12. The ratio of atoms in the compound A is

$$\text{C : H} :: \frac{85.7}{12} : \frac{14.3}{1} :: 7.14 : 14.3 :: 1 : 2$$

Thus, Empirical formula of A is  $\text{CH}_2$ .

Since the compound A consumes 1 mol of hydrogen, the molecule of A contains only one carbon-carbon double bond. From the data on the absorption of bromine, we can calculate the molar mass of A as shown in the following.

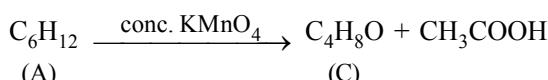
$$\text{Mass of bromine absorbed by } 1.0 \text{ g of hydrocarbon} = \frac{5}{100} \times 38.05 \text{ g}$$

$$\begin{aligned} \text{Mass of hydrocarbon absorbing } 160 \text{ g} (= 1 \text{ mol}) \text{ of Br}_2 \\ = \frac{1.0}{(5 \times 38.05/100)} \times 160 \text{ g} = 84.1 \text{ g.} \end{aligned}$$

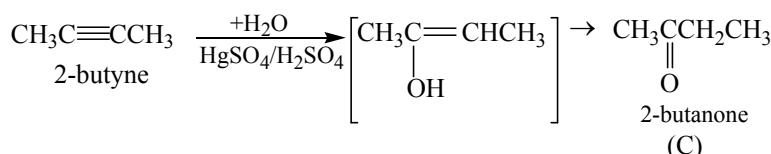
Hence, Molar mass of A is  $84.1 \text{ g mol}^{-1}$ .

The number of repeating  $\text{CH}_2$  group in one molecule of A will be  $6 (= 84.1/14)$ . Hence,

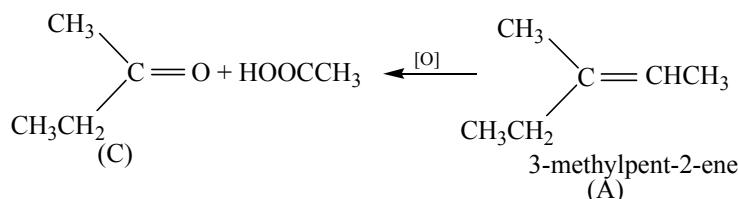
Molecular formula of A is  $\text{C}_6\text{H}_{12}$ . Now, it is given that



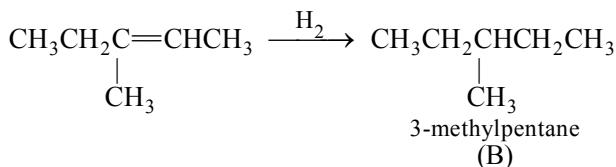
The compound C is obtained by the hydration of 2-butyne. Hence, its structure obtained from the reaction is



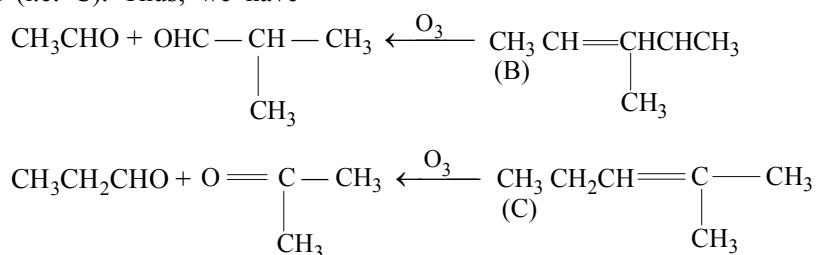
Finally, the structure of A would be



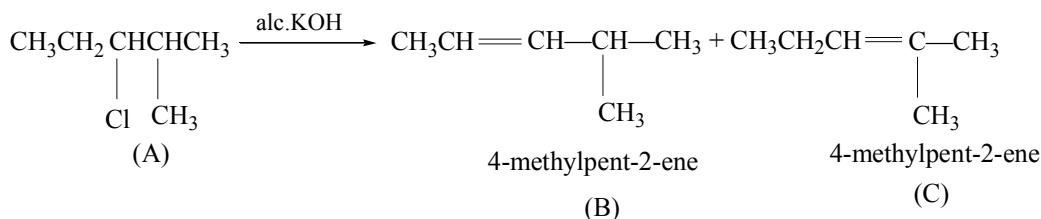
The structure of B is



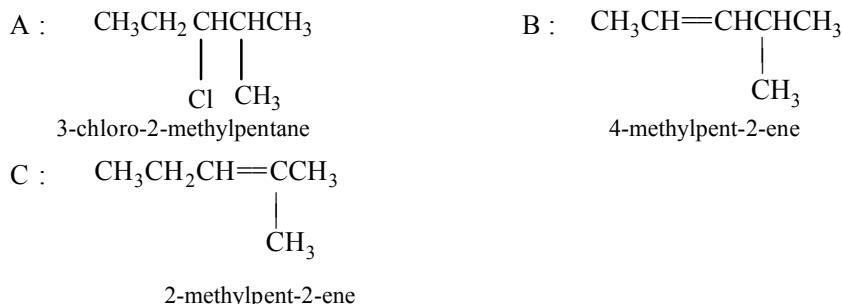
13. Since during ozonolysis, no loss of carbon occurs, we conclude that  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3-\underset{\text{CH}_3}{\overset{|}{\text{CHCHO}}}$  are the products of one of the compounds (say, B) and  $\text{C}_2\text{H}_5\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  are the products of the other compound (i.e. C). Thus, we have



Since the compounds B and C are obtained when A is treated with hot alcoholic potassium hydroxide, we will have



Since the chlorine atom in A is an aliphatic chlorine, it will be slowly precipitated with silver nitrate. Hence, the structures of A, B and C are

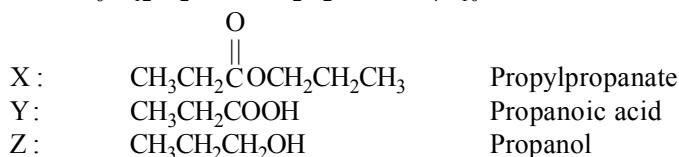


14. Since the hydrolysis of X gives a carboxylic acid (Y) and an alcohol (Z), the compound X must be an ester. Let it be  $\text{RCOOR}'$ . The compounds Y and Z will be  $\text{RCOOH}$  and  $\text{R}'\text{OH}$ , respectively. Since the oxidation of Z gives Y, we will have



Hence, the given compound X may be written as  $\text{RCOOCH}_2\text{R}$ . From this it follows that

2R is C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> minus C<sub>2</sub>H<sub>2</sub>O, i.e. C<sub>4</sub>H<sub>10</sub>



15. The given compound is a ketone as it does not reduce Fehling's solution, but forms a bisulphite addition compound. It will also contain  $\text{CH}_3\text{CO}$  group as it shows positive iodoform test. The ratios of atoms in the compound are

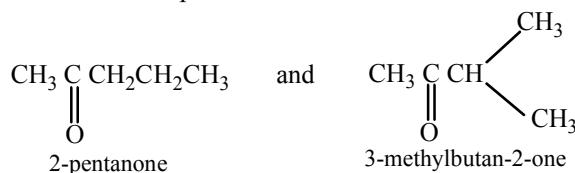
$$\text{C : O : H} :: \frac{69.77}{12} : \frac{18.60}{16} : \frac{11.63}{1} :: 5.81 : 1.16 : 11.63 :: 5 : 1 : 10$$

Hence Empirical formula is  $\text{C}_5\text{H}_{10}\text{O}$ .

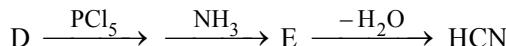
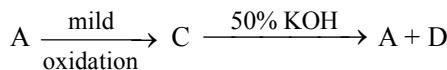
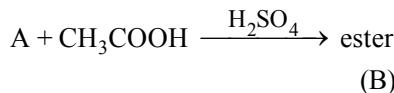
Molar empirical mass = 86 g mol<sup>-1</sup>; same as the given molar mass

Thus, Molecular formula is  $\text{C}_5\text{H}_{10}\text{O}$ .

The structure of the compound will be

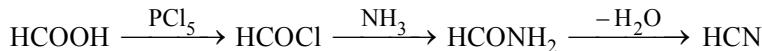
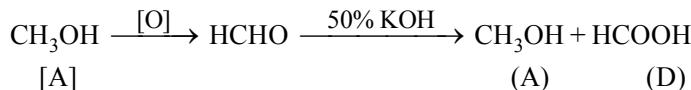
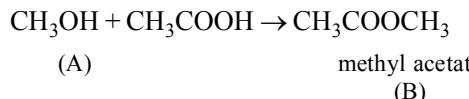


16. The given reactions are



The reaction  $\text{C} \xrightarrow{50\% \text{ KOH}} \text{A} + \text{D}$  is a Cannizzaro reaction and thus the compound C is an aldehyde with no  $\alpha$ -hydrogen, C must be  $\text{HCHO}$ . From this it follows that A must be  $\text{CH}_3\text{OH}$  as its mild oxidation gives  $\text{HCHO}$ .

With this fact, we can write the given reactions as shown below.



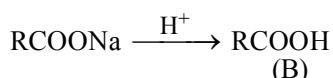
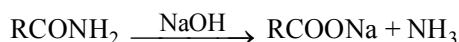
Hence,    A :  $\text{CH}_3\text{OH}$     methanol                      B :  $\text{CH}_3\text{COOCH}_3$     methylethionate  
           C :  $\text{HCHO}$     methanal                      D :  $\text{HCOOH}$     methanoic acid  
           E :  $\text{HCONH}_2$     methanamide

17. The ratios of atoms present in the molecule are

$$\text{C : H : N : O} :: \frac{49.32}{12} : \frac{9.59}{1} : \frac{19.18}{14} : \frac{21.91}{16} :: 4.11 : 9.58 : 1.37 : 1.37 :: 3 : 7 : 1 : 1$$

Hence, Empirical formula;  $\text{C}_3\text{H}_7\text{NO}$ .

Since A on boiling with NaOH gives of  $\text{NH}_3$  and salt of monobasic nitrogen free acid, the compound A must be an amide. Let it be  $\text{RCONH}_2$ . The reaction is



Let  $M$  be the molar mass of  $\text{RCOO}$ . From the data on silver salt, we get

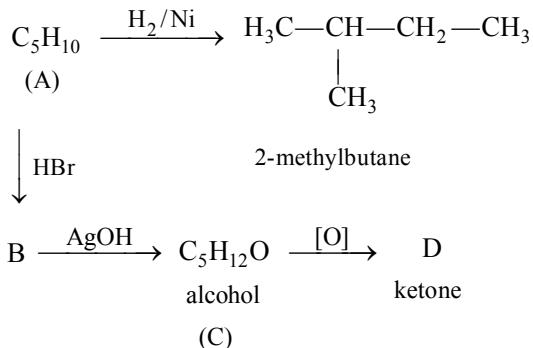
$$\frac{M_{\text{Ag}}}{M_{\text{Ag}} + M_{\text{RCOO}}} \times 100 = 59.67$$

$$\text{or } M_{\text{RCOO}} = M_{\text{Ag}} \left( \frac{0.4033}{0.5967} \right) = (108 \text{ g mol}^{-1}) \left( \frac{0.4033}{0.5967} \right) = 73 \text{ g mol}^{-1}.$$

Molar mass of R =  $(73 - 12 - 32) \text{ g mol}^{-1} = 29 \text{ g mol}^{-1}$

Hence, the alkyl group R is  $\text{C}_2\text{H}_5$  and the compounds A and B are  $\text{C}_2\text{H}_5\text{NH}_2$  and  $\text{C}_2\text{H}_5\text{COOH}$ , respectively.

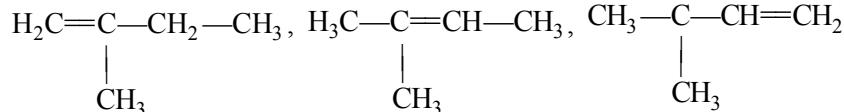
**18.** The given reactions are



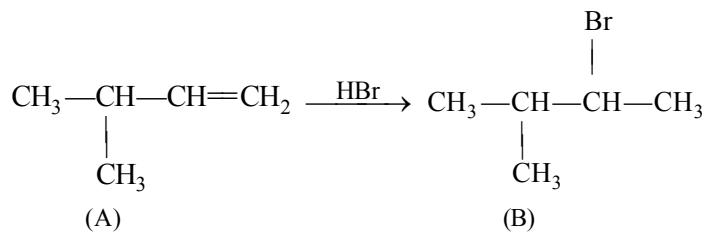
The compound C must be a secondary alcohol as it gives ketone on oxidation.

The compound B will be a secondary bromo derivative.

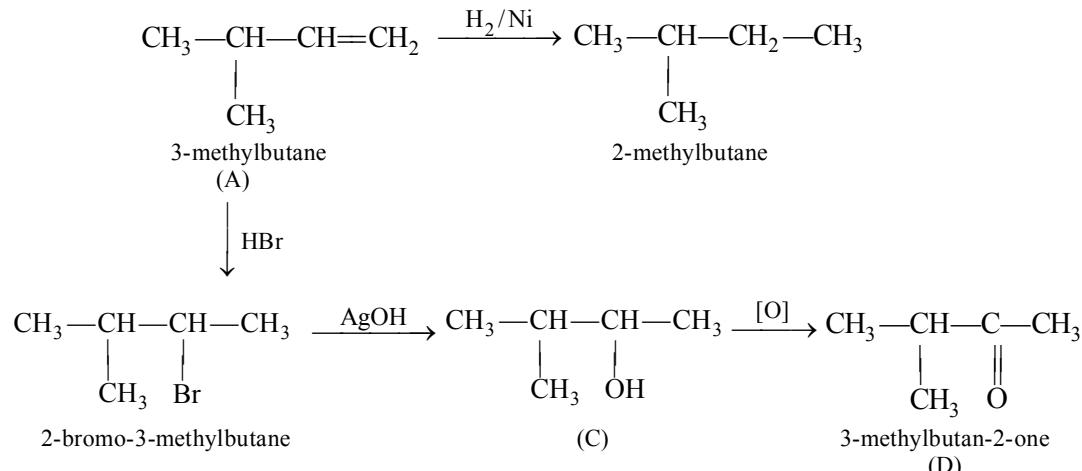
Since the compound A gives 2-methylbutane on reduction, it must have any one of the following structures.



Of these structures, only the last one will produce secondary bromo derivative when HBr adds in accordance with Markovnikov's rule:



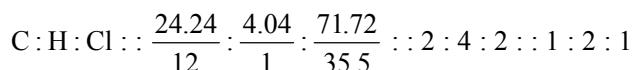
Thus, the reactions involved are as follows.



19. Mass per cent of chlorine in the organic compound X

$$= \frac{M_{\text{Cl}}}{M_{\text{AgCl}}} \frac{m_{\text{AgCl}}}{m_{\text{compound}}} \times 100 = \frac{35.5}{143.5} \times \frac{2.90}{1.0} \times 100 = 71.21$$

The ratios of atoms in the molecule of X are



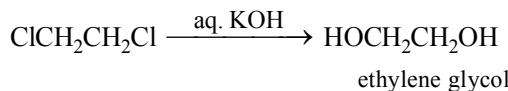
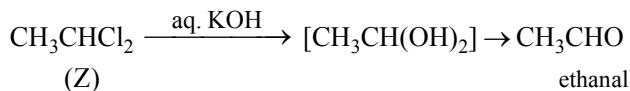
Empirical formula of X is  $\text{CH}_2\text{Cl}$

Since the isomer Y of the compound gives a dihydroxy compound on treating with aqueous KOH, it follows that the compound must contain two Cl atoms. Hence,

Molecular formula of X is  $\text{C}_2\text{H}_4\text{Cl}_2$ .

Its two isomers are  $\text{CH}_3\text{CHCl}_2$  and  $\text{ClCH}_2\text{CH}_2\text{Cl}$ .  
(Z) (Y)

The reaction are



20. The equations are



Mass of *n*-butane to be produced = 55 g

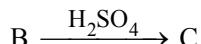
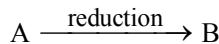
$$\text{Amount of } n\text{-butane to be produced} = \frac{m_{\text{butane}}}{M_{\text{butane}}} = \frac{55 \text{ g}}{58 \text{ g mol}^{-1}} = 0.948 \text{ mol}$$

Amount of  $\text{C}_2\text{H}_5\text{Br}$  required to obtain 0.948 mol of  $\text{C}_4\text{H}_{10}$  would be  $2 \times 0.948 \text{ mol} = 1.896 \text{ mol}$ . But the per cent conversion is 85. Thus, the amount of  $\text{C}_2\text{H}_5\text{Br}$  required would be  $(1.896 \text{ mol}) \left( \frac{100}{85} \right) = 2.23 \text{ mol}$

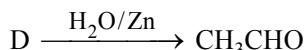
Amount of  $\text{C}_2\text{H}_6$  required would also be 2.23 mol. But the per cent conversion of  $\text{C}_2\text{H}_6$  to  $\text{C}_2\text{H}_5\text{Br}$  is 90. Thus, the actual amount of  $\text{C}_2\text{H}_6$  required would be  $(2.23 \text{ mol}) \left( \frac{100}{90} \right) = 2.478 \text{ mol}$

Volume of  $\text{C}_2\text{H}_6$  required at STP would be  $(2.478 \text{ mol}) (22414 \text{ mL mol}^{-1}) = 55.54 \times 10^3 \text{ mL}$ .

21. We are given that



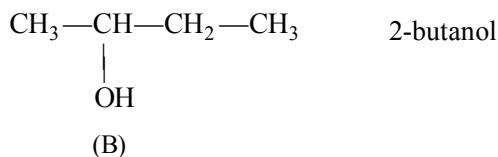
C forms mono-ozonoide, D



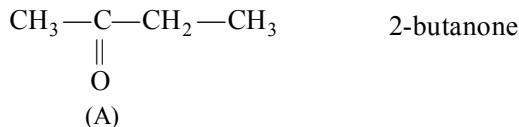
The compound A gives a haloform reaction; it must contain  $\text{CH}_3\text{CO}$  group. The compound C contains a double bond as it forms mono-ozonoide D. Since, the compound D on hydrolysis gives only  $\text{CH}_3\text{CHO}$ , the structure of C would be



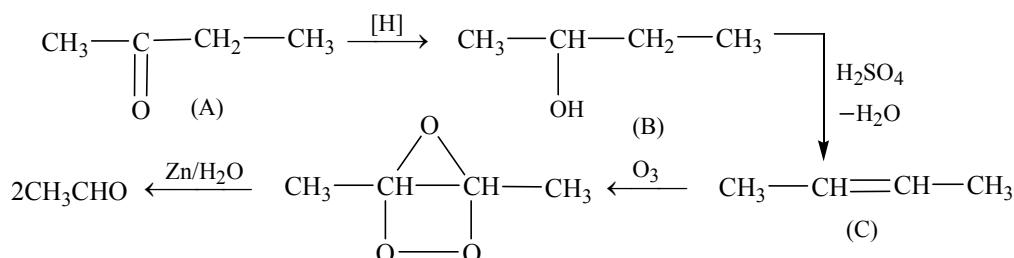
The compound C is obtained by dehydration of B, the latter should be



Finally, B is obtained by the reduction of A. Hence, the compound A should be



The equations involved are as follows.

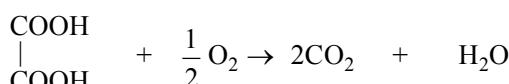


22. From the given data, we can determine the molar mass of dicarboxylic acid. Since on ignition, 2 mol of Ag ( $\equiv 215.8$  g Ag) will be left per mole of dicarboxylic acid, we have

$$\frac{1.0 \text{ g of silver salt of dicarboxylic acid}}{0.71 \text{ g Ag}} \times 215.8 \text{ g Ag} = 303.94 \text{ g of silver salt of dicarboxylic acid.}$$

$$\begin{aligned} \text{Hence, } M_{\text{acid}} &= 303.94 \text{ g mol}^{-1} - 2 M_{\text{Ag}} + 2M_{\text{H}} \\ &= 303.94 \text{ g mol}^{-1} - 215.8 \text{ g mol}^{-1} + 2 \text{ g mol}^{-1} \\ &= 90.14 \text{ g mol}^{-1} \end{aligned}$$

Now, since the molar mass of two carboxylic groups ( $2\text{COOH}$ ) is  $90 \text{ g mol}^{-1}$ , the dicarboxylic acid (C) is oxalic acid ( $\text{HCOOH}-\text{COOH}$ ). The nature of dicarboxylic acid may be confirmed from the combustion data.



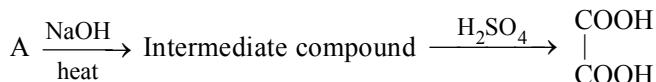
$$\begin{array}{lll} \text{Molar mass} & 90 \text{ g mol}^{-1} & \\ \text{Given data} & 0.4 \text{ g} & 44 \text{ g mol}^{-1} \\ & & 0.39 \text{ g} \end{array}$$

The calculated values of masses of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced during the combustion of 0.4 g of oxalic acid are

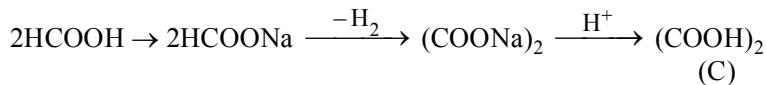
$$\frac{2 \times 44 \text{ g CO}_2}{90 \text{ g oxalic acid}} \times 0.4 \text{ g oxalic acid} = 0.39 \text{ g CO}_2$$

$$\frac{18 \text{ g H}_2\text{O}}{90 \text{ g oxalic acid}} \times 0.4 \text{ g oxalic acid} = 0.08 \text{ g H}_2\text{O}$$

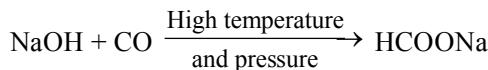
These values tally with the given data. Hence, the compound C is confirmed to be oxalic acid. The production of C from A is as follows.



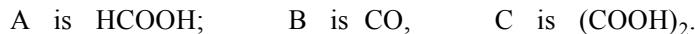
The compound A must be formic acid as the above reactions are used in the manufacture of oxalic acid. The reactions are



The sodium salt of A is produced by passing a gas B into an aqueous solution of caustic alkali at an elevated temperature and pressure. The reaction involved here is



Hence, the gas B is carbon monoxide. Thus, the structures of A, B and C are



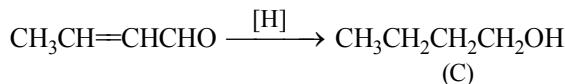
23. The compound A is an ester. The equations involved in the given reactions are as follows.

The compound F is a monobasic acid (molar mass = 60 g mol<sup>-1</sup>). This may be represented as RCOOH. From the molar mass of F, it is evident that the molar mass of R is 15 g mol<sup>-1</sup> [= (60 - 45) g mol<sup>-1</sup>]. Hence, the compound F is CH<sub>3</sub>COOH (ethanoic acid).

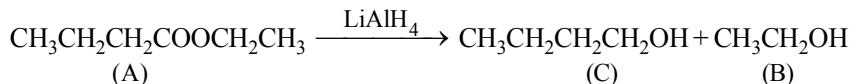
F is obtained by the oxidation of D. Hence, the compound D must be an aldehyde with the structure CH<sub>3</sub>CHO (ethanal). The compound D was obtained from the oxidation of B which must be an alcohol. Hence, the structure of B is CH<sub>3</sub>CH<sub>2</sub>OH (ethanol). D undergoes an aldol condensation (treatment with aqueous alkali) which subsequently gives E on heating. The reactions involved here are



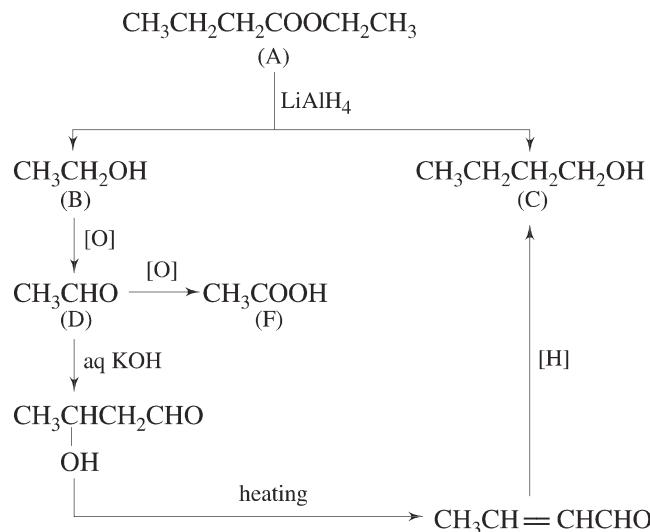
The reduction of E gives compound C. Hence, we have



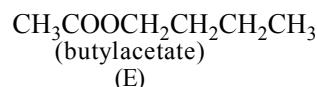
Finally, the structure of A can be obtained from the two alcohols (CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH) produced on treating A with LiAlH<sub>4</sub>. Thus, we have



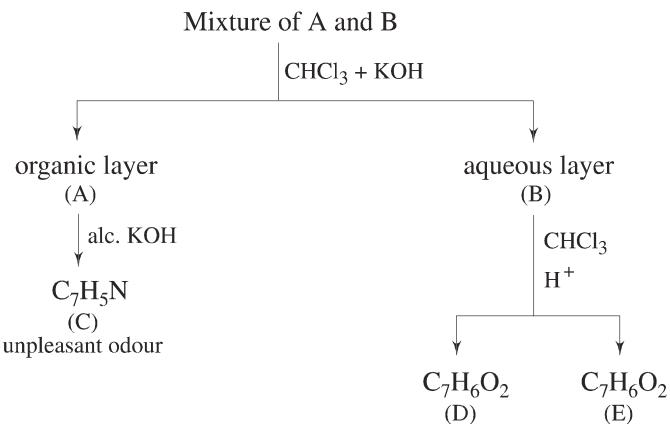
Thus, the reactions involved are as follows.



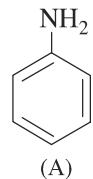
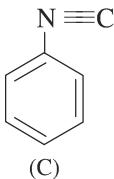
Alternatively, the compound A may be



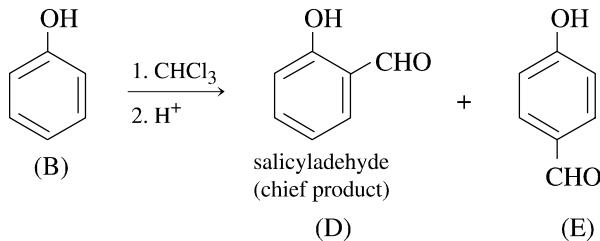
24. We have



The compound C is an isocyanide which is produced from a primary amine. Hence, the structures of C and A are



The compound B exhibits Reimer-Tiemann reaction. Thus, the compound B must be phenol. The reaction is



25. We have

$$\text{Per cent of carbon in the compound} = \frac{M_C}{M_{CO_2}} \frac{m_{CO_2}}{m_{\text{compound}}} \times 100 = \left( \frac{12}{44} \right) \left( \frac{0.308}{0.108} \right) (100) = 77.78$$

$$\text{Per cent of hydrogen in the compound} = \frac{2M_H}{M_{H_2O}} \frac{m_{H_2O}}{m_{\text{compound}}} \times 100 = \left( \frac{2}{18} \right) \left( \frac{0.072}{0.108} \right) (100) = 7.41$$

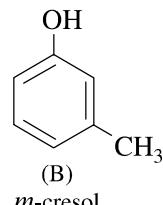
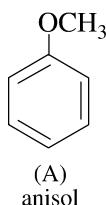
$$\text{Per cent of oxygen in the compound} = 100 - (77.78 + 7.41) = 14.81.$$

The ratios of atoms in the compound are

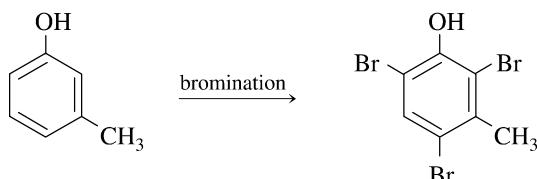
$$C : H : O :: \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} :: 6.48 : 7.41 : 0.926 :: 7 : 8 : 1$$

Hence, Empirical formula of the compound is  $C_7H_8O$ .

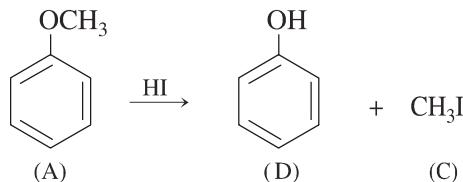
Since the isomer B on reacting with bromine water gives compound E ( $C_7H_5OBr_3$ ), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and  $NaHCO_3$  and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are



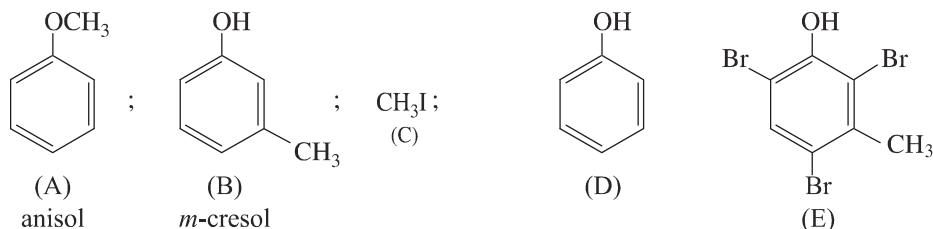
The bromination of B gives



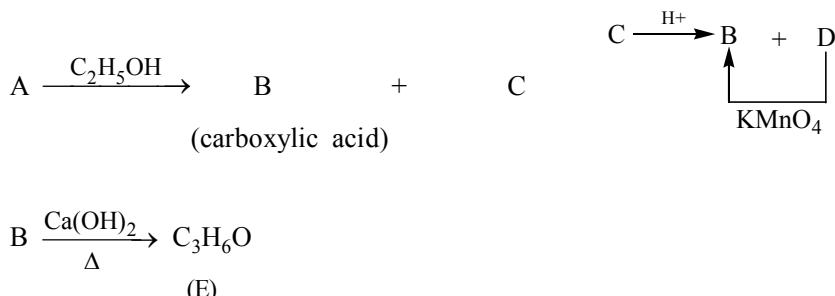
The reaction of compound A with HI is



The compound C can be separated from D by use of ethanolic  $\text{AgNO}_3$  solution as it is soluble in it whereas D will remain insoluble. The compound D will be soluble in NaOH as it is phenol. Hence, the structures of A, B, C, D and E are



26. The given reaction are as follows.



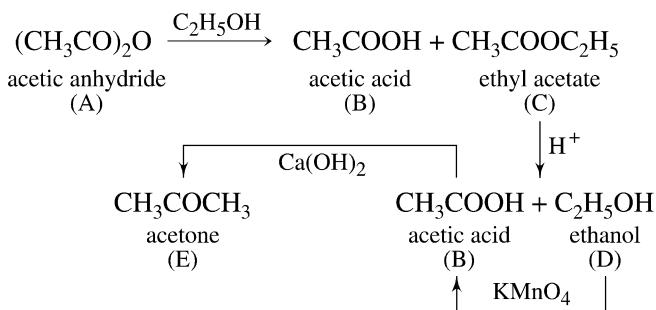
The compound E must be a ketonic compound as it does not give Tollens test and does not reduce Fehling's solution but forms a 2, 4-dinitrophenylhydrazone. Therefore, its structure would be  $\text{CH}_3\text{COCH}_3$  (acetone). Since E is obtained by heating B with  $\text{Ca}(\text{OH})_2$ , the compound B must be  $\text{CH}_3\text{COOH}$  (acetic acid).

Since B is obtained by oxidation of D with  $\text{KMnO}_4$ , the compound D must be an alcohol with molecular formula  $\text{CH}_3\text{CH}_2\text{OH}$  (ethanol).

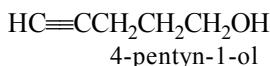
Since B and D are obtained by acid hydrolysis of C, the compound C must be an ester  $\text{CH}_3\text{COOC}_2\text{H}_5$  (ethyl acetate).

Since the compounds B (acetic acid) and C (ethyl acetate) are obtained by treating A with ethanol, the compound A must be an anhydride  $(\text{CH}_3\text{CO})_2\text{O}$  (acetic anhydride).

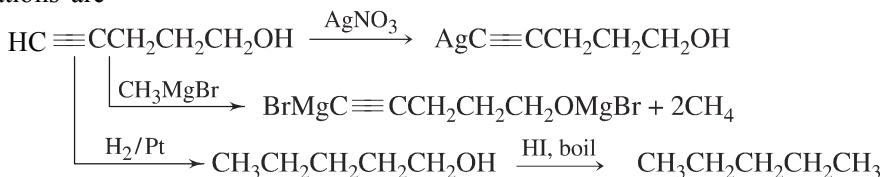
The given reactions are



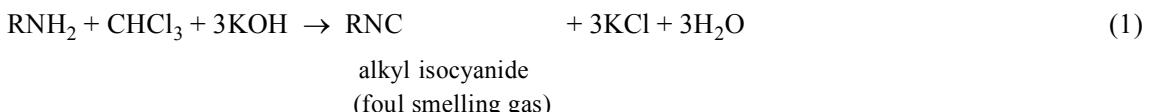
27. Since the given compound does not react appreciably with Lucas reagent, it may be primary alcohol. It is given that 0.42 g of the compound (which is 0.005 mol) produces 22.4 mL of  $\text{CH}_4$  at STP (which is 0.01 mol) with excess  $\text{CH}_3\text{MgBr}$ . This shows that the compound X contains two active hydrogen atoms. Of these, one is due to hydroxyl group and the other must be due to acetylinic hydrogen, i.e. the compound must contain a triple bond with one hydrogen directly attached to it. This is possible only if  $-\text{C}\equiv\text{C}-$  group is present at one of the extreme ends of the molecule. The presence of acetylinic hydrogen is also supported by the fact that the compound X gives a precipitate with ammoniacal silver nitrate. Moreover, the treatment of X with  $\text{H}_2/\text{Pt}$  followed by boiling with excess of HI gives *n*-pentane. This shows that the compound X contains a straight chain. With these facts, we can write the structure of X as



The equations are



28. Since the compound gives a foul smelling gas on treating with  $\text{CHCl}_3$  and alcoholic KOH, the compound must be a primary amine.



Since the compound on treating with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$  produces a colourless gas, the compound must be an aliphatic primary amine.



Thus, the gas produced is nitrogen.

$$\text{Amount of gas liberated} = \frac{112 \text{ mL}}{22400 \text{ mL mol}^{-1}} = \frac{1}{200} \text{ mol}$$

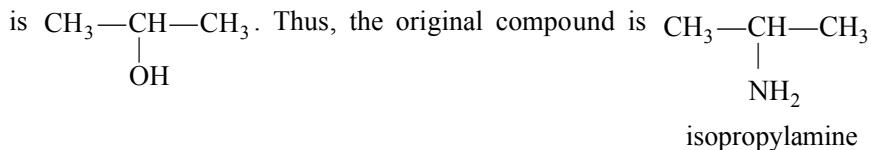
From the above equation, it is obvious that

$$\text{Amount of compound RNH}_2 = \frac{1}{200} \text{ mol}$$

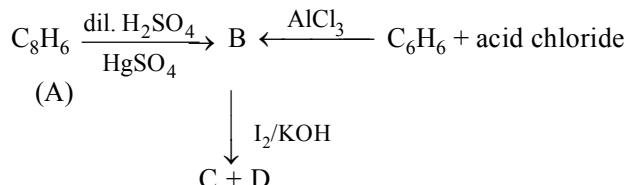
If  $M$  is the molar mass of  $\text{RNH}_2$ , then

$$\frac{2.295 \text{ g}}{M} = \frac{1}{200} \text{ mol} \quad \text{or} \quad M = 0.295 \times 200 \text{ g mol}^{-1} = 59 \text{ g mol}^{-1}.$$

Thus, the molar mass of alkyl group R is  $(59 - 16) \text{ g mol}^{-1}$ , i.e.  $43 \text{ g mol}^{-1}$ . Hence, R must be  $\text{C}_3\text{H}_7$ . From Eq. (2), it is obvious that the liquid obtained after distillation is ROH. Since this gives yellow precipitate with alkali and iodine (iodoform test), it must contain  $\text{CH}_3-\overset{|}{\underset{|}{\text{C}}}-$  group. Hence, it is concluded that ROH

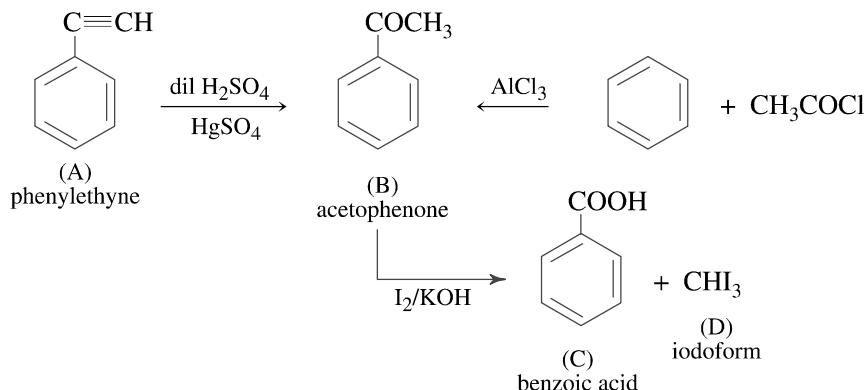


29. The given reactions are

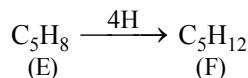


The reaction of B with  $\text{I}_2$  in KOH is iodoform reaction. The compound D is iodoform,  $\text{CHI}_3$ . The compound B must contain  $-\text{COCH}_3$  group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ). The compound C must be an acid.

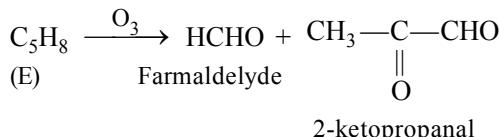
The compound A may be represented as  $\text{C}_6\text{H}_5\text{C}_2\text{H}$ . Since it gives  $\text{C}_6\text{H}_5\text{COCH}_3$  on treating with dilute  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$ , it must contain a triple bond ( $-\text{C}\equiv\text{CH}$ ) in the side chain. Hence, the given reactions may be represented as



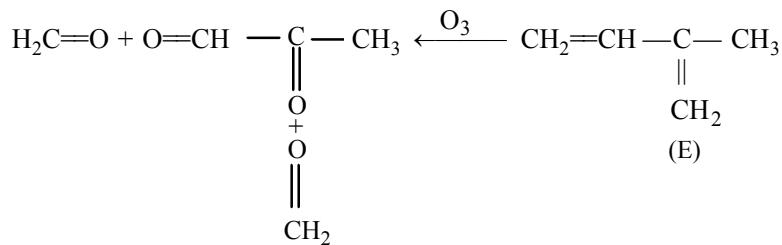
30. Since there are four hydrogen atoms added in the reaction



the compound E may contain two double bonds. The ozonolysis reaction is

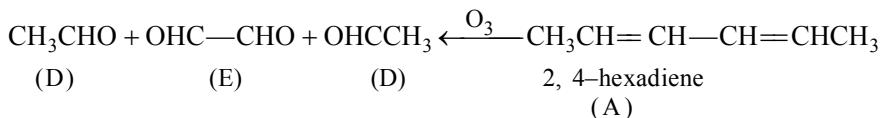


Since there is no loss of carbon atoms in an ozonolysis reaction, probably 2 molecules of formaldehyde are formed. In 2-ketopropanal,  $-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-$  and  $-\text{CHO}$  groups must have resulted due to the cleavage of double bonds. Hence, the net reaction can be explained as follows.

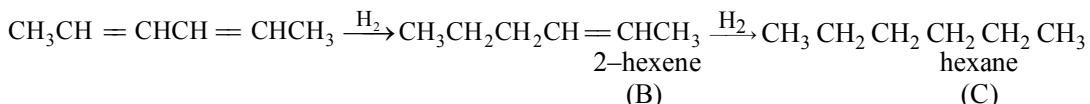


Hence, the compound E is 2-methyl-1, 3-butadiene.

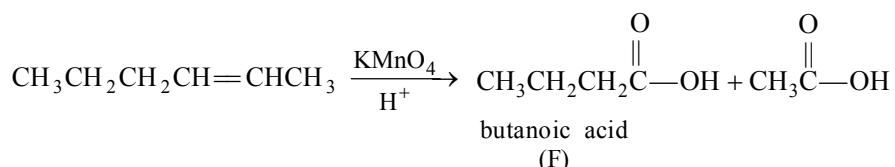
31. Since ozonolysis of A gives two aldehydes, the compound A contains the carbon-carbon double bond. In fact, the molecule of A contains two double bonds as it is successively reduced to  $C_6H_{12}$  and  $C_6H_{14}$ . The number of carbon and hydrogen in the ozonolysis products will remain same as in the compound A. Hence, it may be concluded that the ozonolysis products include two molecules of D( $CH_3CHO$ ) and one molecule of E( $OHC-CHO$ ). From this, we derive the structure of A as shown in the following.



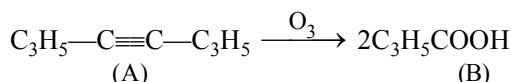
The structures of B and C are as follows.



The structure of F is as follows.



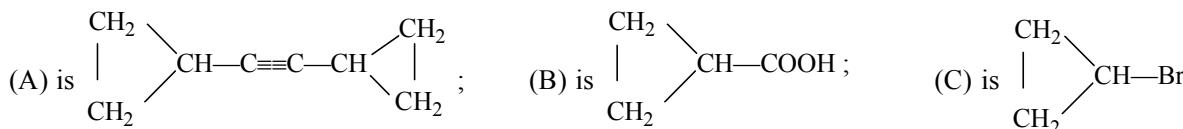
32. Since there is no loss of carbon content on ozonolysis and the fact that the products are carboxylic acid, the compound A may be represented as  $C_3H_5-C\equiv C-C_3H_5$ . The ozonolysis reaction is



The compound B may be obtained as follows.

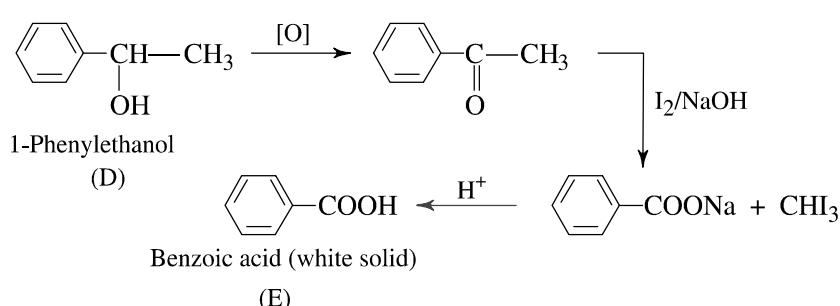


The species  $C_3H_5$  must be saturated alkyl group. The only possibility is the cyclopropyl group. Hence,



33. The reaction of  $C_8H_{10}O$  with alkaline solution of iodine is an iodoform reaction. This reaction is possible if the compound D has  $\begin{array}{c} || \\ -C-O-CH_3 \end{array}$  or  $\begin{array}{c} | \\ -CH-OH-CH_3 \end{array}$  group. The high carbon content in D indicates that D

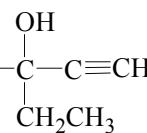
is an aromatic compound containing a benzene ring. To account for the given formula, the compound D may be  $C_6H_5CH(OH)CH_3$ . The given reactions are



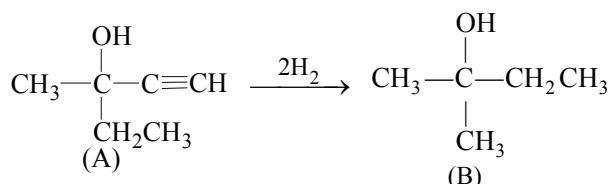
34. The given compound A has the following features.

- One alcoholic group as it contains one oxygen atom.
- One asymmetric carbon as it is an optically active compound.
- One triple bond as two moles of hydrogen can be added.
- The carbon atom bearing  $\text{—OH}$  group does not contain H atom as the compound B is resistant to oxidation.

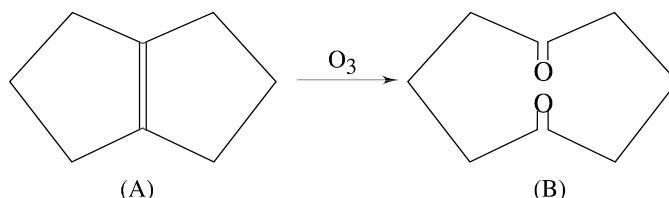
Consistent with the molecular formula, the structure of A may be



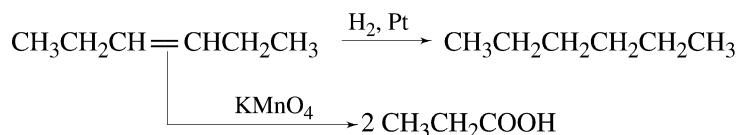
Hence, we have



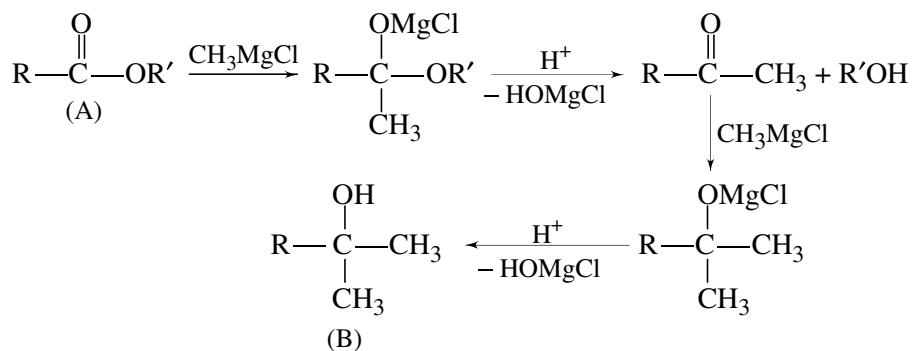
35. Since the compound A on ozonolysis gives only one symmetric diketone B with the same number of carbon atoms and also since A consumes only one mole of hydrogen, the structures of A and B are as follows.



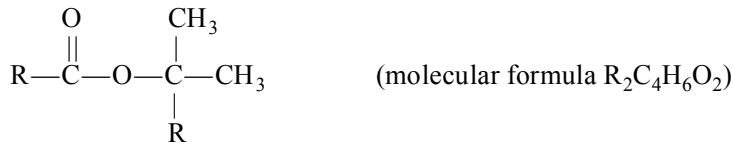
36. The hydrocarbon A is  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ . The given reactions are



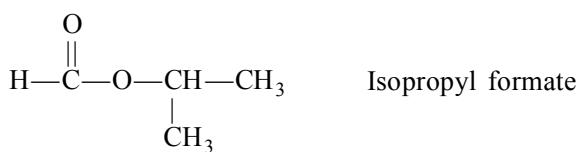
37. The reactions of an ester with methyl magnesium chloride are as follows.



Since the given ester ( $\text{C}_4\text{H}_8\text{O}_2$ ) produces only one alcohol B, it follows that  $\text{RC}(\text{CH}_3)_2\text{OH}$  and  $\text{R}'\text{OH}$  must be identical. Thus, the alkyl group R' must be  $\text{RC}(\text{CH}_3)_2$ — and the given ester A is



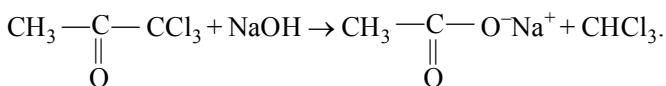
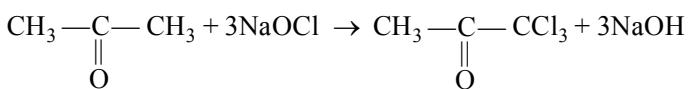
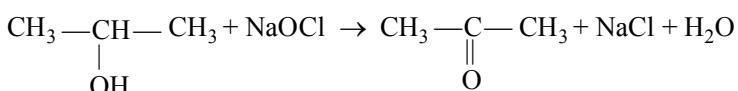
From the molecular formula of A, we conclude that R must be H atom. Hence, the given ester is



The alcohol B is a secondary alcohol.

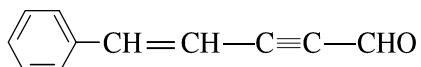


The oxidation of alcohol B with NaOCl will give a ketone which further undergoes a haloform reaction.

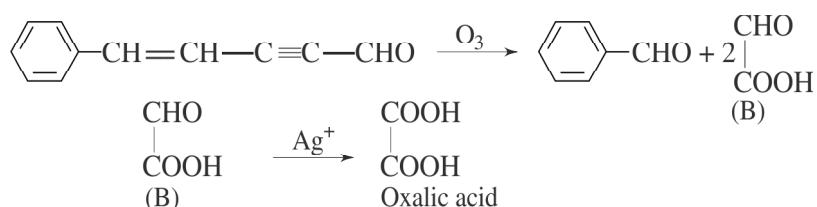


The acidification of sodium acetate will produce acetic acid.

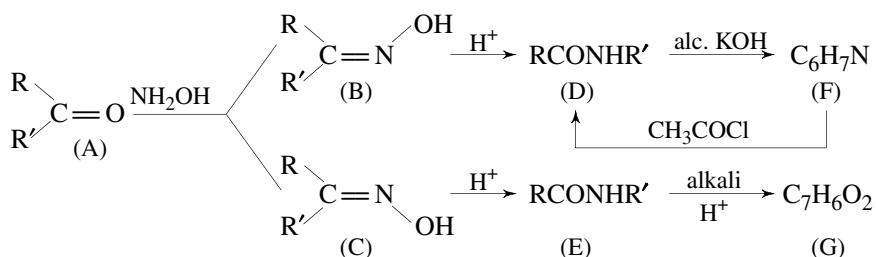
38. Since the given aldehyde does not undergo self aldol condensation, it will not contain alpha hydrogen atom. Since the given aldehyde undergoes ozonolysis, it must include unsaturation, probably at two places as the products are benzaldehyde and two moles of the compound B. With these informations, we can write the structure of the given aldehyde ( $\text{C}_{11}\text{H}_8\text{O}$ ) as



The given reactions are as follows.

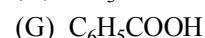
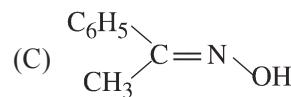
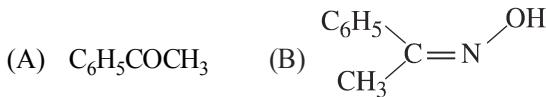
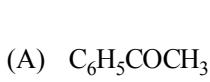


39. The compound A must contain a keto group as it combines with hydroxylamine hydrochloride. Let it be represented as  $\text{RCOR}'$ . The given reaction may be represented as follows.

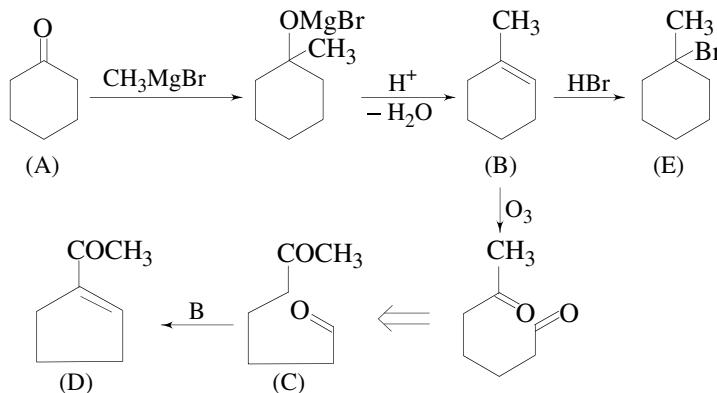


The conversion of F to D is an acetylation reaction implying that the compound F is an amine, i.e.  $\text{R}'\text{NH}_2$  with  $\text{R}'$  probably a phenyl group. The group R must be a methyl group.

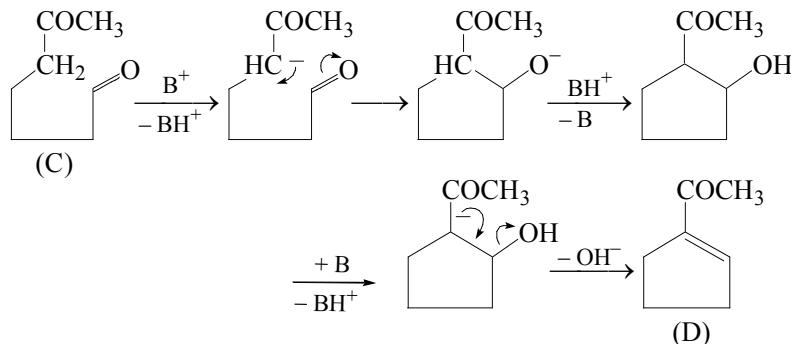
The reactions B to D and C to E are rearrangement reactions, since all these are isomers. In fact, these rearrangement which gives *N*-substituted acetamide due to the migration of R group in the *anti*-position. With these informations, the compounds A to G are as follows.



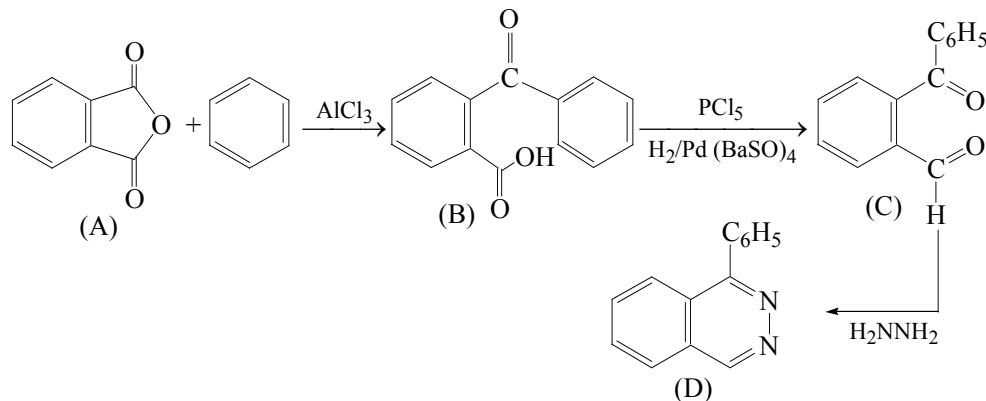
40. The given reactions are as follows.



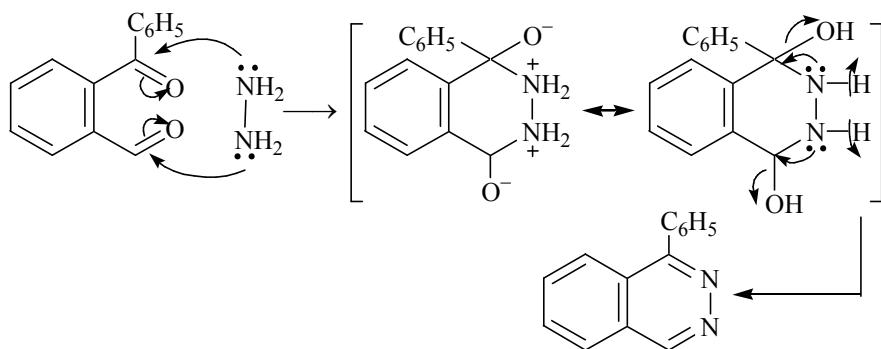
The conversion of C into D may involve the following mechanism.



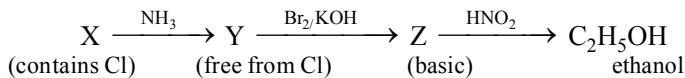
41. The given reactions are as follows.



The formation of D from C may be explained as follows.



42. The given reactions are



From the given composition of Y, we compute its molecular formula as follows:

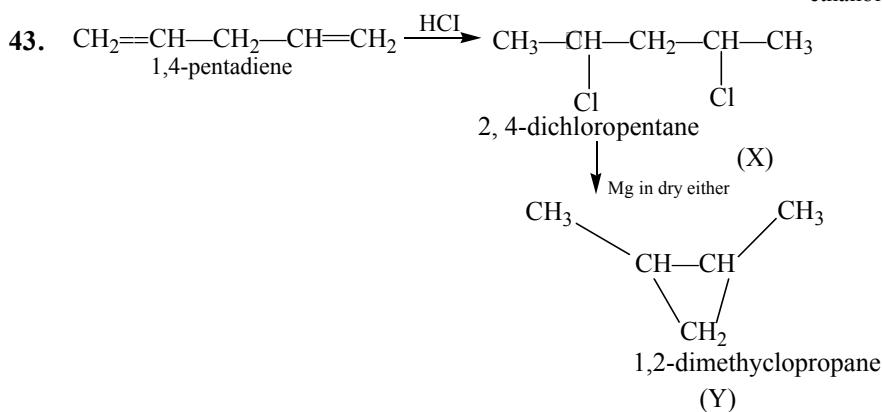
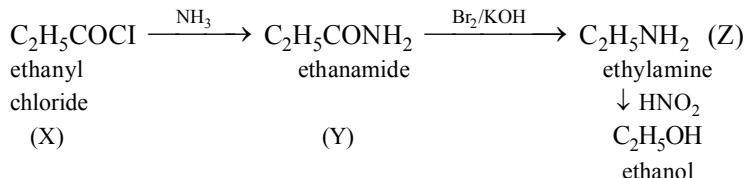
Element	Mass taken (= its per cent)	Number of atoms	Ratio of atoms
C (12 amu)	49.31 amu	49.31/12 = 4.11	4.11/1.37 = 3
H (1 amu)	9.59 amu	9.59/1 = 9.59	9.59/1.37 = 7
N (14 amu)	19.18 amu	19.18/14 = 1.37	1.37/1.37 = 1
O (16 amu)	21.92 amu	21.92/16 = 1.37	1.37/1.37 = 1

Hence, Empirical formula: C<sub>3</sub>H<sub>7</sub>NO

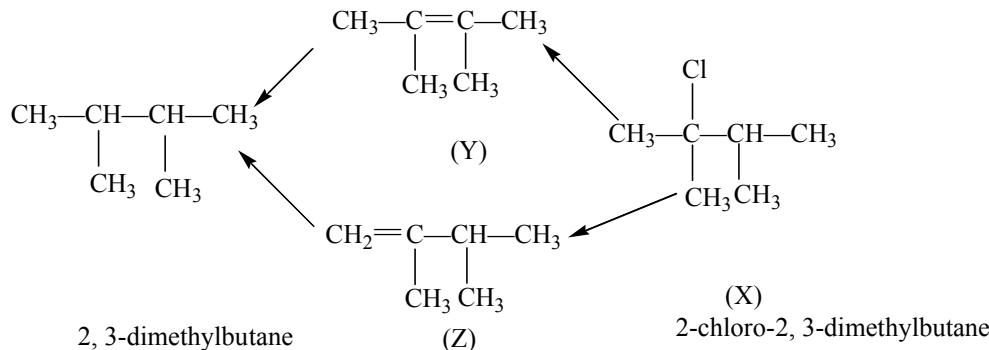
The compound Z will be an aliphatic primary amine as this compound on treating with HNO<sub>2</sub> gives alcohol. Hence, Z is C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>.

The compound Y will be an amide as this on treating with Br<sub>2</sub>/KOH produces an amine. Hence, Y must be C<sub>2</sub>H<sub>5</sub>CONH<sub>2</sub>. The also agrees with the empirical formula computed above.

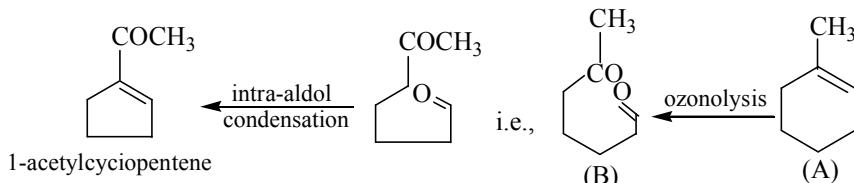
The compound X must be C<sub>2</sub>H<sub>5</sub>COCl as this on treating with concentrated NH<sub>3</sub> would produce an amide. Hence, the given reaction are



44.



45. Since the ozonolysis of the hydrocarbon A (molecular formula,  $C_7H_{12}$ ) gives only one compound B, the compound A must be a cyclic alkene. Moreover, since the number of carbon atoms in the product obtained from the aldol condensation of B is the same as that of A (or B as no loss of carbon atom occurs during ozonolysis), the compound B must have undergone intra-aldol condensation. We arrive at the compounds A and B as shown in the following.



46. The ratios of atoms in the minor product are

$$\begin{aligned}
 \text{C : H : N : O} &:: \frac{42.86}{12} : \frac{2.40}{1} : \frac{16.67}{14} : \frac{38.07}{16} \\
 &:: 3.57 : 2.40 : 1.19 : 2.38 \\
 &:: 3 : 2 : 1 : 2
 \end{aligned}$$

Empirical formula of the minor product:  $C_3H_2NO_2$

Molar empirical formula mass of the minor product

$$= (3 \times 12 + 2 \times 1 + 1 \times 14 + 2 \times 16) \text{ g mol}^{-1} = 84 \text{ g mol}^{-1}$$

Let  $M$  be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality of the solution is

$$m = \frac{5.5 \text{ g}/M}{0.045 \text{ kg}}$$

Substituting this in the expression of elevation of boiling point, we get

$$\Delta T_b = K_b m$$

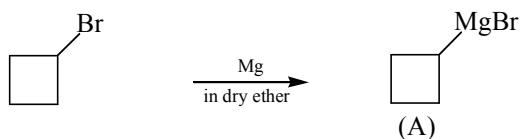
$$1.84 \text{ K} = (2.53 \text{ K kg mol}^{-1}) \left( \frac{55 \text{ g}/M}{0.045 \text{ kg}} \right)$$

$$\text{i.e. } M = \left( \frac{2.53 \times 55}{1.84 \times 0.045} \right) \text{ g mol}^{-1} = 168 \text{ g mol}^{-1}$$

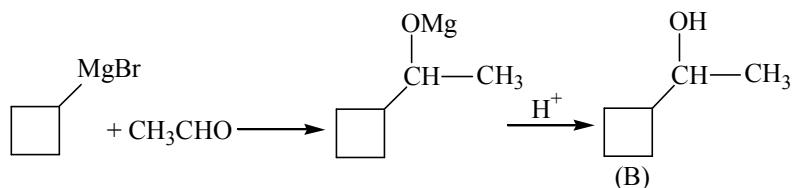
$$\text{Number of unit of empirical formula in molecular formula} = \frac{168 \text{ g mol}^{-1}}{84 \text{ g mol}^{-1}} = 2$$

Hence, the molecular formula of the minor product is  $2(C_3H_2NO_2)$ , i.e.  $C_6H_4(NO_2)_2$ . The product is *m*-dinitrobenzene.

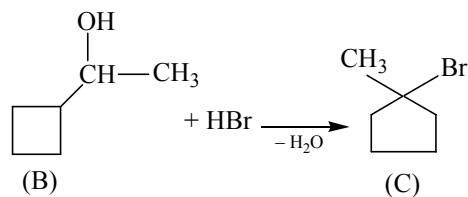
47. The reaction of cyclobutyl bromide with magnesium in dry ether is



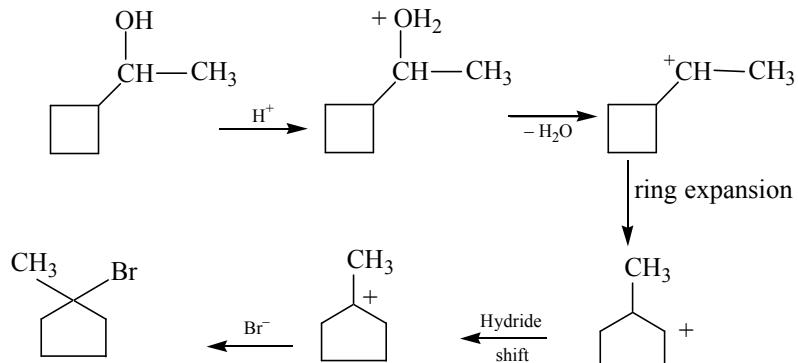
The reaction of A with ethanal followed by acidification to give alcohol are



The reaction of B with HBr is

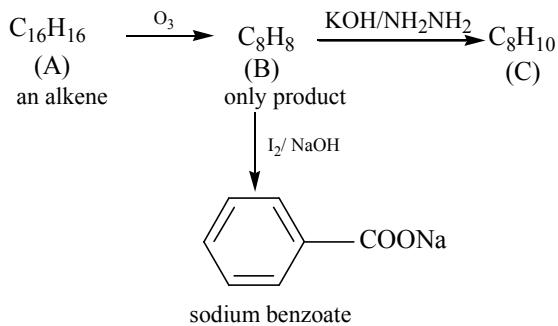


The formation of C from B precedes as follows:

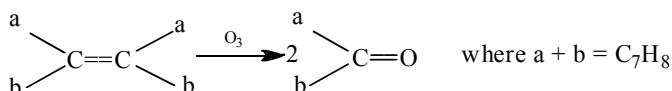


Ring expansion occurs due to more stable five-membered ring. Hydride shift occurs due to more stable 3° carbocation.

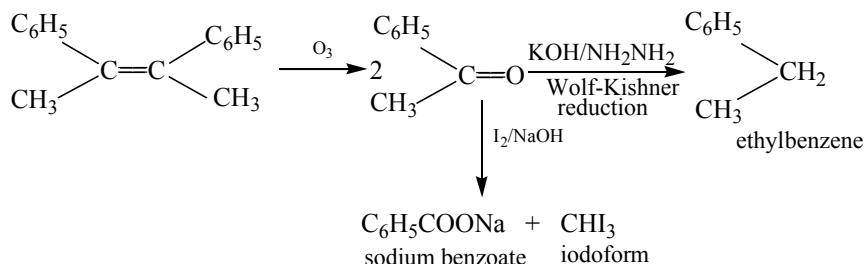
48. The given reactions are as follows:



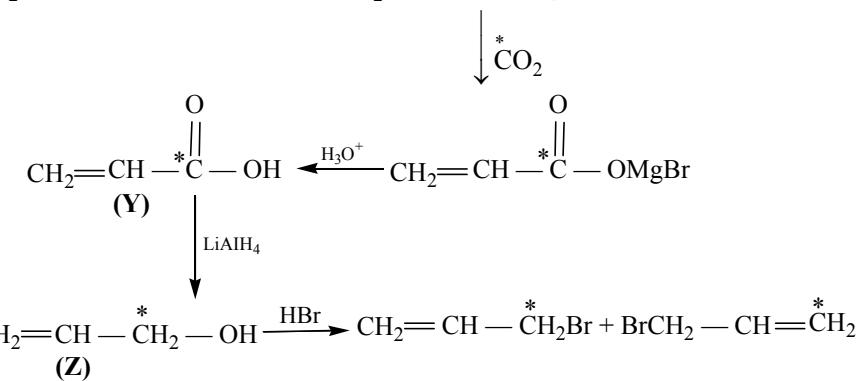
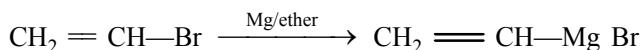
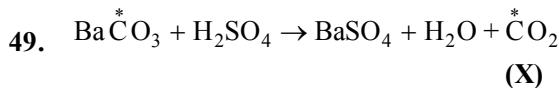
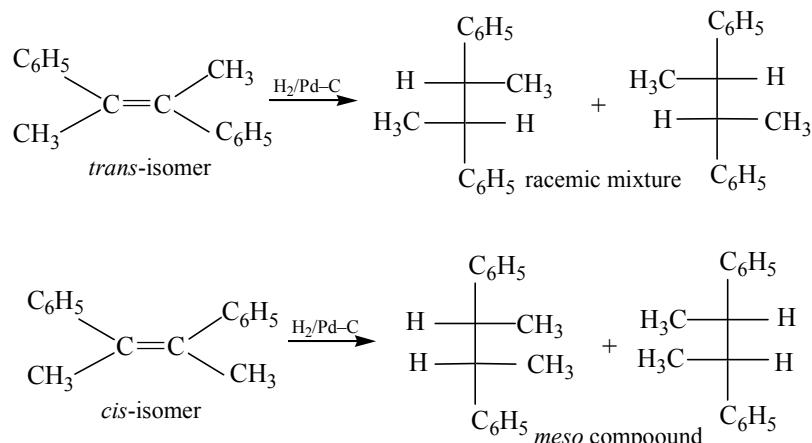
Since A on ozonolysis gives only one product B, the alkene must be a symmetrical one. This reaction may be written as



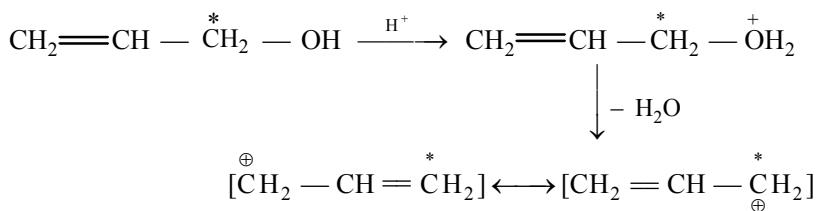
Since **B** on treatment with  $I_2/NaOH$  gives sodium benzoate, one of the groups a and b may be identified with  $C_6H_5$  and hence the other one must be  $CH_3$  group ( $= C_7H_8 - C_6H_5$ ). The given reactions are follows.



The alkene **A** will have two isomers *cis* and *trans*. The catalytic hydrogenation ( $H_2/Pd-C$ ) involves syn-addition of hydrogen. The *trans* isomer gives racemic mixture while *cis* isomeric gives a *meso* compound.



The ozonolysis of  $\text{BrCH}_2\text{CH} = \overset{*}{\text{CH}_2}$  produces formaldehyde,  $\text{H}_2\overset{*}{\text{CO}}$ . Replacement of  $-\text{OH}$  by  $-\text{Br}$  proceeds through the formation of carbocation which can undergo rearrangement as depicted in the following.

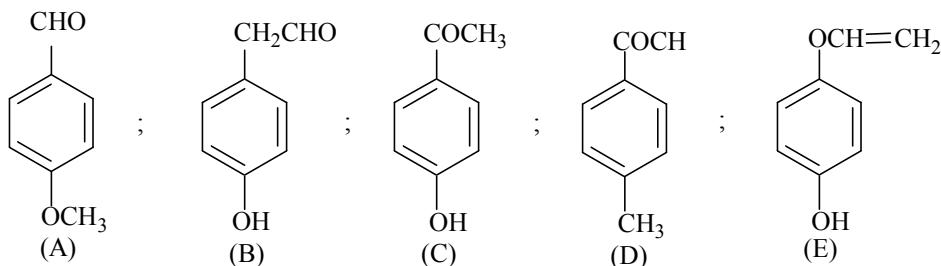


The products are  $\text{BrCH}_2-\text{CH}=\overset{*}{\text{CH}_2}$  and  $\text{CH}_2=\text{CH}-\overset{*}{\text{CH}_2}\text{Br}$

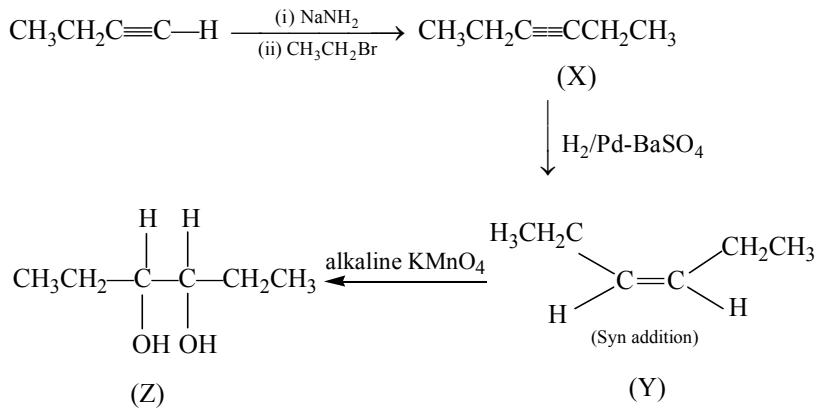
The former on ozonolysis produces  $\text{H}\overset{*}{\text{CH}}\text{O}$ .

50. Since the compounds A to E are *para*-disubstituted aromatic compounds (probably disubstituted benzenes), the substituents are represented by the formula  $\text{C}_2\text{H}_4\text{O}_2$  ( $=\text{C}_8\text{H}_8\text{O}_2$  minus  $\text{C}_6\text{H}_4$ ). The substituents present in the given compounds are as follows.

- (i)  $-\text{OCH}_3$  and  $-\text{CHO}$ . These are present in compound A. The positive silver mirror test is due to  $-\text{CHO}$  group.
- (ii)  $-\text{OH}$  and  $-\text{CH}_2\text{CHO}$ . These are present in the compound B. The positive silver mirror test is due to  $-\text{CHO}$  and the positive test with  $\text{FeCl}_3$  solution is due to phenolic  $-\text{OH}$ .
- (iii)  $-\text{OH}$  and  $-\text{COCH}_3$ . These are present in the compound C. The positive iodoform test is due to  $-\text{COCH}_3$  group.
- (iv)  $-\text{CH}_3$  and  $-\text{COOH}$ . These are present in the compound D. The readily extraction by aqueous  $\text{NaHCO}_3$  solution is due to the presence of carboxylic acid group.
- (v)  $-\text{OH}$  and  $-\text{OCH}=\text{CH}_2$ . These are present in the compound E. The acid hydrolysis of the substituent  $-\text{OCH}=\text{CH}_2$  produces  $-\text{OH}$  group. Hence, the structure of the compounds A to E are as follows.

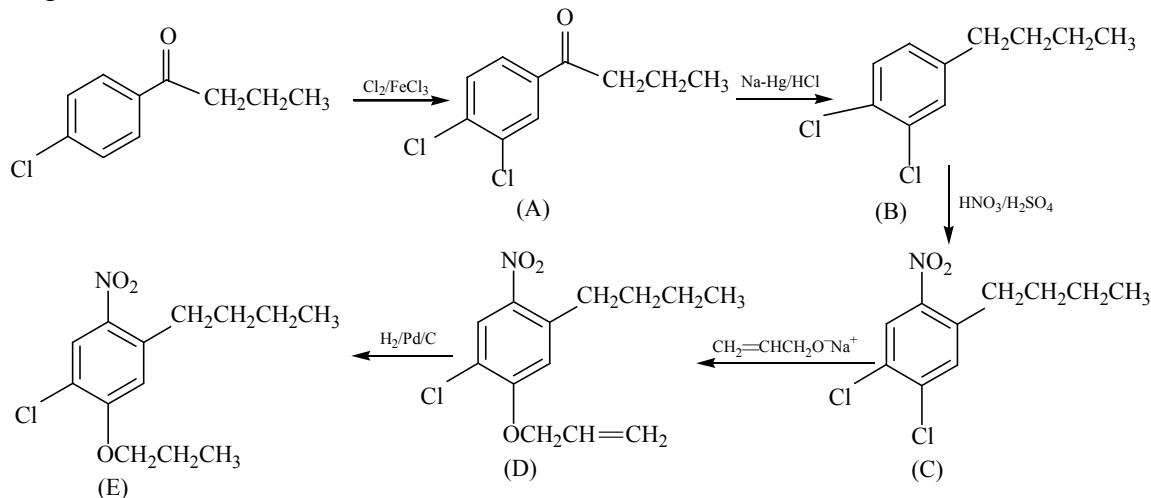


51. The given reactions are as follows.

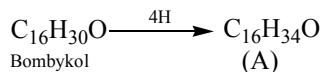


The compound Z is a *meso* compound and is thus optically inactive.

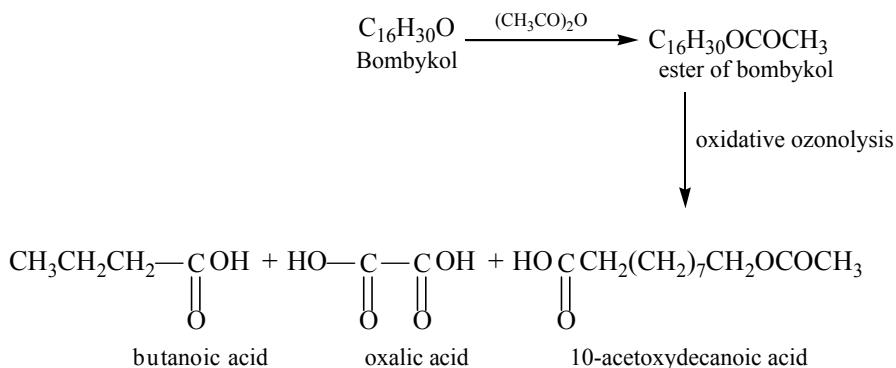
52. The given reaction are as follows.



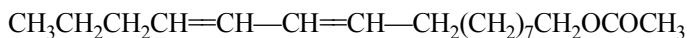
53. From the hydrogenation reaction



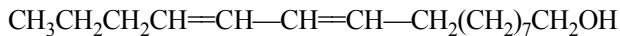
It may be concluded that bombykol contains either two double bonds or a single triple bond. However, the presence of a triple bond is excluded based on the products obtained in the oxidative ozonolysis of the ester of Bombykol.



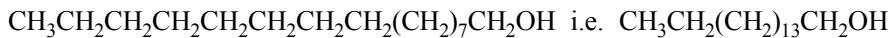
From the products, one can write the structure of ester of bombykol:



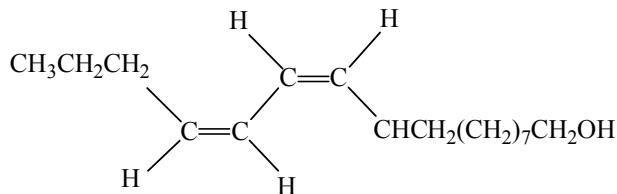
The structure of bombykol is

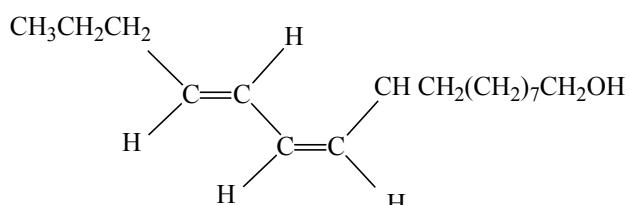
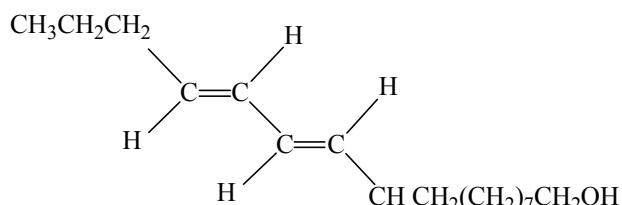
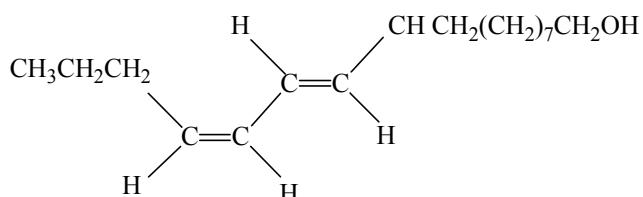


The structure of compound A is

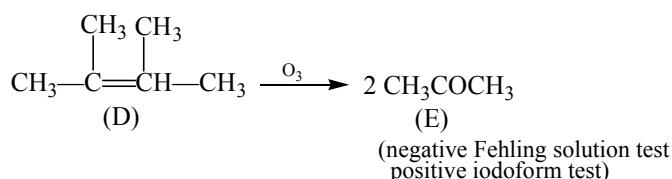
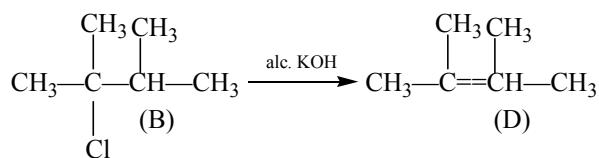
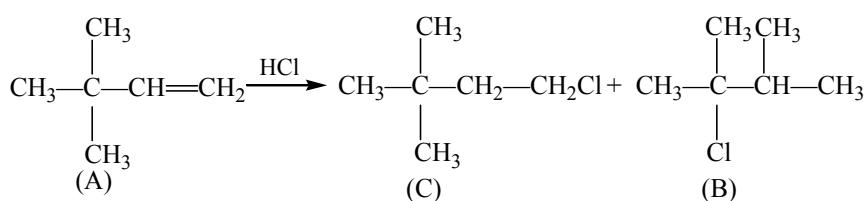


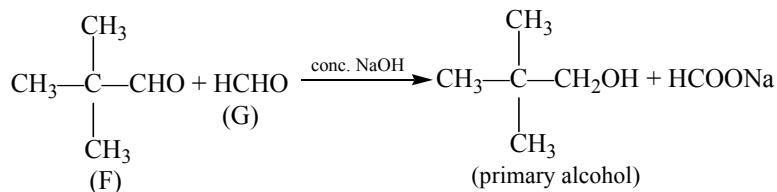
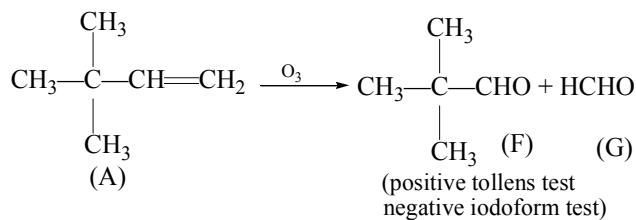
The bombykol can exhibit the following four geometrical isomers due to the presence of two double bonds.



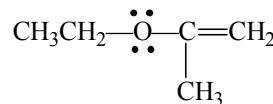


54. The given reactions can be explained as follows.

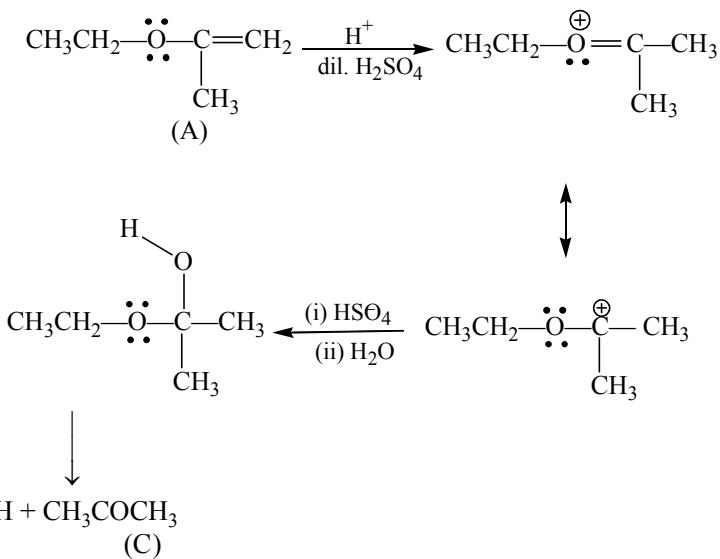




55. (a) Since the reactivity of the compound A with respect to dilute  $\text{H}_2\text{SO}_4$  is  $10^{15}$  times larger than ethylene, it follows that the compound A also contains a carbon-carbon double bond attached to a group which has enhanced its reactivity. Based on this fact, one can write the structure of the compound A as



The reaction of the compound A with dilute  $\text{H}_2\text{SO}_4$  may be formulated as follows.



Both the compounds B and C exhibit iodoform test. Ethyl alcohol is first oxidized to acetaldehyde (which contains  $\text{CH}_3\text{CO}-$  group).

- (b) The extraordinary reactivity of A is due to the oxygen atom attached to the doubly-bonded carbon atom. The unshared pair of electrons of oxygen atom stabilises the intermediate carbocation thereby enhances the reactivity of the double bond.



# **CHEMISTRY**

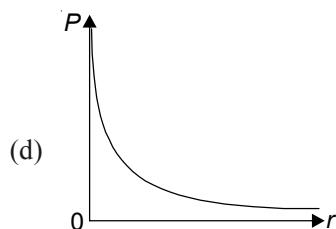
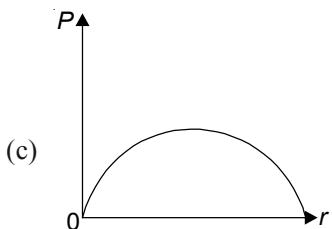
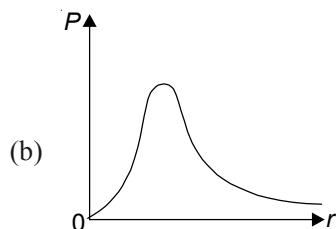
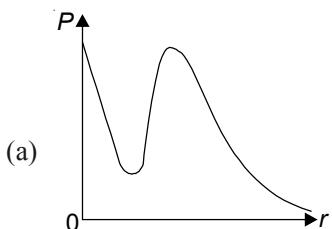
## **JEE (ADVANCED)-2016**

### ***Paper-I***

**SECTION-1 (Maximum Marks : 15)**

- This section contains **FIVE** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is correct.
  - For each question, darken the bubble corresponding to the correct option in the ORS.
  - For each question, marks will be awarded in one of the following categories:  
*Full Marks* : +3 If only the bubble corresponding to the correct option is darkened.  
*Zero Marks* : 0 If none of the bubbles is darkened.  
*Negative Marks* : -1 In all other cases.

1.  $P$  is the probability of finding the 1s electron of hydrogen atom in a spherical shell of infinitesimal thickness,  $dr$ , at a distance  $r$  from the nucleus. The volume of this shell is  $4\pi r^2 dr$ . The qualitative sketch of the dependence of  $P$  on  $r$  is



## P-1.2 IIT Chemistry: Topic-wise Solved Questions



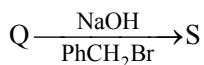
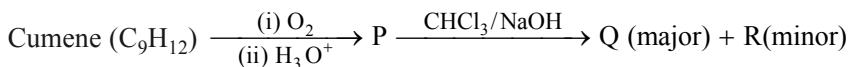
**SECTION-2 (Maximum Marks : 32)**

- This section contains **EIGHT** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is(are) correct.
  - For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
  - For each question, marks will be awarded in one of the following categories:  
*Full Marks* : +4 If only the bubble corresponding to all the correct option(s) is(are) darkened.  
*Partial Marks* : +1 For darkening a bubble corresponding to **each correct option**, provided NO incorrect option is darkened.  
*Zero Marks* : 0 If none of the bubbles is darkened.  
*Negative Marks* : -2 In all other cases.
  - For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (a) and (d) will result in result in +2 marks, and darkening (a) and (b) will result in -2 marks, as a wrong option is also darkened.

6. A plot of the number of neutrons (N) against the number of protons (P) of stable nuclei exhibits upward deviation from linearity for atomic number,  $Z > 20$ . For an unstable nucleus having  $N/P$  ratio less than 1, the possible mode(s) of decay is(are)

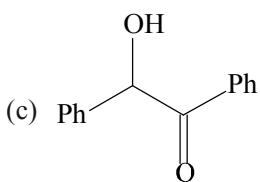
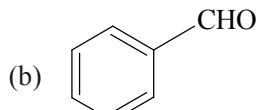
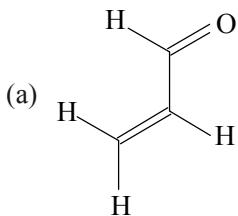
  - (a)  $\beta^-$  decay ( $\beta$  emission)
  - (b) orbital or K-electron capture
  - (c) Neutron emission
  - (d)  $\beta^+$  decay (positron emission)

7. The correct statement(s) about the following reaction sequence is(are)–

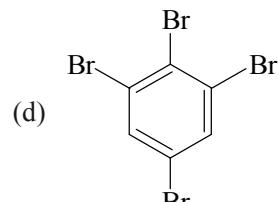
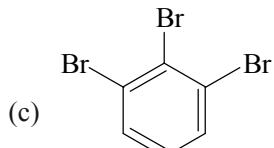
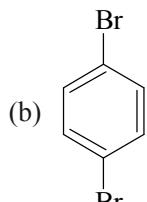
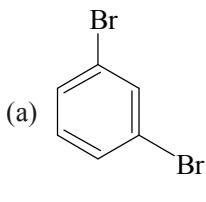
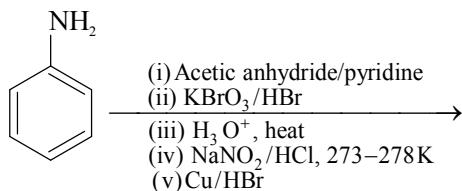


- (a) R is steam volatile
  - (b) Q gives dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution.
  - (c) S gives yellow precipitate with 2, 4-dinitrophenylhydrazine.
  - (d) S gives dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution.

8. Positive Tollens test is observed for



9. The product(s) of the following reaction sequence is(are)



10. The compounds with **TWO** lone pairs of electrons on the central atom is(are)

- (a)  $\text{BrF}_5$       (b)  $\text{ClF}_3$       (c)  $\text{XeF}_4$       (d)  $\text{SF}_4$

**11.** The crystalline form of borax has

- (a) Tetranuclear  $[B_4O_5(OH)_4]^{2-}$  unit
  - (b) All boron atoms in the same plane
  - (c) Equal number of  $sp^2$  and  $sp^3$  hybridized boron atoms
  - (d) One terminal hydroxide per boron atom

12. The reagent(s) that can selectively precipitate  $S^{2-}$  from a mixture of  $S^{2-}$  and  $SO_4^{2-}$  in aqueous solution is(are)

- (a) CuCl<sub>2</sub>, (b) BaCl<sub>2</sub>, (c) Pb(OOCCH<sub>3</sub>)<sub>2</sub>, (d) Na<sub>2</sub>[Fe(CN)<sub>5</sub>NO]

**13.** According to Arrhenius equation,

- (a) A high activation energy usually implies a fast reaction.
  - (b) Rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.
  - (c) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.
  - (d) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energies.

### **SECTION-3 (Maximum Marks : 15)**

- This section contains **FIVE** questions.
  - The answer to each question is a **SINGLE DIGIT INTEGER** ranging from 0 to 9, both inclusive.
  - For each question, darken the bubble corresponding to the correct option in the ORS.
  - For each question, marks will be awarded in one of the following categories:

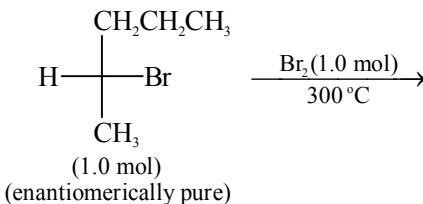
**Full Marks** : +3 If only the bubble corresponding to the correct option is darkened.

*Zero Marks* : 0 In all other cases.

14. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is  $2.0 \text{ g cm}^{-3}$ . The ratio of the molecular weights of the solute and solvent,  $(M_{\text{solute}} / M_{\text{solvent}})$ , is \_\_\_\_\_.

**P-1.4** IIT Chemistry: Topic-wise Solved Questions

15. In the following monobromination reaction, the number of possible chiral products is \_\_\_\_\_.



16. The diffusion coefficient of an ideal gas is proportional to mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases  $x$  times. The value of  $x$  is \_\_\_\_\_.
17. The number of geometric isomers possible for the complex  $[\text{CoL}_2\text{Cl}_2]^-$ , where  $\text{L} = \text{H}_2\text{NCH}_2\text{CH}_2\text{O}^-$ , is \_\_\_\_\_.
18. The neutral or faintly alkaline solution, 8 mol of permanganate anions quantitatively oxidize thiosulphate anions to produce  $X$  mol of sulphur containing product. The magnitude of  $X$  is \_\_\_\_\_.

**Answer Key**

- |                   |             |                   |        |              |
|-------------------|-------------|-------------------|--------|--------------|
| 1. (b)            | 2. (c)      | 3. (b)            | 4. (a) | 5. (b)       |
| 6. (b), (d)       | 7. (b), (c) | 8. (a), (b), (c)  | 9. (b) | 10. (b), (c) |
| 11. (a), (c), (d) | 12. (a)     | 13. (b), (c), (d) | 14. 9  | 15. 5        |
| 16. 4             | 17. 5       | 18. 6             |        |              |

## Hints & Solutions

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1. The  $r$ -dependent part of the wave function of 1s orbital of hydrogen atom is

$$R_{1,0} = 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

where  $a_0$  is the Bohr radius ( $= 52.9 \text{ pm}$ ). The probability of finding the 1s electron in a spherical shell of infinitesimal thickness,  $dr$ , at a distance  $r$  from the nucleus is

$$P = 4\pi r^2 R_{1,0}^2 dr = 4\pi r^2 \left[ 4\left(\frac{1}{a_0}\right)^3 e^{-2r/a_0} \right] dr$$

For shorter distances, the variation of  $r^2$  is larger than that of  $e^{-2r/a_0}$ , with the result that  $P$  increases with increase in the value of  $r$ . For larger distance, the reverse is true, consequently,  $P$  decreases exponentially with increase in the value of  $r$ . These characteristics are displayed in the Choice (b).

2. From the first law of thermodynamics, we have  $\Delta U = q + w$

Since temperature of the ideal gas remains constant,  $\Delta U = 0$ . Hence

$$\begin{aligned} q &= -w = -(-p_{\text{ext}} \Delta V) = p_{\text{ext}} \Delta V \\ &= 3.0 \text{ atm} (2.0 \text{ L} - 1.0 \text{ L}) \\ &= 3.0 \text{ atm L} \equiv 3.0 \times 101.3 \text{ J} \\ &= 303.9 \text{ J} \end{aligned}$$

Now

$$q_{\text{surr}} = -q = -303.9 \text{ J}$$

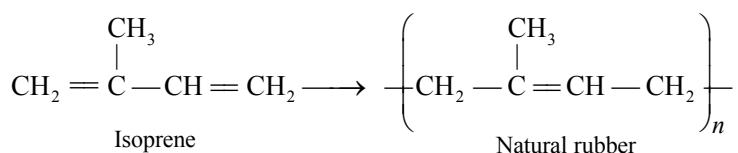
$$\Delta_{\text{surr}} S = \frac{q_{\text{surr}}}{T} = \frac{-303.9 \text{ J}}{300 \text{ K}} = -1.013 \text{ J K}^{-1}$$

3. The descending order of elements is  ${}_{13}\text{Al}$ ,  ${}_{31}\text{Ga}$ ,  ${}_{49}\text{In}$ ,  ${}_{81}\text{Tl}$

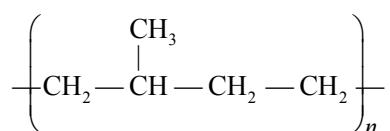
In general, the radius of atom increases on descending a group. This is due to outmost shell of higher principal quantum number. However, due to the poor shielding of nucleus by 3d electrons, the size of Ga is smaller than that of Al.

The size of Tl is a little larger than In due to lanthanide contraction.

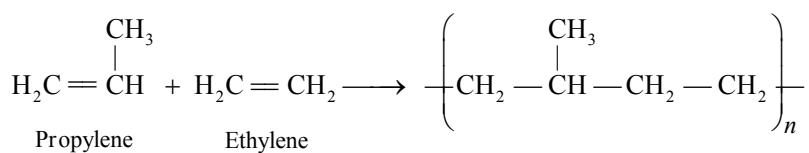
4. The natural rubber results from the polymerization of isoprene:



The complete hydrogenation of natural rubber gives

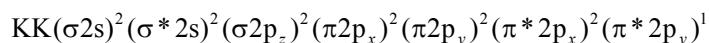
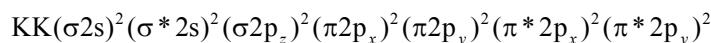
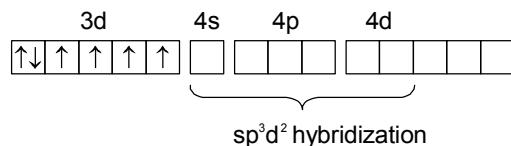
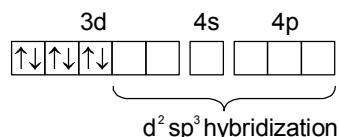
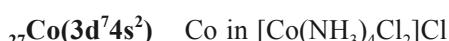
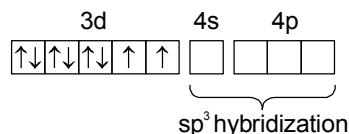
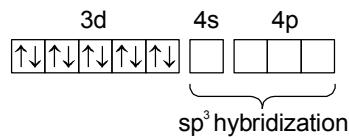


This may be obtained by the copolymerization of ethylene and propylene:



## P-1.6 IIT Chemistry: Topic-wise Solved Questions

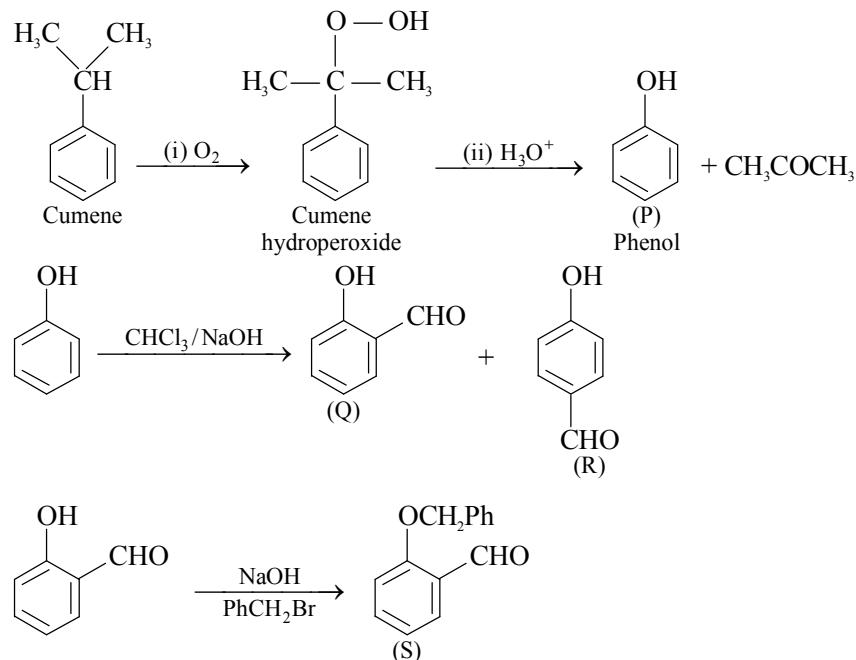
5. We have the following facts.



The species  $[\text{NiCl}_4]^{2-}$ ,  $\text{Na}_3[\text{CoF}_6]$  and  $\text{CsO}$ , have unpaired electrons and thus are paramagnetic.

6. To attain stability, the ratio N/P has to be increased. From the given choices, the Choice b (K-electron capture) and the Choice d (positron emission) will decrease the number of protons and hence increase in the ratio N/P.

7. The given reactions are as follows:

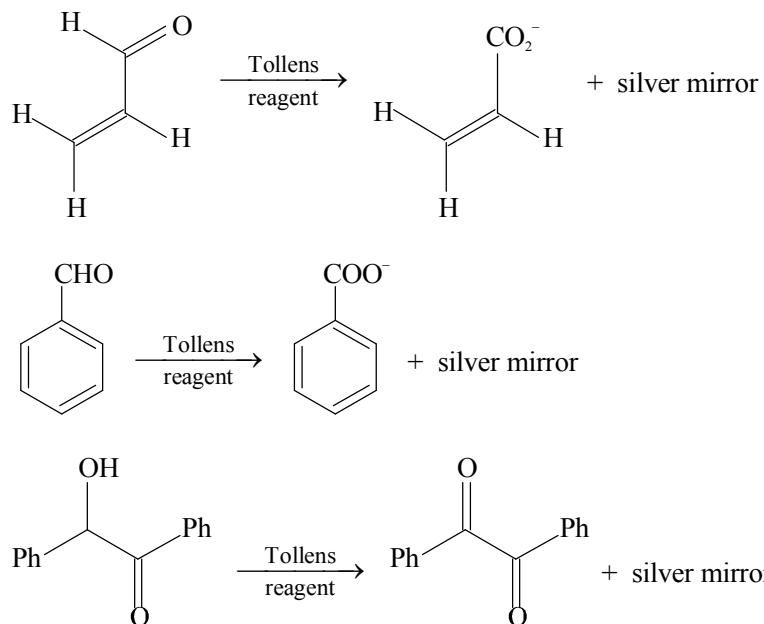


Q is steam volatile as it involves intramolecular hydrogen bonding. R is *not* steam volatile as it involves intermolecular hydrogen bonding.

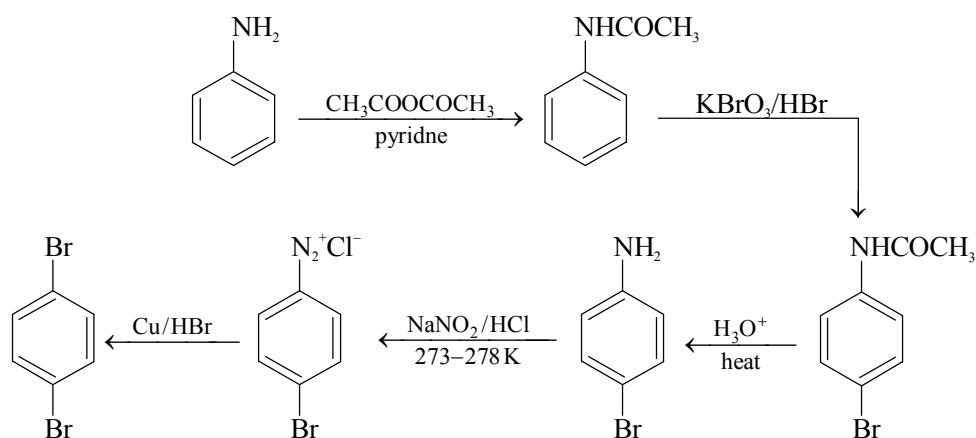
Q gives dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution due to phenolic group.

S gives yellow precipitate with 2, 4-dinitrophenylhydrazine due to  $-\text{CHO}$  group. It will not give dark violet coloration with 1% aqueous  $\text{FeCl}_3$  solution as there is no free phenolic group.

8. The Tollens reagent is an ammoniacal solution of silver nitrate. Aldehydes (Choices a and b) reduce Tollens reagent to a bright silver mirror. Also,  $\alpha$ -hydroxy carbonyl compound (Choice c) is oxidised by Tollens reagent. The reactions are:



9. The given reactions are: (i) acetylation of  $-\text{NH}_2$ , (ii) monobromination due to liberated bromine ( $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ ), (iii) deacetylation of  $-\text{NH}_2$ , (iv) diazotisation of  $-\text{NH}_2$  and (v) its replacement with Br.

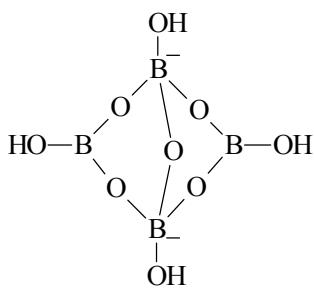


**P-1.8** IIT Chemistry: Topic-wise Solved Questions

10. Molecule	Valence electrons	Lewis structure
$\text{BrF}_5$	$7 + 5 \times 7 = 42$	
$\text{ClF}_3$	$7 + 3 \times 7 = 28$	
$\text{XeF}_4$	$8 + 4 \times 7 = 36$	
$\text{SF}_4$	$6 + 4 \times 7 = 34$	

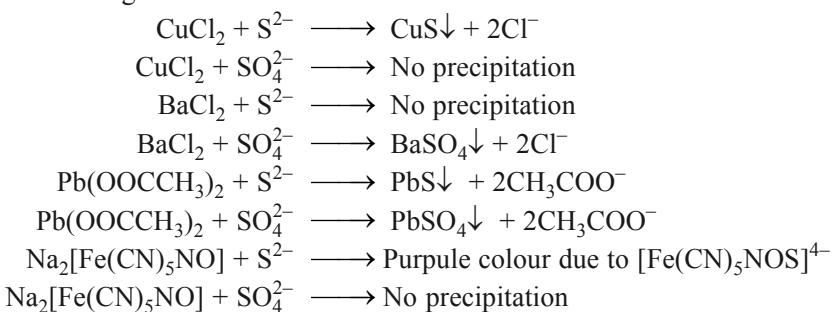
The molecule  $\text{ClF}_3$  (Choice b) and  $\text{XeF}_4$  (Choice c) have two lone pairs of electrons on the central atom.

11. The borax is  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ . The structure of  $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$  is



This structure has a tetranuclear (boron) unit. Two boron atoms are  $\text{sp}^2$  hybridized while the other two are  $\text{sp}^3$  hybridized. There is one terminal hydroxide per boron atom. The entire unit is **not** planar due to  $\text{sp}^3$  hybrid orbital.

12. We have the following facts.



Only  $\text{CuCl}_2$  (Choice a) can cause selective precipitation of  $\text{S}^{2-}$  ions.

**Note:** The solubility products of  $\text{PbS}$  and  $\text{PbSO}_4$  are:

$K_{\text{sp}}^{\circ}(\text{PbS}) = 3 \times 10^{-28}$  and  $K_{\text{sp}}^{\circ}(\text{PbSO}_4) = 2.53 \times 10^{-8}$ . Since  $K_{\text{sp}}^{\circ}(\text{PbS}) \ll K_{\text{sp}}^{\circ}(\text{PbSO}_4)$ ,  $\text{S}^{2-}$  ions can be preferentially precipitated out from a solution containing both these ions.

13. The Arrhenius equation is  $k = Ae^{-E_a/RT}$

(a) High activation energy leads to a slower reaction because the rate constant,  $k$  has a lower value.

- (b) With increase in temperature, the number of molecules having energies more than activation energy is increased.  
 (c) We have

$$\frac{dk}{dT} = A \left( \frac{E_a}{RT^2} \right) e^{-E_a/RT}$$

Since  $dk/dT \propto E_a$ , there will be large change in the value of  $k$  for a large value of  $E_a$

- (d) If all collisions between molecules lead to the reaction, the rate of reaction or the rate constant will have a maximum value. According to the Arrhenius equation, the maximum value of  $k$  is  $A$  (where  $E_a = 0$ ). Thus, the pre-exponential factor is a measure of the rate at which collision occurs, irrespective of their energies.

- 14.** Let the subscripts 1 and 2 represent solvent and solute, respectively. It is given that

$$x_2 = \frac{n_2}{n_1 + n_2} = 0.1$$

Let  $n_2 = 0.1$  mol and thus  $n_1 = 0.9$  mol

Mass of solute,  $m_2 = n_2 M_2$

Mass of solvent,  $m_1 = n_1 M_1$

$$\text{Volume of solution, } V = \frac{m_1 + m_2}{\rho}$$

$$\text{Molarity of solution, } M = \frac{n_2}{V} = \frac{n_2}{(m_1 + m_2)/\rho}; (V \text{ expressed in dm}^3)$$

$$\text{Molality of solution, } b = \frac{n_2}{m_1}; (m_1 \text{ expressed in kg})$$

Since the numerical values of molarity and molality are identical, we write

$$\frac{n_2 / \text{mol}}{m_1 / \text{kg}} = \frac{n_2 / \text{mol}}{\{(m_1 + m_2) / \rho\} / \text{dm}^3}$$

$$\text{This gives } \frac{m_1}{\text{kg}} = \frac{(m_1 + m_2)}{\rho} \frac{1}{\text{dm}^3}$$

$$\text{or } \{(kg^{-1} dm^3) \rho - 1\} m_1 = m_2$$

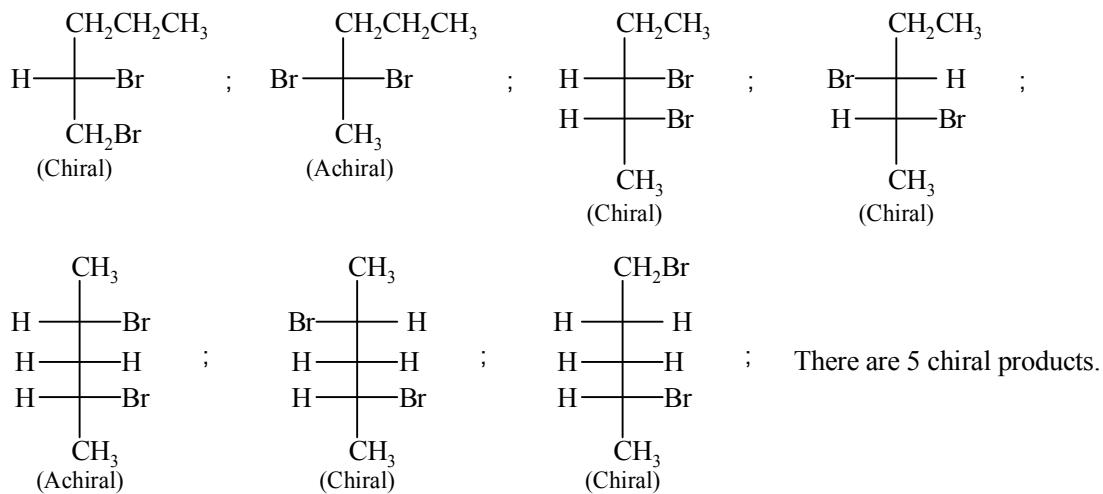
Since  $1 \text{ kg}^{-1} \text{ dm}^3 \equiv 1 \text{ g}^{-1} \text{ cm}^3$ , we have

$$\frac{m_2}{m_1} = \{(g^{-1} \text{ cm}^3) \rho - 1\} = (g^{-1} \text{ cm}^3) (2 \text{ g cm}^{-3}) - 1 = 1$$

$$\text{i.e. } \frac{n_2 M_2}{n_1 M_1} = 1 \quad \text{or} \quad \frac{M_2}{M_1} = \frac{n_1}{n_2} = \frac{0.9 \text{ mol}}{0.1 \text{ mol}} = 9$$

**P-1.10** IIT Chemistry: Topic-wise Solved Questions

15. The possible products are:



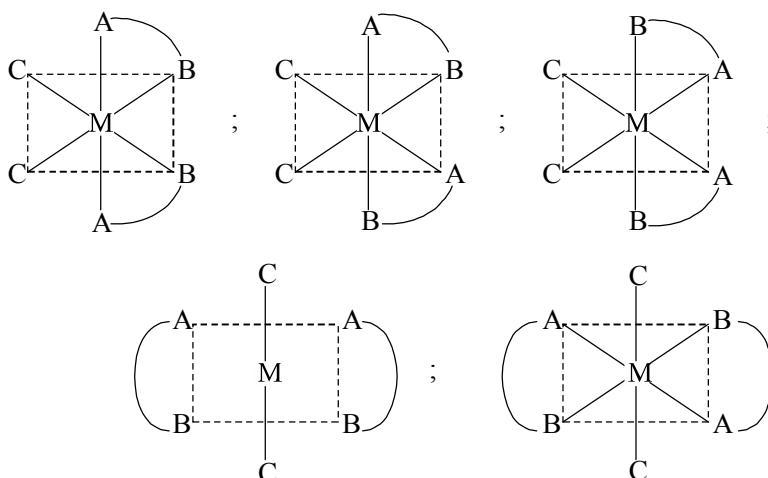
16. It is given that  $D \propto \lambda u_{av}$

Now  $\lambda = \frac{1}{\sqrt{2\pi\sigma^2 N^*}} = \frac{1}{\sqrt{2\pi\sigma^2(p/kT)}} \quad \text{and} \quad u_{av} = \sqrt{\frac{8kT}{\pi m}}$

Hence,  $\lambda \propto \frac{T^{3/2}}{p}$ .

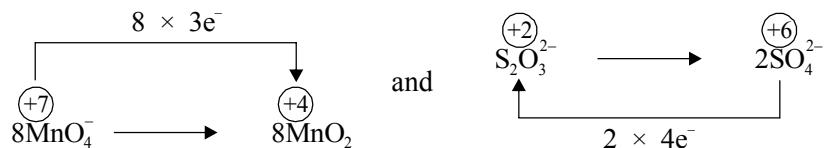
Thus,  $\frac{\lambda_2}{\lambda_1} = \frac{(4T)^{3/2}/2p}{T^{3/2}/p} = \frac{4^{3/2}}{2} = \frac{4 \times 2}{2} = 4$

17. The given complex is of the type  $[\text{M(AB)}_2\text{C}_2]$ . Its possible geometrical isomers are:

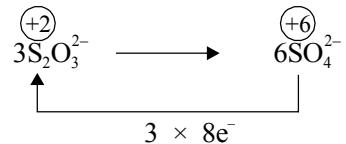


There are 5 geometrical isomers.

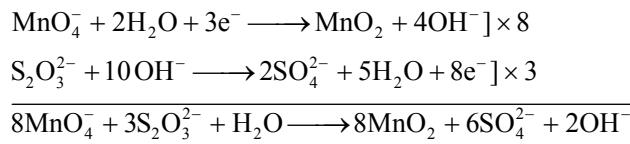
18. The basic reactions are:



To make electrons equal, the oxidation reaction of  $\text{S}_2\text{O}_3^{2-}$  will have to multiplied by 3, i.e.



The value of X is 6. The complete reaction is



■ ■



# CHEMISTRY

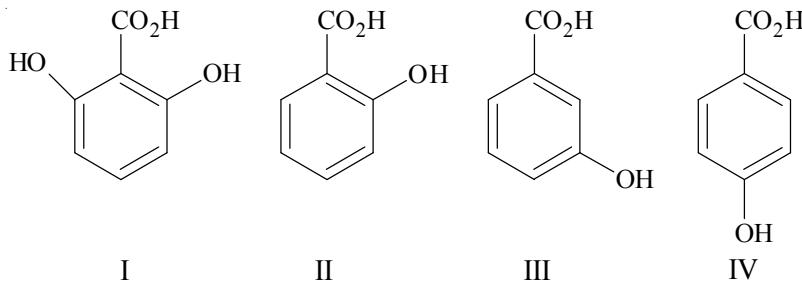
## JEE (ADVANCED)-2016

### Paper-II

#### SECTION-1 (Maximum Marks : 18)

- This section contains SIX questions.
- Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories:  
*Full Marks* : +3 If only the bubble corresponding to the correct option is darkened.  
*Zero Marks* : 0 If none of the bubbles is darkened.  
*Negative Marks* : -1 In all other cases.

1. The correct order of acidity for the following compounds is



- (a) I > II > III > IV      (b) III > I > II > IV      (c) III > IV > II > I      (d) I > III > IV > II

2. The geometries of the ammonia complexes of  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Zn}^{2+}$ , respectively, are

- (a) octahedral, square planar and tetrahedral      (b) square planar, octahedral and tetrahedral  
(c) tetrahedral, square planar and octahedral      (d) octahedral, tetrahedral and square planar

3. For the following electrochemical cell at 298 K,



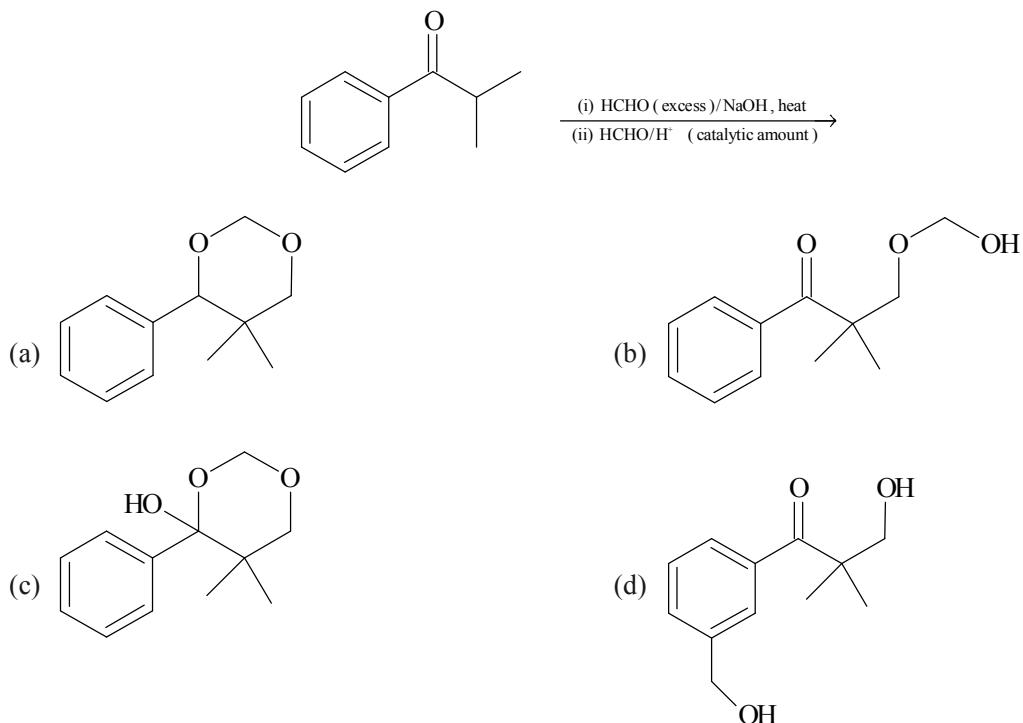
$$E_{\text{cell}} = 0.092 \text{ V when } \frac{[\text{M}^{2+}(\text{aq})]}{[\text{M}^{4+}(\text{aq})]} = 10^x.$$

Given :  $E_{\text{M}^{4+}|\text{M}^{2+}}^{\circ} = 0.151 \text{ V}$ ;  $2.303 \frac{RT}{F} = 0.059 \text{ V}$ . The value of  $x$  is

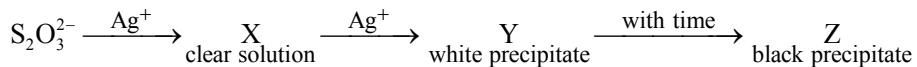
- (a) -2      (b) -1      (c) 1      (d) 2

**P-2.2** IIT Chemistry: Topic-wise Solved Questions

4. The major product of the following reaction sequence is

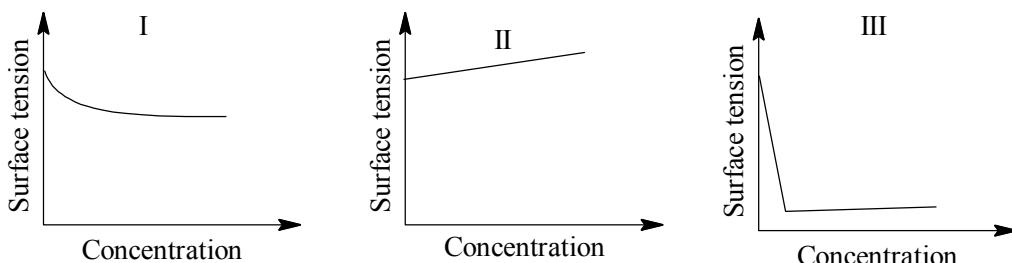


5. In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are



- (a)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ,  $\text{Ag}_2\text{S}_2\text{O}_3$ ,  $\text{Ag}_2\text{S}$   
 (b)  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ,  $\text{Ag}_2\text{SO}_3$ ,  $\text{Ag}_2\text{S}$   
 (c)  $[\text{Ag}(\text{SO}_3)_2]^{3-}$ ,  $\text{Ag}_2\text{S}_2\text{O}_3$ ,  $\text{Ag}$   
 (d)  $[\text{Ag}(\text{SO}_3)_3]^{3-}$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{Ag}$

6. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of  $\text{KCl}$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$  at room temperature. The correct assignment of the sketches is



- |   |  |   |
|---|--|---|
| (a) I : $\text{KCl}$  | II : $\text{CH}_3\text{OH}$                                    | III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ |
| (b) I : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ | II : $\text{CH}_3\text{OH}$                                    | III : $\text{KCl}$  |
| (c) I : $\text{KCl}$  | II : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ | III : $\text{CH}_3\text{OH}$                                    |
| (d) I : $\text{CH}_3\text{OH}$                                    | II : $\text{KCl}$  | III : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$ |

## SECTION-2 (Maximum Marks : 32)

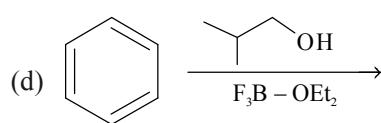
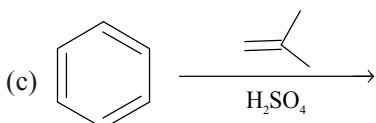
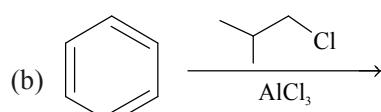
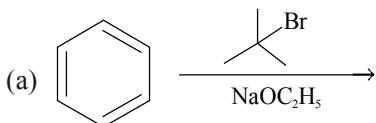
- This section contains **EIGHT** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONE OR MORE THAN ONE** of these four option(s) is(are) correct.
  - For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.
  - For each question, marks will be awarded in one of the following categories:
- Full Marks* : +4 If only the bubble corresponding to all the correct option(s) is(are) darkened.
- Partial Marks* : +1 For darkening a bubble corresponding to **each correct option**, provided NO incorrect option is darkened.
- Zero Marks* : 0 If none of the bubbles is darkened.
- Negative Marks* : -2 In all other cases.
- For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (a) and (d) will result in result in +2 marks, and darkening (a) and (b) will result in -2 marks, as a wrong option is also darkened.

7. For ‘invert sugar’, the correct statement(s) is(are):

Given: specific rotations of (+)-sucrose, (+)-maltose, L-(+)-glucose and L-(+)-fructose in aqueous solution are +66°, +140°, -52° and +92°, respectively.

- ‘invert sugar’ is prepared by acid catalyzed hydrolysis of maltose
- ‘invert sugar’ is an equimolar mixture of D-(+)-glucose and D-(+)-fructose
- specific rotation of ‘invert sugar’ is -20°
- on reaction with Br<sub>2</sub> water, ‘invert sugar’ forms saccharic acid as one of the products.

8. Among the following reaction(s) which gives(give) *tert*-butylbenzene as the major product is(are):



9. Extraction of copper from copper pyrite (CuFeS<sub>2</sub>) involves

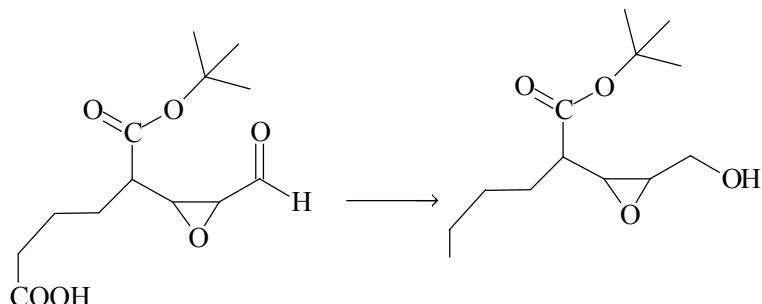
- crushing followed by concentration of the ore by froth-flotation
- removal of iron as slag
- self-reduction step to produce ‘blister copper’ following evolution of SO<sub>2</sub>
- refining of ‘blister copper’ by carbon reduction

10. The **correct** statement(s) for cubic-close packed (ccp) three dimensional structure is(are):

- The number of the nearest neighbours of an atom present in the topmost layer is 12.
- The efficiency of atom packing is 74%.
- The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively.
- The unit cell edge length is  $2\sqrt{2}$  times the radius of the atom.

**P-2.4** IIT Chemistry: Topic-wise Solved Questions

11. Reagent(s) which can be used to bring about the following transformation is(are)



- (a) LiAlH<sub>4</sub> in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O      (b) BH<sub>3</sub> in THF  
 (c) NaBH<sub>4</sub> in C<sub>2</sub>H<sub>5</sub>OH      (d) Raney Ni/H<sub>2</sub> in THF

12. Mixture(s) showing positive deviation from Raoult's law at 35 °C is(are)

- (a) carbon tetrachloride + methanol      (b) carbon disulphide + acetone  
 (c) benzene + toluene      (d) phenol + aniline

13. The nitrogen containing compound produced in the reaction of HNO<sub>3</sub> and P<sub>4</sub>O<sub>10</sub>

- (a) can also be prepared by reaction of P<sub>4</sub> and HNO<sub>3</sub>  
 (b) is diamagnetic  
 (c) contains one N—N bond  
 (d) reacts with Na metal producing a brown gas.

14. According to molecular orbital theory,

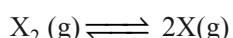
- (a) C<sub>2</sub><sup>2-</sup> is expected to be diamagnetic  
 (b) O<sub>2</sub><sup>2+</sup> expected to have a longer bond length than O<sub>2</sub>  
 (c) N<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>-</sup> have the same bond order  
 (d) He<sub>2</sub><sup>+</sup> has the same energy as two isolated He atoms

**SECTION-3 (Maximum Marks : 12)**

- This section contains **TWO** paragraphs.
  - Based on each paragraph, there are **TWO** questions.
  - Each question has **FOUR** options (a), (b), (c) and (d). **ONLY ONE** of these four options is correct.
  - For each question, darken the bubble corresponding to the correct option in the ORS.
  - For each question, marks will be awarded in one of the following categories:
- Full Marks* : +3 If only the bubble corresponding to the correct option is darkened.  
*Zero Marks* : 0 If none of the bubbles is darkened.  
*Negative Marks* : -1 In all other cases.

**PARAGRAPH-1**

Thermal decomposition of gaseous X<sub>2</sub> to gaseous X at 298 K takes place according to the following equation:



The standard reaction Gibbs energy, Δ<sub>r</sub>G°, of this reaction is positive. At the start of the reaction, there is one mole of X<sub>2</sub> and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, β<sub>eq</sub> is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given : R = 0.083 L bar K<sup>-1</sup> mol<sup>-1</sup>.)

15. The standard equilibrium constant  $K_p^0$  for this reaction at 298 K, in terms of  $\beta'_{\text{eq}}$  ( $= \beta_{\text{eq}} / \text{mol}$ ), is

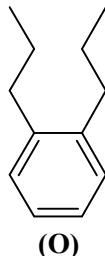
- (a)  $\frac{8\beta_{\text{eq}}'^2}{2 - \beta_{\text{eq}}'}$       (b)  $\frac{8\beta_{\text{eq}}'^2}{4 - \beta_{\text{eq}}'^2}$       (c)  $\frac{4\beta_{\text{eq}}'^2}{2 - \beta_{\text{eq}}'}$       (d)  $\frac{4\beta'^2}{4 - \beta_{\text{eq}}'^2}$

16. The **incorrect** statement among the following, for this reaction, is

- (a) Decrease in the total pressure will result in formation of more moles of gaseous X.  
 (b) At the start of the reaction, dissociation of gaseous  $X_2$ , takes place spontaneously.  
 (c)  $\beta_{\text{eq}} = 0.7 \text{ mol}$ .  
 (d)  $K_c < 1$ .

#### PARAGRAPH-2

Treatment of compound **O** with  $\text{KMnO}_4/\text{H}^+$  gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with  $\text{Br}_2/\text{NaOH}$  produced **R**. On strong heating, **Q** gave **S**, which on further treatment with ethyl-2-bromopropanoate in the presence of KOH followed by acidification, gave a compound **T**.



17. The compound **R** is

- (a)
- (b)
- (c)
- (d)

18. The compound **T** is

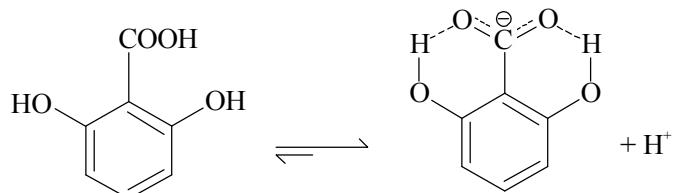
- (a) Glycine      (b) Alanine      (c) Valine      (d) Serine

#### Answer Key

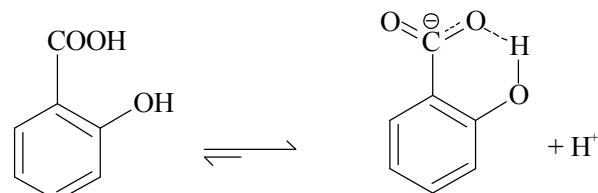
- |         |              |                  |                  |                   |
|---------|--------------|------------------|------------------|-------------------|
| 1. (a)  | 2. (a)       | 3. (d)           | 4. (a)           | 5. (a)            |
| 6. (d)  | 7. (b), (c)  | 8. (b), (c), (d) | 9. (a), (b), (c) | 10. (b), (c), (d) |
| 11. (c) | 12. (a), (b) | 13. (b), (d)     | 14. (a), (c)     | 15. (b)           |
| 16. (c) | 17. (a)      | 18. (b)          |                  |                   |

## Hints & Solutions

1. Structure I involves strongest ortho effect due to the chelation of two —OH groups with the —COO<sup>-</sup> group. This makes structure I a strongest acid.



Structure II also involves ortho effect due to the chelation of one —OH group with the —COO<sup>-</sup> group. This makes structure II a stronger acid as compared to structures III and IV but a weaker acid than the structure I.



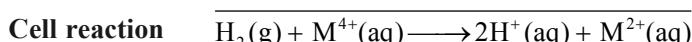
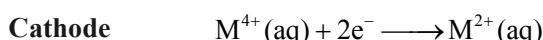
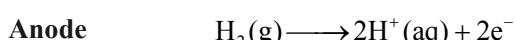
Structure III is a stronger acid than structure IV as the latter involves more effective +R effect. The —OH group is electron-donating group which makes ionization of H<sup>+</sup> less effective. Therefore, the correct order of acidity is I > II > III > IV (Choice a).

2. The complexes are [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>, [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>.

The six ammonia in [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> are accommodated in octahedral geometry. Zinc in [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> has (3d)<sup>10</sup> configuration, and involves sp<sup>3</sup> hybridization to accommodate four ammonia in tetrahedral geometry.

Platinum complexes have square planar geometry.

3. The cell reaction is



The cell potential is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{2F} \log \left\{ \frac{[\text{H}^+ / \text{M}]^2}{(p_{\text{H}_2} / \text{bar}) [\text{M}^{4+}]} \right\}$$

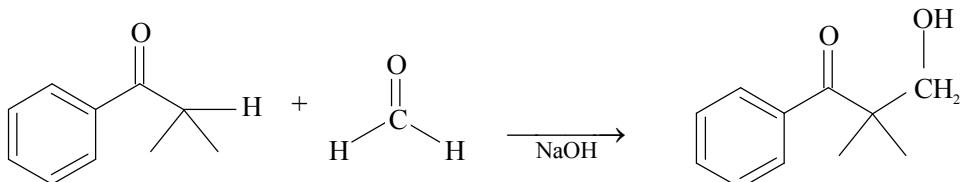
where       $E_{\text{cell}}^{\circ} = E_{\text{R}}^{\circ} - E_{\text{L}}^{\circ} = 0.151 \text{ V} - 0 \text{ V} = 0.151 \text{ V}$ .

Substituting the given values in the above expression, we get

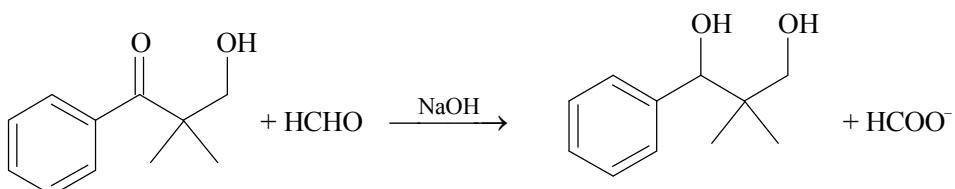
$$0.092 \text{ V} = 0.151 \text{ V} - \left( \frac{0.059 \text{ V}}{2} \right) \log \left\{ \frac{(1)^2}{(1)} (10^x) \right\} = 0.151 \text{ V} - \left( \frac{0.059 \text{ V}}{2} \right) x$$

This gives       $x = \frac{0.151 \text{ V} - 0.092 \text{ V}}{(0.059 \text{ V} / 2)} = 2$

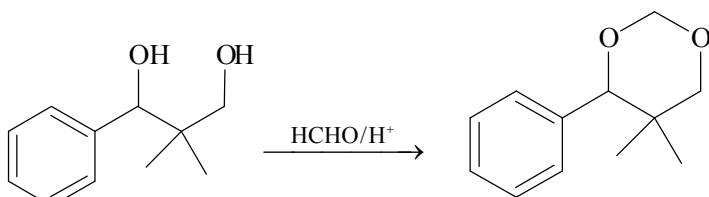
4. The given compound contains  $\alpha$ -hydrogen adjacent to CO group. With HCHO/NaOH, it undergoes cross aldol condensation.



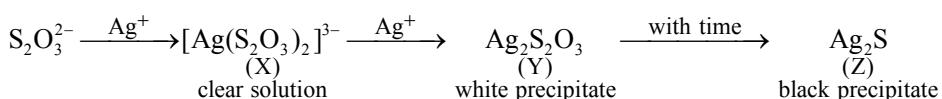
The resultant compound does not contain  $\alpha$ -hydrogen. It undergoes cross Cannizzaro reaction with HCHO/NaOH.



The resultant compound forms a cyclic acetal with HCHO/H<sup>+</sup> (catalytic amount).



5. The reaction sequence is as follows:



6.  $\text{CH}_3\text{OH}$  has more concentration at the surface than in the bulk of aqueous solution. Its effect is to decrease the surface tension as more and more  $\text{CH}_3\text{OH}$  is added (Choice a).

KCl has more concentration in the bulk than at the surface of aqueous solution. Its effect is to increase the surface tension as more and more KCl is added (Choice b).

$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$  is a surface active substance. It is mostly concentrated at the surface with specific orientation ( $-\text{OSO}_3^-$  group pointing to the surface and  $\text{CH}_3(\text{CH}_2)_{11}-$ group pointing away from the surface) and thus causes steep decrease in the surface tension of aqueous solution.

This is continued till the surface is completely covered. Thereafter, the surface tension remains constant.

7. The hydrolysis of sucrose produces ‘invert sugar’ which is equimolar mixture of D-(+)-glucose and D-(-)-fructose (Choice b).

Specific rotation of D<sup>+</sup>(+)-glucose = - specific rotation of L<sup>-</sup>(-)-glucose = 52°

Specific rotation of D-(-)-fructose = - specific rotation of L-(+)-fructose = -92°

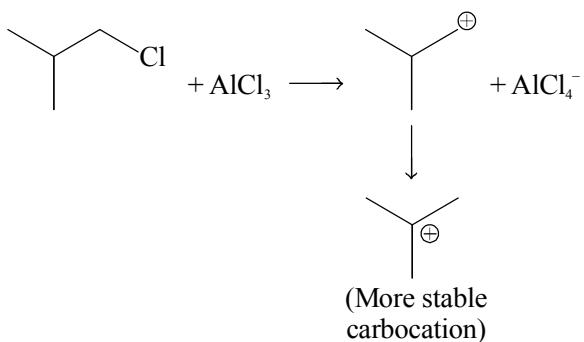
Specific rotation of 'invert sugar' is  $\frac{+52^\circ - 92^\circ}{2} = -20^\circ$  (Choice c)

With  $\text{Br}_2$ , water, D-glucose forms D-gluconic acid whereas D-fructose shows no reaction.

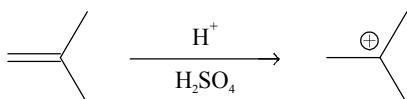
**P-2.8** IIT Chemistry: Topic-wise Solved Questions

8. Choice (b), (c) and (d) produce *tert*-butyl carbocation which can be substituted in the benzene ring to form *tert*-butylbenzene. This is shown in the following:

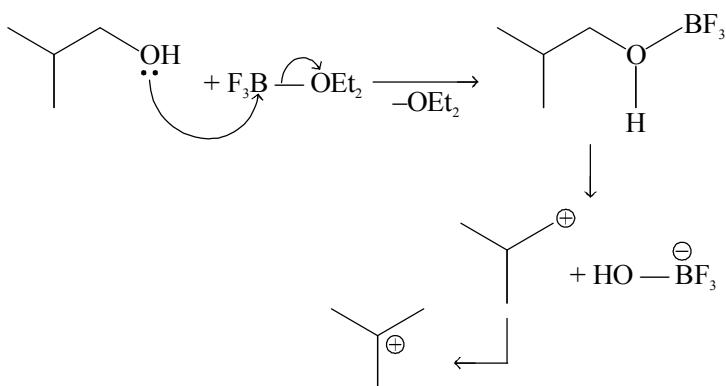
**Choice (b)**



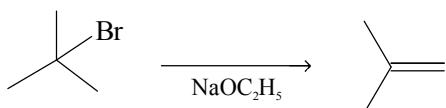
**Choice (c)**



**Choice (d)**



Choice a does not produce *tert*-butyl carbocation.



9. The Choice (a), (b) and (c) are correct. The Choice (d) is not correct as the refining is carried out electrolytically.
10. The unit cell of cubic-close packed structure is face-centred cube. In this unit cell, atoms touch each other along the face diagonal (which has a length of  $\sqrt{2}a$ ). If  $r$  is the radius of atom, then

$$4r = \sqrt{2}a \quad \text{i.e. } a = \left(\frac{4}{\sqrt{2}}\right)r = (2\sqrt{2})r \quad (\text{Choice d})$$

There are 4 atoms per unit cell. Thus, packing efficiency is

$$\frac{4\left(\frac{4}{3}\pi r^3\right)}{a^3} \times 100 = \frac{4\left(\frac{4}{3}\pi r^3\right)}{\left(2\sqrt{2}r\right)^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\% \quad (\text{Choice b})$$

A face-centred cubic unit cell can be divided into 8 smaller cubes of edge length  $a/2$ . The centre of each smaller cube is the tetrahedral void.

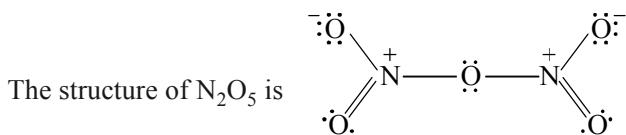
The octahedral void lies at the centre of unit cell and at the mid point of edges. The former belongs exclusively to the unit cell. Each of the octahedral void at the edge is shared by four unit cells. Thus, the total number of octahedral voids is

$$\frac{1}{(\text{from the centre})} + \frac{12 \text{ edges}}{4 (\text{from the edges})} = 4$$

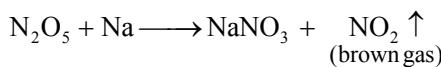
Since there are 4 atoms (one from the corners ( $= 8 \times 1/8 = 1$ ) and three from the centre of faces ( $= 6 \times 1/2 = 3$ ). Hence the number of tetrahedral and octahedral voids per atom will be 2 ( $= 8/4$ ) and 1 ( $= 4/4$ ), respectively (Choice c).

In the top most layer, the coordination of number of atom is 9 (six surrounding the atom and three in the layer just below it). Therefore, the Choice (a) is incorrect.

11. In the given transformation, —CHO group is reduced to —CH<sub>2</sub>OH. The reagent in Choice (c), i.e. NaBH<sub>4</sub> in C<sub>2</sub>H<sub>5</sub>OH, can be used for this purpose.
12. If the interaction A ... B are weaker than those existing in A ... A and B ... B, the system displays positive deviation from Raoult's law. The Choices (a) and (b) are the examples. The Choice (c) exhibits ideal behaviour and the Choice (d) exhibits negative deviation.
13. P<sub>4</sub>O<sub>10</sub> is a strong dehydrating agent. It converts HNO<sub>3</sub> into the corresponding anhydride (N<sub>2</sub>O<sub>5</sub>). The reaction is P<sub>4</sub>O<sub>10</sub> + 4HNO<sub>3</sub> → 4HPO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub>



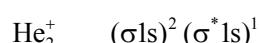
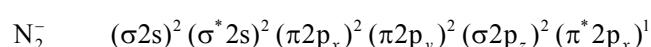
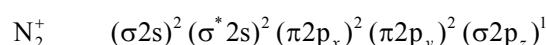
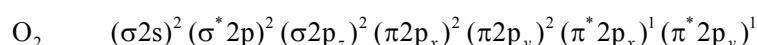
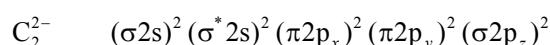
There is no unpaired electron, and, hence it is diamagnetic (Choice b)  
N<sub>2</sub>O<sub>5</sub> on reacting with Na produces brown gas NO<sub>2</sub> (Choice d)



The reaction of P<sub>4</sub> with HNO<sub>3</sub> produces NO<sub>2</sub>.



14. The electronic configuration of C<sub>2</sub><sup>2-</sup> (valence electron = 10), O<sub>2</sub> (valence electrons = 12), N<sub>2</sub><sup>+</sup> (valence electron = 9), N<sub>2</sub><sup>-</sup> (valence electrons = 11) and He<sub>2</sub><sup>+</sup> (valence electrons = 3) are as follows:



**P-2.10** IIT Chemistry: Topic-wise Solved Questions

$\text{C}_2^{2-}$  does not have unpaired electrons. It is diamagnetic (Choice a).

By definition,

$$\text{Bond order} = \frac{(\text{bonding} - \text{antibonding}) \text{ electrons}}{2}$$

$$\text{Bond order of } \text{O}_2 = \frac{6-2}{2} = 2 \quad \text{and} \quad \text{Bond order of } \text{O}_2^{2+} = \frac{6-0}{2} = 3$$

Since bond length is inversely proportional to bond order, bond length of  $\text{O}_2^{2+}$  is expected to be smaller than  $\text{O}_2$ .

$$\text{Bond order of } \text{N}_2^+ = \frac{5-0}{2} = 2.5 \quad \text{and} \quad \text{Bond order of } \text{N}_2^- = \frac{6-1}{2} = 2.5$$

$\text{He}_2^+$  will have smaller energy than the two isolated He atom as there is a net one electron in bonding orbital.

15. We have  $\text{X}_2(\text{g}) \rightleftharpoons 2\text{X}(\text{g})$

Total amount of gases =  $1 + \beta_{\text{eq}}/2$

$$\text{Partial pressure of } \text{X}_2 = \left( \frac{1\text{mol} - \beta_{\text{eq}}/2}{1\text{mol} + \beta_{\text{eq}}/2} \right) p \quad \text{and} \quad \text{Partial pressure of } \text{X} = \left( \frac{\beta_{\text{eq}}}{1\text{mol} + \beta_{\text{eq}}/2} \right) p$$

$$K_p = \frac{p_x^2}{p_{x_2}} = \frac{\{\beta_{\text{eq}} / (1\text{mol} + \beta_{\text{eq}}/2)\}^2 p^2}{\{(1\text{mol} - \beta_{\text{eq}}/2) / (1\text{mol} + \beta_{\text{eq}}/2)\} p}$$

$$= \left( \frac{\beta_{\text{eq}}^2}{(1\text{mol})^2 - (\beta_{\text{eq}}/2)^2} \right) p = \left( \frac{4\beta_{\text{eq}}^2}{4\text{mol}^2 - \beta_{\text{eq}}^2} \right) (2 \text{ bar})$$

$$K_p^\circ = \frac{K_p}{1 \text{ bar}} = \frac{8\beta_{\text{eq}}^2}{4\text{mol}^2 - \beta_{\text{eq}}^2} = \frac{8\beta_{\text{eq}}'^2}{4 - \beta_{\text{eq}}'^2}; \quad (\text{where } \beta' = \beta / \text{mol}) \quad (\text{Choice b})$$

16. (a) If the total pressure is decreased, the reaction will shift in a direction which tends to increase pressure. This is achieved if more of gaseous species is formed. This is achieved by shifting the reaction in the forward direction.

- (b) At the start of reaction, the reaction quotient,  $Q^\circ = 0$ . Since

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q^\circ$$

we have  $\Delta_r G$  = negative. Thus, dissociation of  $\text{X}_2$  will take place spontaneously.

- (c) For  $\beta_{\text{eq}} = 0.7 \text{ mol}$ , the value of standard equilibrium constant will be

$$K_p^\circ = \frac{8(0.7 \text{ mol})^2}{4\text{mol}^2 - (0.7 \text{ mol})^2} = 1.12$$

Since  $\Delta_r G^\circ = -RT \ln K_p^\circ$ , we will have

$$\ln K_p^\circ = -\frac{\Delta_r G^\circ}{RT} = \text{negative}$$

This will give  $K_p^\circ < 1$ .

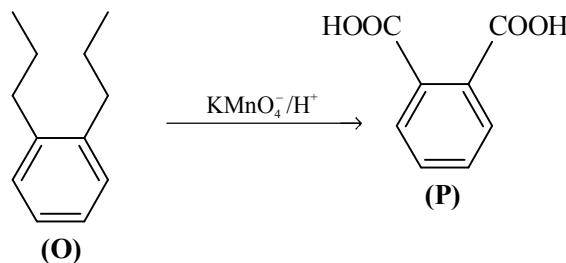
The Choice (b) is incorrect.

(d)  $\Delta\nu_g = +1$

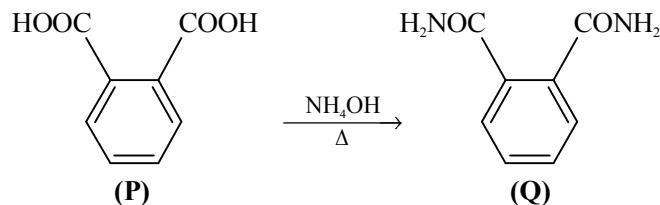
We have  $K_p = K_c (RT)^{\Delta\nu_g}$  or  $K_c = K_p / (RT)^{\Delta\nu_g}$

Since  $(RT)^{\Delta\nu_g}$  is a positive quantity and has a value more than 1, it is expected that  $K_c < K_p$ . Since  $K_p^o < 1$ , it follows that  $K_c^o < 1$ . (correct statement)

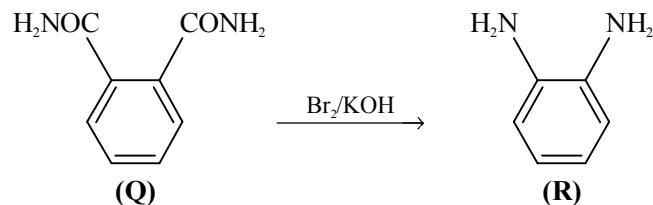
**17, 18.** Treatment with  $\text{KMnO}_4/\text{H}^+$  causes side chain oxidation:



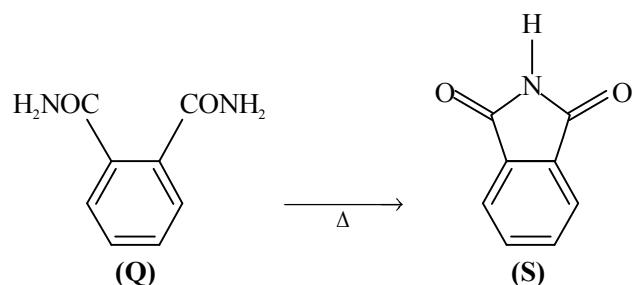
Treatment of the compound **P** with ammonia forms ammonium salt which on heating gives amides.



Treatment of the compound **Q** with  $\text{Br}_2/\text{KOH}$  converts amides into amines. This reaction is Hofmann degradation of amides.

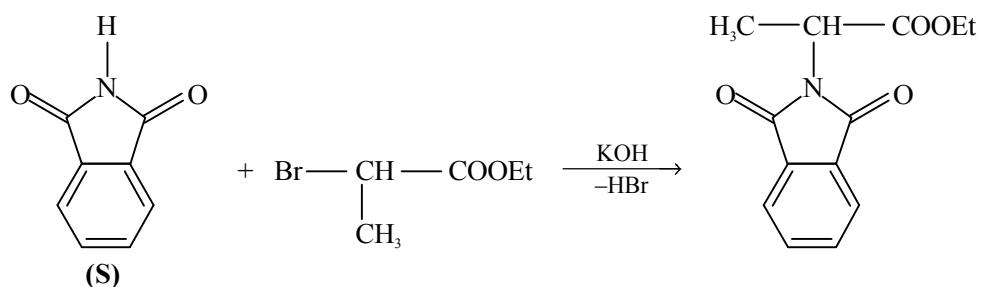


Strong heating of **Q** causes cyclization of side chains with elimination of  $\text{NH}_3$

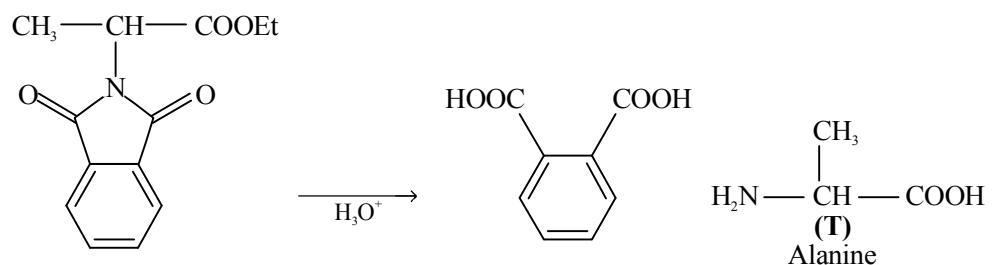


Treatment S with ethyl-2-bromopropanoate in the presence of KOH causes the following reaction.

**P-2.12** IIT Chemistry: Topic-wise Solved Questions



Acidification of the resultant compound causes the following reaction.



The conversion of **S** into **T** is Gabriel's phthalimide synthesis.

The compound **R** is an *ortho*-diamine.

The compound **T** is alanine.

