

Chapter

1

Some Basic Concepts
of Chemistry

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The weight of a single atom of oxygen is : [1997]
 - (a) 1.057×10^{23} g
 - (b) 3.556×10^{23} g
 - (c) 2.656×10^{-23} g
 - (d) 4.538×10^{-23} g
2. Volume of a gas at NTP is 1.12×10^{-7} cc. The number of molecule in it is : [1998]
 - (a) 3.01×10^{12}
 - (b) 3.01×10^{18}
 - (b) 3.01×10^{24}
 - (d) 3.01×10^{30}
3. The oxide of an element contains 67.67% oxygen and the vapour density of its volatile chloride is 79. Equivalent weight of the element is: [1998]
 - (a) 2.46
 - (b) 3.82
 - (c) 4.36
 - (d) 4.96
4. 60 gm of an organic compound on analysis is found to have C = 24 g, H = 4 g and O = 32 g. The empirical formula of compound is: [1998]
 - (a) CH_2O
 - (b) CHO
 - (c) $\text{C}_2\text{H}_2\text{O}$
 - (d) $\text{C}_2\text{H}_2\text{O}_2$
5. The molar concentration of 20 g of NaOH present in 5 litre of solution is : [1998]
 - (a) 0.1 moles/litre
 - (b) 0.2 moles/litre
 - (c) 1.0 moles/litre
 - (d) 2.0 moles/litre
6. The normality of solution obtained by mixing 10 ml of N/5 HCl and 30 ml of N/10 HCl is : [1999]
 - (a) $\frac{\text{N}}{15}$
 - (b) $\frac{\text{N}}{5}$
 - (c) $\frac{\text{N}}{7.5}$
 - (d) $\frac{\text{N}}{8}$
7. The empirical formula of a compound is CH_2O . Its molecular weight is 180. The molecular formula of compound is : [1999]
 - (a) C_4HO_4
 - (b) $\text{C}_3\text{H}_6\text{O}_3$
 - (c) $\text{C}_6\text{H}_{12}\text{O}_6$
 - (d) $\text{C}_5\text{H}_{10}\text{O}_5$
8. 0.4 moles of HCl and 0.2 moles of CaCl_2 were dissolved in water to have 500 mL of solution, the molarity of Cl^- ion is: [2000]
 - (a) 0.8 M
 - (b) 1.6 M
 - (c) 1.2 M
 - (d) 10.0 M
9. 10^{21} molecules are removed from 200 mg of CO_2 . The moles of CO_2 left are : [2001]
 - (a) 2.88×10^{-3}
 - (b) 28.8×10^{-3}
 - (c) 288×10^{-3}
 - (d) 28.8×10^3
10. The weight of NaCl decomposed by 4.9g of H_2SO_4 , if 6 g of sodium hydrogen sulphate and 1.825 g of HCl, were produced in the reaction is:
 - (a) 6.921 g
 - (b) 4.65 g [2001]
 - (c) 2.925 g
 - (d) 1.4 g
11. Temperature does not affect : [1997, 2001]
 - (a) Molality
 - (b) Formality
 - (c) Molarity
 - (d) Normality
12. The molarity of H_2SO_4 solution, which has a density 1.84 g/cc. at 35°C and contains 98% by weight, is : [2001]
 - (a) 1.84 M
 - (b) 18.4 M
 - (c) 20.6 M
 - (d) 24.5 M
13. The normality of orthophosphoric acid having purity of 70 % by weight and specific gravity 1.54 is : [2001]
 - (a) 11 N
 - (b) 22 N
 - (c) 33 N
 - (d) 44 N
14. The weight of one molecule of a compound of molecular formula $\text{C}_{60}\text{H}_{122}$ is [2002]
 - (a) 1.2×10^{-20} g
 - (b) 5.025×10^{23} g
 - (c) 1.4×10^{-21} g
 - (d) 6.023×10^{-20} g
15. During electrolysis of water the volume of O_2 liberated is 2.24 dm^3 . The volume of hydrogen liberated, under same conditions will be [2008]
 - (a) 2.24 dm^3
 - (b) 1.12 dm^3
 - (c) 4.48 dm^3
 - (d) 0.56 dm^3

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c-2*Topicwise AIIMS Solved Papers – CHEMISTRY*

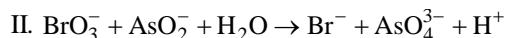
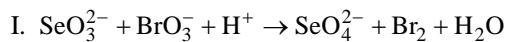
- 16.** Calculate the millimoles of SeO_3^{2-} in solution on the basis of following data : [2009]

70ml of $\frac{M}{60}$ solution of KBrO_3 was added to SeO_3^{2-} solution. The bromine evolved was removed by boiling and excess of KBrO_3 was

back titrated with 12.5 mL of $\frac{M}{25}$ solution of

NaAsO_2 .

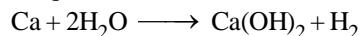
The reactions are given below.



(a) 1.6×10^{-3} (b) 1.25

(c) 2.5×10^{-3} (d) None of these

- 17.** The reaction of calcium with water is represented by the equation



What volume of H_2 at STP would be liberated when 8 gm of calcium completely reacts with water? [2010]

(a) 0.2 cm^3 (b) 0.4 cm^3
(c) 2240 cm^3 (d) 4480 cm^3

- 18.** A solution is prepared by dissolving 24.5 g of sodium hydroxide in distilled water to give 1 L solution. The molarity of NaOH in the solution is [2010]

(a) 0.2450 M (b) 0.6125 M
(c) 0.9800 M (d) 1.6326 M

(Given that molar mass of NaOH = 40.0 g mol⁻¹)

- 19.** Which of the following pairs of solutions are expected to be isotonic, temperature being the same? [2011]

(a) 0.1 M glucose and 0.1M $\text{C}_6\text{H}_5\text{N}^+\text{H}_3\text{Cl}^-$
(b) 0.1 M NaCl and 0.05 M BaCl_2
(c) 0.1 M Na_2SO_4 and 0.1 M KNO_3
(d) 0.1 M BaCl_2 and 0.075 M FeCl_3

- 20.** For preparing 0.1 N solution of a compound from its impure sample of which the percentage purity is known, the weight of the substance required will be [2012]

(a) less than the theoretical weight
(b) more than the theoretical weight
(c) same as the theoretical weight
(d) none of these

- 21.** In a hydrocarbon, mass ratio of hydrogen and carbon is 1:3, the empirical formula of hydrocarbon is [2012]

- (a) CH_4 (b) CH_2
(c) C_2H (d) CH_3

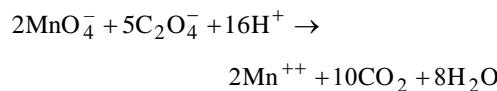
- 22.** The vapour density of a mixture containing NO_2 and N_2O_4 is 27.6. Mole fraction of NO_2 in the mixture is [2012]

(a) 0.8 (b) 0.6
(c) 0.4 (d) 0.2

- 23.** An aqueous solution of 6.3 g of 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 [2013]

(a) 20ml (b) 40ml
(c) 10ml (d) 4ml

- 24.** KMnO_4 reacts with oxalic acid according to the equation: [2013]



Here 20 mL of 0.1 M KMnO_4 is equivalent to:

(a) 20 mL of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$
(b) 50 mL of 0.5 M $\text{H}_2\text{C}_2\text{O}_4$
(c) 50 mL of 0.1 M $\text{H}_2\text{C}_2\text{O}_4$
(d) 20 mL of 0.1 M $\text{H}_2\text{C}_2\text{O}_4$

- 25.** Calculate the normality of 10 volume H_2O_2 ?

(a) 1.7 N (b) 12 N [2013]
(c) 30.3 N (d) 0.0303 N

- 26.** Which has the maximum number of molecules among the following ? [2014]

(a) 44 g CO_2 (b) 48 g O_3
(c) 8 g H_2 (d) 64 g SO_2

- 27.** Sulphur forms the chlorides S_2Cl_2 and SCl_2 . The equivalent mass of sulphur in SCl_2 is [2015]

(a) 8 g/mol (b) 16 g/mol
(c) 64.8 g/mol (d) 32 g/mol

- 28.** Arrange the following in the order of increasing mass (atomic mass: O = 16, Cu = 63, N = 14)

I. one atom of oxygen
II. one atom of nitrogen
III. 1×10^{-10} mole of oxygen
IV. 1×10^{-10} mole of copper [2016]

(a) II < I < III < IV (b) I < II < III < IV
(c) III < II < IV < I (d) IV < II < III < I

- 29.** Volume of water needed to mix with 10 mL 10N HNO_3 to get 0.1 N HNO_3 is : [2017]

(a) 1000mL (b) 990mL
(c) 1010mL (d) 10mL

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 30-32) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
 - (e) If the Assertion is incorrect but the Reason is correct.
- 30.** **Assertion :** Atoms can neither be created nor destroyed.

Reason : Under similar condition of temperature and pressure, equal volume of gases does not contain equal number of atoms. **[2002]**

- 31.** **Assertion :** Equivalent weight of a base

$$= \frac{\text{Molecular weight}}{\text{Acidity}}$$

Reason : Acidity is the number of replaceable hydrogen atoms in one molecule of the base.

[2008]

- 32.** **Assertion :** One molal aqueous solution of glucose contains 180g of glucose in 1 kg water.

Reason : Solution containing one mole of solute in 1000 g of solvent is called one molal solution.

[2008]

Directions for (Qs.33-34) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

- 33.** **Assertion :** The normality of 0.3 M aqueous solution of H_3PO_3 is equal to 0.6 N.

Reason : Equivalent weight of H_3PO_3
 $= \frac{\text{Molecular weight of } \text{H}_3\text{PO}_3}{3}$ **[2011, 13]**

- 34.** **Assertion :** Equal moles of different substances contain same number of constituent particles.

[2017]

Reason : Equal weights of different substances contain the same number of constituent particles.

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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (c) Weight of single atom of oxygen

$$= \frac{16}{6.02 \times 10^{23}} = 2.656 \times 10^{-23} \text{ g}$$

2. (a) No. of molecules

$$\begin{aligned} &= \frac{6.02 \times 10^{23} \times 1.12 \times 10^{-7}}{22400} \\ &= \frac{6.02 \times 10^{-7} \times 1.12 \times 10^{23}}{2.24 \times 10^4} = 3.01 \times 10^{12} \end{aligned}$$

3. (b) Equivalent weight of an element is its weight which reacts with 8 gm of oxygen to form oxide.

Thus eq. weight of the given element

$$= \frac{32.33}{67.67} \times 8 = 3.82$$

4. (a) Ratio of no. of atoms = $\frac{24}{12} : \frac{4}{1} : \frac{32}{16}$
 $= 2 : 4 : 2 = 1 : 2 : 1$

Empirical formula = CH_2O .

5. (a) molar concentration = $\frac{\text{Mole}}{\text{Vol. in L}} = \frac{20/40}{5}$
 $= \frac{20}{5 \times 40} = 0.1 \text{ mole/litre.}$

6. (d) Normality of a mixture of two or more acids is given by

$$\begin{aligned} N &= \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \\ &= \frac{\frac{1}{5} \times 10 + \frac{1}{10} \times 30}{10 + 30} = \frac{5}{40} = \frac{1}{8} \text{ or } \frac{N}{8} \end{aligned}$$

7. (c) Empirical formula weight
 $= 12 + 2 + 16 = 30$

$$n = \frac{180}{30} = 6$$

Molecular formula = $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.

8. (b) $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$
 $0.4 \text{ moles} \quad 0.4 \text{ moles}$
 $\text{CaCl}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^-$
 $0.2 \text{ moles} \quad 2 \times 0.2 = 0.4 \text{ moles}$

Total Cl^- moles = $0.4 + 0.4 = 0.8$ moles

$$\text{Molarity} = \frac{\text{Moles}}{\text{Vol.in L}}$$

$$\therefore \text{Molarity of Cl}^- = \frac{0.8}{0.5} = 1.6 \text{ M.}$$

9. (a) No. of moles = $\frac{\text{Wt. in g}}{\text{Mol. wt}}$

$$\begin{aligned} \text{No. of moles in 200 mg} &= \frac{200}{1000 \times 44} \\ &= 4.5 \times 10^{-3} \text{ moles} \end{aligned}$$

No. of moles in 10^{21} molecules

$$= \frac{10^{21}}{6.02 \times 10^{23}} = 1.67 \times 10^{-3} \text{ moles}$$

$$\begin{aligned} \text{No. of moles left} &= (4.5 - 1.67) \times 10^{-3} \\ &= 2.88 \times 10^{-3} \end{aligned}$$

10. (c) $\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}$
 $x \text{ g} \qquad 4.9 \text{ g} \qquad \qquad \qquad 6 \text{ g} \qquad 1.825 \text{ g}$

According to law of conservation of mass
"mass is neither created nor destroyed during a chemical change"

$$\therefore \text{Mass of the reactants} = \text{Mass of products}$$

$$x + 4.9 = 6 + 1.825$$

$$\text{or} \qquad x = 2.925 \text{ g}$$

11. (a) Temperature does not affect molality as it does not depend upon volume factor.

12. (b) 100 gm solution contains 98 gm H_2SO_4 .

$$\frac{100}{1.84} \text{ c.c contains 98 gm H}_2\text{SO}_4.$$

1000 c.c solution contains

$$= \frac{98}{100} \times 1.84 \times 1000 \text{ gm H}_2\text{SO}_4$$

$$= \frac{98}{100} \times \frac{1.84 \times 1000}{98} \text{ moles of H}_2\text{SO}_4$$

$$= 18.4 \text{ M.}$$

13. (c) 70% by weight means

$$\text{Wt. of solute} = 70 \text{ g}$$

$$\text{Wt of solution} = 100 \text{ g}$$

$$\therefore V_{cc} \text{ of solution} = \frac{\text{mass}}{\text{density}} = \frac{100}{1.54}$$

We know that

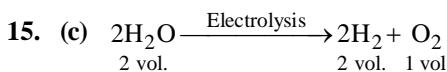
$$N = \frac{W \times 1000}{\text{Eq. Wt} \times V_{cc}}$$

$$= \frac{70 \times 3}{98} \times \frac{1000 \times 1.54}{100} = 33N$$

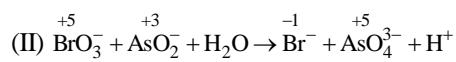
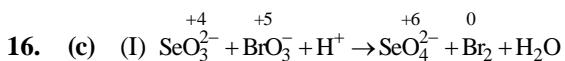
14. (c) M.W. = $60 \times 12 + 122 = 842$

$$\text{Weight of one molecule} = \frac{842}{6.02 \times 10^{23}} \text{ gm}$$

$$= 140 \times 10^{-23} \text{ gm} = 1.4 \times 10^{-21} \text{ gm}$$



Thus, the volume of hydrogen liberated is twice that of the volume of oxygen liberated. When 2.24 dm^3 of oxygen is liberated the volume of hydrogen liberated will be $2 \times 2.24 \text{ dm}^3$ or 4.48 dm^3



In reaction (II)

gm. eq. of BrO_3^- = gm. eq. of AsO_2^-

$$n_{\text{BrO}_3^-} \times 6 = n_{\text{AsO}_2^-} \times 2$$

$$= \frac{12.5}{1000} \times \frac{1}{25} \times 2 = 10^{-3}$$

$$n_{\text{BrO}_3^-} = \frac{10^{-3}}{6}$$

In reaction (I)

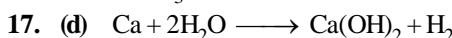
moles of BrO_3^- consumed

$$= \frac{70}{1000} \times \frac{1}{60} - \frac{10^{-3}}{6} = 10^{-3}$$

gm eq. of SeO_3^{2-} = gm. eq. of BrO_3^-

$$n_{\text{SeO}_3^{2-}} \times 2 = 10^{-3} \times 5;$$

$$n_{\text{SeO}_3^{2-}} = 2.5 \times 10^{-3}$$



According to the stoichiometry of reaction, 40 gm of Ca on complete reaction with water liberates = 2 gm H_2

\therefore 8 gm of Ca, on complete reaction with

$$\text{water liberates} = \frac{2}{40} \times 8 \text{ gm } \text{H}_2$$

$$= 0.40 \text{ gm } \text{H}_2$$

$$= \frac{0.40}{2} \times 22400 \text{ cm}^3$$

$$= 4480 \text{ cm}^3 \text{ of } \text{H}_2 \text{ at S.T.P.}$$

18. (b) Given $W_{\text{NaOH}} = 24.5 \text{ g}$

$$\text{No. of moles of NaOH} = \frac{24.5}{40} \text{ moles}$$

$$= 0.6125 \text{ moles}$$

\ Molarity of solution

$$= \frac{0.6125 \text{ moles}}{1 \text{ L}} = 0.6125 \text{ M}$$

19. (d) Effective molarity of $\text{BaCl}_2 = 3 \times 0.1 = 0.3$; effective molarity of $\text{FeCl}_3 = 4 \times 0.075 = 0.3$

20. (b) More than theoretical weight since impurity will not contribute.

21. (a) Mass ratio of H : C = 1 : 12

However, given mass ratio of H : C = 1 : 3
Therefore, for every C atom, there are 4 H atoms, hence empirical formula = CH_4

22. (a) V.D_{max} =

$$X_{\text{NO}_2} (\text{V.D})_{\text{NO}_2} + X_{\text{N}_2\text{O}_4} (\text{V.D})_{\text{N}_2\text{O}_4}$$

$$27.6 = X \times 23 + (1 - X) \times 46$$

$$\therefore X_{\text{NO}_2} = 0.8$$

23. (b) Normality of oxalic acid

$$= \frac{6.3 \times 1000}{63 \times 250} = 0.4 \text{ N}$$

$$\text{N}_1 \text{V}_1 = \text{N}_2 \text{V}_2 \quad 10 \times 0.4 = \text{V} \times 0.1 = 40 \text{ ml.}$$

24. (c) Meq of A = Meq of B.

$$0.1 \text{ M } \text{KMnO}_4 = 0.5 \text{ N } \text{KMnO}_4$$

$$\therefore \text{Meq of KMnO}_4 = 20 \times 0.5 = 10 \text{ (n factor = 5)}$$

$$\text{Meq of 50 ml of } 0.1 \text{ M } \text{H}_2\text{C}_2\text{O}_4 = 50 \times 0.2 = 10$$

$$(0.1 \text{ M } \text{H}_2\text{C}_2\text{O}_4 = 0.2 \text{ N } \text{H}_2\text{C}_2\text{O}_4)$$

25. (a) Normality of 10V of H_2O_2

$$\frac{68 \times 10}{22.4} = 17 \times \text{N} \quad \therefore \text{N} = 1.78$$

26. (c) No. of molecules

$$\text{Moles of CO}_2 = \frac{44}{44} = 1 \quad \text{N}_A$$

$$\text{Moles of O}_3 = \frac{48}{48} = 1 \quad \text{N}_A$$

$$\text{Moles of H}_2 = \frac{8}{2} = 4 \quad 4\text{N}_A$$

$$\text{Moles of SO}_2 = \frac{64}{64} = 1 \quad \text{N}_A$$

27. (b) The atomic weight of sulphur = 32

In SCl_2 valency of sulphur = 2

$$\text{So equivalent mass of sulphur} = \frac{32}{2} = 16$$

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28. (a) Mass of 6.023×10^{23} atoms of oxygen = 16 g
Mass of one atom of oxygen

$$= \frac{16}{6.023 \times 10^{23}} = 2.66 \times 10^{-23} \text{ g}$$

- Mass of 6.023×10^{23} atoms of nitrogen = 14 g
Mass of one atom of nitrogen

$$= \frac{14}{6.023 \times 10^{23}} = 2.32 \times 10^{-23} \text{ g}$$

- Mass of 1×10^{-10} mole of oxygen = 16×10^{-10}

- Mass of 1 mole of copper = 63 g

- Mass of 1 mole of oxygen = 16 g

Mass of 1×10^{-10} mole of copper
 $= 63 \times 1 \times 10^{-10}$
 $= 63 \times 10^{-10}$

So, the order of increasing mass is

II < I < III < IV.

29. (b) Given $N_1 = 10\text{N}$, $V_1 = 10 \text{ ml}$, $N_2 = 0.1\text{N}$, $V_2 = ?$

$$N_1 V_1 = N_2 V_2$$

$$\text{or } 10 \times 10 = 0.1 \times V_2$$

$$\text{or } V_2 = \frac{10 \times 10}{0.1}, V_2 = 1000 \text{ ml}$$

Volume of water to be added

$$= V_2 - V_1 = 1000 - 10 = 990 \text{ ml.}$$

Type B : Assertion Reason Questions

30. (d) Atoms can be created and can be destroyed.
At N.T.P., number of molecules or atoms contained in same volume remains equal.

31. (c) Yes, Eq. wt of a base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Thus, assertion is correct.

Acidity is the number of replaceable –OH groups (not hydrogen atoms) present in a molecule. Thus, reason is false.

32. (a) Molality = $\frac{\text{No.of moles of solute}}{\text{Wt of solvent in kg.}}$

Here, No. of moles = $\frac{\text{Molecular mass}}{\text{Wt of solvent}}$

$$= \frac{180}{180} = 1$$

$$\therefore \text{Molality} = \frac{1}{1} = 1$$

Hence assertion and reason, both are correct, and reason is the correct explanation of assertion.

33. (c) Assertion is true, reason is false.

$$\text{Eq. wt. of H}_3\text{PO}_3 = \frac{\text{mol.wt}}{2} [\because \text{Basicity of}$$

$$\text{H}_3\text{PO}_3 = 2]$$

34. (c) Equal moles of different substances contain same number of constituent particles but equal weights of different substances do not contain the same number of constituent particles.

Chapter

2

Structure of Atom

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The configuration $1s^2 \cdot 2s^2 2p^5, 3s^1$ shows : [1997]
 - (a) excited state of O_2^-
 - (b) excited state of neon atom
 - (c) excited state of fluorine atom
 - (d) ground state of fluorine atom

2. The total number of orbitals in a shell with principal quantum number ' n ' is : [1997]
 - (a) n^2
 - (b) $n + 1$
 - (c) $2n$
 - (d) $2n^2$

3. Positron is : [1997]
 - (a) electron with positive charge
 - (b) a nucleus with one neutron and one proton
 - (c) a nucleus with two protons
 - (d) a helium nucleus

4. The wavelength of visible light is : [1998]
 - (a) $2000\text{ \AA} - 3700\text{ \AA}$
 - (b) $7800\text{ \AA} - 8900\text{ \AA}$
 - (c) $3800\text{ \AA} - 7600\text{ \AA}$
 - (d) None of these

5. The wavelength of a 150 g rubber ball moving with a velocity of 50 ms^{-1} is : [1998]
 - (a) $3.43 \times 10^{-33}\text{ cm}$
 - (b) $5.86 \times 10^{-33}\text{ cm}$
 - (c) $7.77 \times 10^{-33}\text{ cm}$
 - (d) $8.83 \times 10^{-33}\text{ cm}$

6. If $e = 1.60206 \times 10^{-19}\text{ C}$, [1999]

$$\frac{e}{m} = 1.75875 \times 10^{11}\text{ C kg}^{-1}$$

then the mass of electron is

 - (a) $7.5678 \times 10^{-31}\text{ kg}$
 - (b) $9.1091 \times 10^{-31}\text{ kg}$
 - (c) $11.2531 \times 10^{-31}\text{ kg}$
 - (d) $13.0513 \times 10^{-31}\text{ kg}$

7. The energy of electron in first energy level is $-21.79 \times 10^{-12}\text{ erg}$ per atom. The energy of electron in second energy level is : [1999]

$$(a) -54.47 \times 10^{-12}\text{ erg atom}^{-1}$$

$$(b) -5.447 \times 10^{-12}\text{ erg atom}^{-1}$$

$$(c) -0.5447 \times 10^{-12}\text{ erg atom}^{-1}$$

$$(d) -0.05447 \times 10^{-12}\text{ erg atom}^{-1}$$

8. Deuterium nucleus contains: [2000]
 - (a) 1 proton, 1 electron
 - (b) 1 proton, 1 neutron
 - (c) 2 protons, 1 electron
 - (d) 1 proton, 2 electrons

9. The outermost configuration of most electronegative element is: [2000]
 - (a) $ns^2 np^5$
 - (b) $ns^2 np^6$
 - (c) $ns^2 np^4$
 - (d) $ns^2 np^3$

10. Bohr's theory is not applicable to: [2000]
 - (a) H
 - (b) He^+
 - (c) Li^{2+}
 - (d) H^+

11. The de-Broglie wavelength of an electron in the ground state of hydrogen atom is : [K.E. = 13.6 eV ; $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$] [2000]

$$(a) 33.28\text{ nm}$$

$$(b) 3.328\text{ nm}$$

$$(c) 0.3328\text{ nm}$$

$$(d) 0.0332\text{ nm}$$

12. The de-Broglie wavelength associated with a particle of mass 10^{-6} kg moving with a velocity of 10 ms^{-1} is : [2001]
 - (a) $6.63 \times 10^{-7}\text{ m}$
 - (b) $6.63 \times 10^{-16}\text{ m}$
 - (c) $6.63 \times 10^{-21}\text{ m}$
 - (d) $6.63 \times 10^{-29}\text{ m}$

13. The velocity of electron in second shell of hydrogen atom is : [2001]
 - (a) $10.94 \times 10^6\text{ ms}^{-1}$
 - (b) $18.88 \times 10^6\text{ ms}^{-1}$
 - (c) $1.888 \times 10^6\text{ ms}^{-1}$
 - (d) $1.094 \times 10^6\text{ ms}^{-1}$

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- 14.** Which of the following element is represented by electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$? [2001]
- (a) nitrogen (b) oxygen
 (c) fluorine (d) sulphur
- 15.** Quantum numbers of an atom can be defined on the basis of [2002]
- (a) Hund's rule
 (b) Pauli's exclusion principle
 (c) Aufbau's principle
 (d) Heisenberg's uncertainty principle
- 16.** Spectrum of Li^{2+} is similar to that of [2002]
- (a) H (b) Be
 (c) He (d) Ne
- 17.** Azimuthal quantum number defines [2002]
- (a) e/m ratio of electron
 (b) angular momentum of electron
 (c) spin of electron
 (d) magnetic momentum of electron
- 18.** The quantum number 'm' of a free gaseous atom is associated with : [2003]
- (a) the effective volume of the orbital
 (b) the shape of the orbital
 (c) the spatial orientation of the orbital
 (d) the energy of the orbital in the absence of a magnetic field
- 19.** For principle quantum number $n = 4$, the total number of orbitals having $l = 3$ is : [2004]
- (a) 3 (b) 7
 (c) 5 (d) 9
- 20.** The isoelectronic pair is : [2005]
- (a) Cl_2O_3 and ICl_2^- (b) ICl_2^- and ClO_2^-
 (c) IF_2^+ and I_3^- (d) ClO_2^- and ClF_2^+
- 21.** The most probable radius (in pm) for finding the electron in He^+ is [2005]
- (a) 0.0 (b) 52.9
 (c) 26.5 (d) 105.8
- 22.** The de Broglie wavelength associated with a ball of mass 1 kg having kinetic energy 0.5 J is : [2006]
- (a) $6.626 \times 10^{-34} \text{ m}$ (b) $13.20 \times 10^{-34} \text{ m}$
 (c) $10.38 \times 10^{-21} \text{ m}$ (d) $6.626 \times 10^{-34} \text{ \AA}$
- 23.** The uncertainties in the velocities of two particles, A and B are 0.05 and 0.02 ms^{-1} respectively. The mass of B is five times to that of the mass of A. What is the ratio of uncertainties $\frac{\Delta x_A}{\Delta x_B}$ in their positions ? [2008]
- (a) 2 (b) 0.25
 (c) 4 (d) 1
- 24.** Find the frequency of light that corresponds to photons of energy $5.0 \times 10^{-5} \text{ erg}$ [2010]
- (a) $7.5 \times 10^{-21} \text{ sec}^{-1}$ (b) $7.5 \times 10^{-21} \text{ sec}$
 (c) $7.5 \times 10^{21} \text{ sec}^{-1}$ (d) $7.5 \times 10^{21} \text{ sec}$
- 25.** Ratio of energy of photon of wavelength 3000 Å and 6000 Å is [2012]
- (a) 3 : 1 (b) 2 : 1
 (c) 1 : 2 (d) 1 : 3
- 26.** Which of the following combinations of quantum numbers is allowed? [2013]
- | | | | |
|-------|-----|-----|----------------|
| n | l | m | m_s |
| (a) 3 | 2 | 1 | 0 |
| (b) 2 | 0 | 0 | $-\frac{1}{2}$ |
| (c) 3 | -3 | -2 | $+\frac{1}{2}$ |
| (d) 1 | 0 | 1 | $+\frac{1}{2}$ |
- 27.** Among the following groupings which represents the collection of isoelectronic species? [2013]
- (a) $\text{NO}^+, \text{C}_2^{2-}, \text{O}_2^-, \text{CO}$
 (b) $\text{N}_2, \text{C}_2^{2-}, \text{CO}, \text{NO}$
 (c) $\text{CO}, \text{NO}^+, \text{CN}^-, \text{C}_2^{2-}$
 (d) $\text{NO}, \text{CN}^-, \text{N}_2, \text{O}_2^-$
- 28.** The electrons, identified by quantum numbers n and l (i) $n = 4, l = 1$ (ii) $n = 4, l = 0$ (iii) $n = 3, l = 2$ (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest, as [2014]
- (a) (iv) < (ii) < (iii) < (i)
 (b) (ii) < (iv) < (i) < (iii)
 (c) (i) < (iii) < (ii) < (iv)
 (d) (iii) < (i) < (iv) < (ii)

29. In hydrogen atomic spectrum, a series limit is found at 12186.3 cm^{-1} . Then it belongs to

[2014]

- (a) Lyman series (b) Balmer series
- (c) Paschen series (d) Brackett series

30. Based on equation $E = -2.178 \times 10^{-18} J \left(\frac{Z^2}{n^2} \right)$,

certain conclusions are written. Which of them is not correct? [2015]

- (a) Larger the value of n , the larger is the orbit radius.
- (b) Equation can be used to calculate the change in energy when the electron changes orbit.
- (c) For $n = 1$, the electron has a more negative energy than it does for $n = 6$ which means that the electron is more loosely bound in the smallest allowed orbit.
- (d) The negative sign in equation simply means that the energy or electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

31. Let m_p be the mass of a proton, m_n that of a neutron, M_1 that of a $^{20}_{10}\text{Ne}$ nucleus and M_2 that of a $^{40}_{20}\text{Ca}$ nucleus. Then [2015]

- (a) $M_2 = 2M_1$ (b) $M_1 < 10(m_p + m_n)$
- (c) $M_2 > 2M_1$ (d) $M_1 = M_2$

32. Which transition in the hydrogen atomic spectrum will have the same wavelength as the transition, $n = 4$ to $n = 2$ of He^+ spectrum?

[2016]

- (a) $n = 4$ to $n = 3$ (b) $n = 3$ to $n = 2$
- (c) $n = 4$ to $n = 2$ (d) $n = 2$ to $n = 1$

33. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen

[2017]

- (a) $5 \rightarrow 2$ (b) $4 \rightarrow 1$
- (c) $2 \rightarrow 5$ (d) $3 \rightarrow 2$

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 34-42) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

34. **Assertion :** An atom is electrically neutral

Reason : Atom contains equal number of protons and neutrons. [1997]

35. **Assertion :** The sum of protons and neutrons is always different in isobars.

Reason : Isobars are atoms of different elements having same mass number but different atomic number. [1997]

36. **Assertion :** All photons possess the same amount of energy.

Reason : Energy of photon does not depend upon wavelength of light used. [1998]

37. **Assertion :** Atoms are not electrically neutral.

Reason : Number of protons and electrons are different [1999]

38. **Assertion :** For Balmer series of hydrogen spectrum, the value $n_1 = 2$ and $n_2 = 3, 4, 5$.

Reason : The value of n for a line in Balmer series of hydrogen spectrum having the highest wave length is 4 and 6. [2002]

39. **Assertion :** Absorption spectrum consists of some bright lines separated by dark spaces.

Reason : Emission spectrum consists of dark lines. [2002]

40. **Assertion :** Nuclear binding energy per nucleon is in the order ${}^9_4\text{Be} > {}^7_3\text{Li} > {}^4_2\text{He}$.

Reason : Binding energy per nucleon increases linearly with difference in number of neutrons and protons. [2004]

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- 41.** **Assertion :** A spectral line will be observed for a $2p_x - 2p_y$ transition.
Reason : The energy is released in the form of wave of light when electron drops from $2p_x$ to $2p_y$ orbital. [2008]
- 42.** **Assertion :** An orbital designated by $n = 3$, $l = 1$ has double dumb-bell shape.
Reason : It belongs to p -subshell. [2011]
- Directions for (Qs.43-46) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- 43.** **Assertion :** Angular momentum of an electron in any orbit is given by angular momentum $= \frac{n.h}{2\pi}$, where n is the principal quantum number.
Reason : The principal quantum number, n , can have any integral value. [2012, 13]
- 44.** **Assertion :** Spin quantum number can have two values, $+\frac{1}{2}$ and $-\frac{1}{2}$.
Reason : + and – signs signify the positive and negative wave functions. [2014]
- 45.** **Assertion :** It is impossible to determine the exact position and exact momentum of an electron simultaneously.
Reason : The path of an electron in an atom is clearly defined. [2016]
- 46.** **Assertion :** The radius of the first orbit of hydrogen atom is 0.529\AA . [2017]
Reason : Radius of each circular orbit (r_n) $= 0.529\text{\AA} \cdot (n^2/Z)$, where $n = 1, 2, 3$ and Z = atomic number.

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Type A : Multiple Choice Questions

1. (b) Atomic number of the given element = 10
Electronic configuration = $1s^2, 2s^22p^6$
 $1s^22s^22p^6$ is electronic configuration of Ne.
 $1s^22s^22p^53s^1$ is excited oxidation state.
2. (a) The total no of orbital in a shell is n^2 .
3. (a) Positron is electron with positive charge,
 $+1e^0$
4. (c) Wavelength of visible light is
3800Å – 7600Å.
5. (d) From the de-Broglie formula for wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{150 \times 50} = 8.83 \times 10^{-33} \text{ cm.}$$

$$6. (b) \frac{e}{m} = 1.75875 \times 10^{11}$$

$$\frac{1.60206 \times 10^{-19}}{m} = 1.75875 \times 10^{11}$$

$$m = \frac{1.60206 \times 10^{-19}}{1.75875 \times 10^{11}} = \frac{1.60206}{1.75875} \times 10^{-30}$$

$$= 9.1091 \times 10^{-31} \text{ kg.}$$

7. (b) For a particular element,

$$E_n = \frac{13.6Z^2}{n^2} \text{ erg atm}^{-1}$$

$$\therefore E_n \propto \frac{1}{n^2}$$

$$\therefore \frac{E_1}{E_2} = \frac{(n_2^2)}{(n_1)^2}$$

$$\text{or } E_2 = \frac{(1)^2 \times (-21.79 \times 10^{-12})}{(2)^2}$$

$$= -5.447 \times 10^{-12} \text{ erg atm}^{-1}$$

8. (b) Deuterium nucleus contains 1 proton and 1 neutron because it is an isotope of hydrogen.
9. (a) Most electronegative element corresponds to ns^2np^5 configuration.
10. (d) Bohr's Theory is not applicable to H^+ as it has no electron.

11. (c) We know that

$$K.E. = \frac{1}{2} mv^2$$

$$\therefore v = \sqrt{\frac{2 \times K.E.}{m}}$$

$$= \sqrt{\frac{2 \times 13.6 \times 1.602 \times 10^{-19}}{9.1 \times 10^{-31}}}$$

$$= 2.18824 \times 10^6 \text{ m/s}$$

$$\text{No since, } \lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18824 \times 10^6}$$

$$= 0.3328 \times 10^{-9} = 0.3328 \text{ nm}$$

12. (d) $\lambda = \frac{h}{mc} = \frac{6.6 \times 10^{-34}}{10^{-6} \times 10} = 6.63 \times 10^{-29} \text{ m}$

13. (d) According to Bohr, velocity (v) of an electron is given by relation.

$$v = 2.188 \times 10^6 \frac{Z}{n} \text{ m/s}$$

Here $n = 2$, and Z (for H) = 1

$$\therefore v = \frac{2.188 \times 10^6 \times 1}{2}$$

$$= 1.094 \times 10^6 \text{ m/s}$$

14. (a) Electronic configuration corresponds to atomic number 7; hence the element is nitrogen.

15. (b) Quantum numbers of an atom can be defined on the basis of Pauli's exclusion principle which states that no two electrons can have the same value of all the four quantum numbers.

16. (a) Li^{2+} will have only one electron in its outermost electron. Its spectrum will be very similar to that of hydrogen.

17. (b) Azimuthal quantum no. ' m ' defines angular momentum of electron.

18. (c) Magnetic quantum no. ' m ' represents the spatial orientation of the orbital.

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- 19.** (b) For $n=4$ and $\ell=3$, the orbital is $4f$.
No. of values of $m=(2\ell+1)=7$
- 20.** (d) No. of electrons in $\text{ClO}_2^- = 17 + 16 + 1 = 34$
No. of electrons in $\text{ClF}_2^+ = 17 + 9 \times 2 - 1 = 34$
- 21.** (c) Bohr's radius (r)

$$= \frac{0.529 \times 10^{-10} n^2}{Z} \text{ m} = \frac{52.9 n^2}{Z} \text{ pm}$$

Here n (No of shell) = 1
Z (At. No) = 2

$$\therefore r = \frac{52.9 \times 1^2}{2} = 26.45 \text{ pm}$$

$$\begin{aligned} \text{22. (a)} \quad \lambda &= \frac{h}{mv} = \frac{h}{\sqrt{2mE}} \\ &= \frac{6.6 \times 10^{-34}}{\sqrt{2 \times 1 \times 0.5}} = 6.6 \times 10^{-34} \text{ m} \end{aligned}$$

- 23.** (a) Using the relation,

$$\Delta x \cdot \Delta v = \frac{h}{4\pi m}$$

[Heisenberg's uncertainty principle]

$$\text{or } \Delta x = \frac{h}{4\pi m \cdot \Delta v}$$

$$\text{Thus, } \Delta x_A = \frac{h}{4\pi \times 0.05 \times m} \quad \dots (\text{i})$$

$$\Delta x_B = \frac{h}{4\pi \times 0.02 \times 5m} \quad \dots (\text{ii})$$

Dividing (i) by (ii), we get

$$\frac{\Delta x_A}{\Delta x_B} = \frac{0.02 \times 5}{0.05} = \frac{10}{5} \text{ or } 2$$

- 24.** (c) Using $E = h\nu$, we get

$$\begin{aligned} v &= \frac{E}{h} = \frac{5.0 \times 10^{-5} \text{ erg}}{6.63 \times 10^{-34} \text{ Js}} \\ &= \frac{5.0 \times 10^{-5} \text{ erg}}{6.63 \times 10^{-34} \times 10^7 \text{ erg sec}} \end{aligned}$$

$$[\because 1 \text{ J} = 10^7 \text{ erg}]$$

$$= 7.54 \times 10^{21} \text{ sec}^{-1}$$

$$\text{25. (b)} \quad E = \frac{hc}{\lambda}; \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1} = \frac{6000}{3000} = 2:1$$

- 26.** (b)
- 27.** (c) The species CO , NO^+ , CN^- and C_2^{2-} contain 14 electrons each.
- 28.** (a) (n + l) rule the higher the value of (n + l), the higher is the energy. When (n + l) value is the same see value of n.

	i	ii	iii	iv
(n + l)	(4 + 1)	(4 + 0)	(3 + 2)	(3 + 1)
	5	4	5	4

$$\therefore \text{iv} < \text{ii} < \text{iii} < \text{i}$$

- 29.** (c) Series limit is the last line of the series, i.e. $n_2 = \infty$.

$$\begin{aligned} \therefore \bar{v} &= \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = R \left[\frac{1}{n_1^2} - \frac{1}{\infty^2} \right] = \frac{R}{n_1^2} \\ \therefore \bar{v} &= 12186.3 = \frac{109677.76}{n_1^2} \\ \Rightarrow n_1^2 &= \frac{109677.76}{12186.3} = 9 \Rightarrow n_1 = 3 \end{aligned}$$

- 30.** (c) The line belongs to Paschen series.
Energy of an electron at infinite distance from the nucleus is zero. As an electron approaches the nucleus, the electron attraction increases and hence the energy of electron decreases and thus becomes negative. Thus as the value of n decreases, i.e. lower the orbit is, more negative is the energy of the electron in it.

- 31.** (a) ${}_{10}^{20}\text{Ne}$ contains 10 protons and 10 neutrons
 $\therefore M_1 = 10 m_p + 10 m_n$
 ${}_{20}^{40}\text{Ca}$ contains 20 protons and 20 neutrons
 $\therefore M_2 = 20 m_p + 20 m_n$
 $\therefore M_2 = 2M_1$

- 32.** (d) For He^+ ion, $\frac{1}{\lambda} = Z^2 R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$(2)^2 R \left[\frac{1}{2^2} - \frac{1}{4^2} \right] = \frac{3R}{4}$$

For hydrogen atom, $\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$

$$\frac{3R}{4} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ or } \frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$

 $n_1 = 1 \text{ and } n_2 = 2.$

Structure of Atom

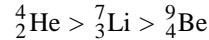
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- 33.** (a) The lines falling in the visible region comprise Balmer series. Hence the third line would be $n_1=2$, $n_2=5$ i.e. $5 \rightarrow 2$.

Type B : Assertion Reason Questions

- 34.** (c) Atom is electrically neutral. Atoms necessarily contain equal number of protons and electrons, but not neutrons.
- 35.** (e) Isobars have the same atomic mass (sum of protons and neutrons) but different atomic numbers.
- 36.** (d) Energy of a photon = $h\nu = h \cdot \frac{c}{\lambda}$.
So, energy depends upon wavelength.
- 37.** (d) Atoms are electrically neutral as number of electrons and protons are same.
- 38.** (c) The value of n for a line in Balmer series of hydrogen spectrum having the highest wave length will be $n_1=2$ and $n_2=3$ because this transition will have lowest energy and so highest wavelength.
- 39.** (d) Absorption spectrum consists of dark lines separated by bright space and emission spectrum consists of bright lines.
- 40.** (d) Binding energy depends on the mass defect (mass lost when the constituent protons and neutrons combine to form nucleus). Binding energy is direct measurement of stability of nucleus Higher the binding energy (means high loss of energy during formation of nucleus from protons and neutrons) per

nucleon, higher is stability of the nucleus.
The order of binding energy is



- 41.** (d) In this case both assertion and reason are false. Both $2p_x$ and $2p_y$ orbitals have equal energy ($2p$ orbitals are degenerate), there is no possibility of electron transition and hence no energy is released and thus no spectral line will be observed.
- 42.** (d) The orbital has dumb-bell shape and belongs to p -subshell.
- 43.** (b) Both assertion and reason are correct. Reason is **not** the correct explanation of assertion.
- 44.** (c) Plus and minus signs of spin quantum numbers imply that spin angular momentum of the electron, a vector quantity, acts in the same or opposite directions of orbital angular momentum.
- 45.** (c)
- 46.** (a) Both assertion and reason are true and reason is the correct explanation of assertion.

$$\text{Radius, } r_n = \frac{n^2 h^2}{4\pi e^2 m Z} = \frac{n^2}{Z} \times 0.529 \text{\AA}.r_n$$

For first orbit of H-atom

$$n = 1$$

$$r_1 = \frac{(1)^2}{1} \times 0.529 \text{\AA} = 0.529 \text{\AA}$$

Chapter

3

Classification of Elements and Periodicity in Properties

TYPE A : MULTIPLE CHOICE QUESTIONS

- (b) $I < Br < F < Cl$:
Increasing electron gain enthalpy
(with negative sign)
- (c) $B < C < N < O$
Increasing first ionization enthalpy
- (d) $Al^{3+} < Mg^{2+} < Na^+ < F^-$
Increasing ionic size
14. The correct decreasing order of first ionisation enthalpies of five elements of the second period is [2016]
(a) Be > B > C > N > F (b) N > F > C > B > Be
(c) F > N > C > Be > B (d) N > F > B > C > Be
15. The law of triads is applicable to a group of [2017]
(a) Cl, Br, I (b) C, N, O
(c) Na, K, Rb (d) H, O, N
- TYPE B : ASSERTION REASON QUESTIONS**
- Directions for (Qs.16-19) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
16. **Assertion :** First ionization energy for nitrogen is lower than oxygen.
Reason : Across a period effective nuclear charge decreases. [2005]
17. **Assertion :** Electron affinity refers to an isolated atom's attraction for an additional electron while electronegativity is the ability of an atom of an element to attract electrons towards itself in a shared pair of electrons.
Reason : Electron affinity is a relative number and electronegativity is experimentally measurable. [2010]
18. **Assertion :** Element has a tendency to lose the electron(s) to attain the stable configuration.
Reason : Ionization enthalpy is the energy released to remove an electron from an isolated gaseous atom in its ground state. [2011]
19. **Assertion :** Both Be and Al can form complexes such as BeF_4^{2-} and AlF_6^{3-} respectively, BeF_6^{3-} is not formed.
Reason : In case of Be, no vacant d-orbitals are present in its outermost shell. [2015]

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Type A : Multiple Choice Questions

1. (d) First ionisation potential is maximum for hydrogen, as electron is withdrawn from the first orbital which is very near to nucleus.
2. (b) Cl has high electron affinity.
3. (c) Group IA and III A contain mostly metals. Group VIII contains transition elements which are metals. Group VII A contains mostly non-metals (F, Cl, Br).
4. (d) Elements having 1, 2 or 3 electrons in its last shell act as metals.
 $32 = [\text{Ar}] 3d^{10} 4s^2 p^2$
 $34 = [\text{Ar}] 3d^{10} 4s^2 p^4$
 $36 = [\text{Ar}] 3d^{10} 4s^2 p^6$
 $38 = [\text{Ar}] 3d^{10}, 4s^2 p^6, 5s^2$

5. (a) Hydration energy $\propto \frac{1}{\text{Size}}$

In a group, size increases on going down the group from top to bottom i.e.,



∴ Increasing order of hydration energy



6. (d) Na ($Z = 11$; $1s^2, 2s^2 2p^6, 3s^1$) readily gives one electron because the resulting Na^+ ($1s^2 2s^2 2p^6$) has stable configuration .

Thus the first IE of Na is less. However, removal of an electron from a stable (noble gas) configuration requires high energy and thus IE_2 of Na will be very high.

7. (c) The atomic no of this element is highest which indicates that it will have highest energy.

8. (d) Electronic configuration of Cr (I) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

Electronic configuration of Fe(III) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

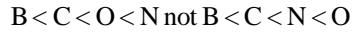
Electronic configuration of Mn (II) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$.

So, all these have valence electrons in $3d$ -subshell. So, option (d) is correct answer.

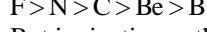
9. (d) The ionisation potential decreases with increase in atomic radii.

10. (c)

11. (b)
12. (c)
13. (c) In a period the value of ionisation potential increases from left to right with breaks where the atoms have some what stable configuration. In this case N has half filled stable orbital. Hence has highest ionisation energy. Thus the correct order is



- not $\text{B} < \text{C} < \text{N} < \text{O}$
14. (c) As we move along the period, the atomic size decreases due to increase in nuclear charge. Therefore, it is more difficult to remove electron from an atom. Hence the sequence of first ionization enthalpy in decreasing order is



But ionization enthalpy of boron is less as compared to beryllium because first electron in boron is to be removed from p -orbital while in beryllium, it is to be removed from s -orbital.

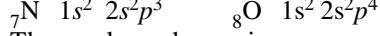
As s -orbital is closer to nucleus in comparison to p -orbital thus energy required to remove an electron from s -orbital is greater.

15. (a) According to the law of triads the atomic wt of the middle element is arithmetic mean of I and III.

$$\text{At wt of Br} = \frac{\text{At.wt of Cl} + \text{At wt of I}}{2}$$

Type B : Assertion Reason Questions

16. (d) The ionisation energy of N is more than that of O because N has exactly half filled valence p orbital.



The nuclear charge increases across a period.

17. (c) Assertion is true but Reason is false. Electron affinity is experimentally measurable while electronegativity is a relative number.

18. (c) Ionization enthalpy is the energy required to remove an electron from an isolated gaseous atom in its ground state.

19. (a) Both assertion and reason are correct and reason is correct explanation of assertion.

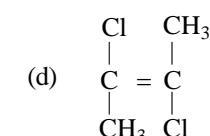
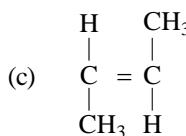
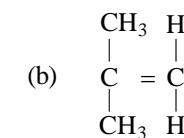
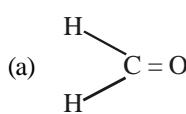
Chapter

4

Chemical Bonding and Molecular Structure

TYPE A : MULTIPLE CHOICE QUESTIONS

- The strongest hydrogen bond is : [1997]
 - O—H.....S
 - S—H.....O
 - F—H.....F
 - F—H.....O
- Shape of XeF_4 molecule is: [1998]
 - Pyramidal
 - Square planar
 - Triangular planar
 - Linear
- The shape of NH_3 molecule is: [2001]
 - Tetrahedral
 - Trigonal planar
 - Trigonal pyramidal
 - Linear
- Which of the following molecule has highest bond energy? [2002]
 - F—F
 - N—N
 - C—C
 - O—O
- Which of the following has the highest dipole moment? [2002]



- The number of σ - and π -bonds present in pent-4-en- 1-yne is [2002]
 - 10, 3
 - 4, 9
 - 3, 10
 - 9, 4
- Which of the following are arranged in the decreasing order of dipole moment? [2003]
 - $\text{CH}_3\text{Cl}, \text{CH}_3\text{Br}, \text{CH}_3\text{F}$
 - $\text{CH}_3\text{Cl}, \text{CH}_3\text{F}, \text{CH}_3\text{Br}$
 - $\text{CH}_3\text{Br}, \text{CH}_3\text{Cl}, \text{CH}_3\text{F}$
 - $\text{CH}_3\text{Br}, \text{CH}_3\text{F}, \text{CH}_3\text{Cl}$
- The paramagnetic species is : [2003]
 - KO_2
 - SiO_2
 - TiO_2
 - BaO_2

- Shape of O_2F_2 is similar to that of : [2004]
 - C_2F_2
 - H_2O_2
 - H_2F_2
 - C_2H_2
- The ONO angle is maximum in : [2004]
 - NO_3^-
 - NO_2^-
 - NO_2
 - NO_2^+
- Among the following molecules
 (i) $\ddot{\text{X}}\text{eO}_3$ (ii) $\ddot{\text{X}}\text{eOF}_4$ (iii) $\ddot{\text{X}}\text{eF}_6$
 Those having same number of lone pair of Xe are : [2005]
 - (i) and (ii) only
 - (i) and (iii) only
 - (ii) and (iii) only
 - (i), (ii) and (iii)
- Among the following, the species having square planar geometry for central atom are [2006]
 - XeF_4
 - SF_4
 - $[\text{NiCl}_4]^{2-}$
 - $[\text{PtCl}_4]^{2-}$
 - (i) and (iv)
 - (i) and (ii).
 - (ii) and (iii)
 - (iii) and (iv)
- In $[\text{Ag}(\text{CN}_2)]^-$, the number of π bonds is : [2006]
 - 2
 - 3
 - 4
 - 6
- Bond length order is [2007]
 - $\text{O}_2 < \text{O}_3 < \text{O}_2^{2-}$
 - $\text{O}_2 < \text{O}_2^{2-} < \text{O}_3$
 - $\text{O}_2^{2-} < \text{O}_3 < \text{O}_2$
 - $\text{O}_2 = \text{O}_2^{2-} > \text{O}_3$
- Sulphur reacts with chlorine in 1 : 2 ratio and forms X. Hydrolysis of X gives a sulphur compound Y. What is the structure and hybridisation of anion of Y? [2008]
 - tetrahedral, sp^3
 - linear, sp
 - pyramidal, sp^3
 - trigonal planar, sp^2
- Which of the following molecule has highest dipole moment? [2010]
 - B_2H_6
 - NF_3
 - NH_3
 - BF_3
- The geometry of ClO_3^- according to valence shell electron pair repulsion (VSEPR) theory will be [2012]
 - Planar triangle
 - Pyramidal
 - Tetrahedral
 - Square planar

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18. N₂ and O₂ are converted into monocations, N₂⁺ and O₂⁺ respectively. Which of the following statements is wrong ? [2013]
- (a) In N₂⁺, the N—N bond weakens
 - (b) In O₂⁺, the O—O bond order increases
 - (c) In O₂⁺, paramagnetism decreases
 - (d) N₂⁺ becomes diamagnetic
19. Match List I and List II and pick out correct matching codes from the given choices : [2015]
- | List I | List II |
|---------------------|-------------------------|
| Compound | Structure |
| A. ClF ₃ | 1. Square planar |
| B. PCl ₅ | 2. Tetrahedral |
| C. IF ₅ | 3. Trigonal bipyramidal |
| D. CCl ₄ | 4. Square pyramidal |
| E. XeF ₄ | 5. T-shaped |
- Codes**
- (a) A-5, B-4, C-3, D-2, E-1
 - (b) A-5, B-3, C-4, D-2, E-1
 - (c) A-5, B-3, C-4, D-1, E-2
 - (d) A-4, B-3, C-5, D-2, E-1
20. XeO₄ molecule is tetrahedral having : [2016]
- (a) Two pπ – dπ bonds
 - (b) One pπ – dπ bonds
 - (c) Four pπ – dπ bonds
 - (d) Three pπ – dπ bonds
21. Among the following species, identify the pair having same bond order CN⁻, O₂⁻, NO⁺, CN⁺ [2016]
- (a) CN⁻ and O₂⁻
 - (b) O₂⁻ and NO⁺
 - (c) CN⁻ and NO⁺
 - (d) CN⁻ and CN⁺
22. Which of the following substances has the least covalent character ? [2017]
- (a) Cl₂O
 - (b) NCl₃
 - (c) PbCl₂
 - (d) BaCl₂

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 23-32) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

23. **Assertion :** Water is liquid but H₂S is a gas.
Reason : Oxygen is paramagnetic. [1999]

24. **Assertion :** Boiling and melting points of amides are higher than corresponding acids.
Reason : It is due to strong intermolecular hydrogen bonding in their molecules. [2002]

25. **Assertion :** Sigma (σ) is a strong bond, while pi (π) is a weak bond.
Reason : Atoms rotate freely about pi (π) bond. [2002]

26. **Assertion :** The O—O bond length in H₂O₂ is shorter than that of O₂F₂.
Reason : H₂O₂ is an ionic compound. [2003]

27. **Assertion :** All F—S—F angle in SF₄ are greater than 90° but less than 180°,
Reason : The lone pair- bond pair repulsion is weaker than bond pair-bond pair repulsion. [2004]

28. **Assertion :** SeCl₄ does not have a tetrahedral structure.
Reason : Se in SeCl₄ has two lone pairs. [2005]

29. **Assertion :** B₂ molecule is diamagnetic.
Reason : The highest occupied molecular orbital is of σ type. [2005]

30. **Assertion :** Ozone is powerful oxidising agent in comparison to O₂.
Reason : Ozone is diamagnetic but O₂ is paramagnetic. [2005]

31. **Assertion :** Molecular nitrogen is less reactive than molecular oxygen.
Reason : The bond length of N₂ is shorter than that of oxygen. [2007, 2006]

32. **Assertion :** Fluorine molecule has bond order one.
Reason : The number of electrons in the antibonding molecular orbitals is two less than that in bonding molecular orbitals. [2008]

Directions for (Qs.33-38) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
33. **Assertion :** Molecules of larger size have higher polarizability.
Reason : Polarizability is observed only in those molecules which has permanent dipole moment. [2010]
34. **Assertion :** Bond angle of H_2S is smaller than H_2O .
Reason : Electronegativity of the central atom increases, bond angle decreases. [2011]
35. **Assertion :** Bond angle of H_2S is smaller than H_2O .
36. **Assertion :** LiCl is predominantly a covalent compound.
Reason : Electronegativity difference between Li and Cl is too small. [2014]
37. **Assertion :** Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{++}) does not.
Reason : Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{++}) is blue in the aqueous solution. [2014]
38. **Assertion :** Lone pair-lone pair repulsive interactions are greater than lone pair-bond pair and bond pair-bond pair interactions.
Reason : The space occupied by lone pair electrons is more as compared to bond pair electrons. [2016]

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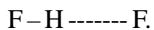
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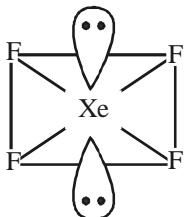
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Type A : Multiple Choice Questions

1. (c) Higher the electronegativity of the other atom, greater is the strength of hydrogen bond. Strongest hydrogen bond is between H and F.

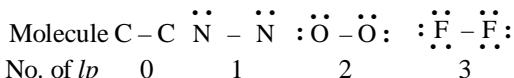


2. (b) Shape of XeF_4 molecule is square planar. It involves sp^3d^2 hybridisation.

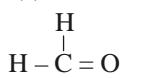


3. (c) In NH_3 , N is sp^3 hybridised ; N of NH_3 has a lone pair of electrons. The lone pair distorts the normal tetrahedral geometry due to $lp-bp$ interaction to trigonal bipyramidal.

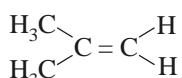
4. (c) Greater the number of lone pairs present on the bonded atoms, greater is the repulsive force between them and hence smaller the bond energy.



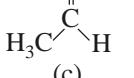
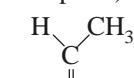
5. (a) Greater the difference in electronegativity between the two atoms, larger will be polarity and hence dipole moment. Thus (a) has maximum dipole moment.



(a)
(C–O bond is
more polar)



(b)
(very less polar)



(c) Symmetrical molecules ($\mu = 0$)

6. (a) $\text{HC} \equiv \text{C} - \text{CH}_2 - \text{CH} = \text{CH}_2$
Pent-4-en-1-yne

Triple bond between C and C contains one σ bond and two π bonds. Double bond between C and C contains one σ bond and one π bond.

Total σ bonds = 10

Total π bonds = 3

7. (b) Fluorine is most electronegative and Br is least electronegative. So CH_3F should have highest dipole moment but as C – F bond length is very small so inspite of greater polarity in CH_3F , it has less dipole moment than CH_3Cl .

8. (a) Species having unpaired electron or odd number of electrons are paramagnetic while species having paired or even number of electrons are called diamagnetic.

KO_2 has 35 electrons — paramagnetic

SiO_2 has 30 electrons — diamagnetic

TiO_2 has 38 electrons — diamagnetic

BaO_2 has 72 electrons — diamagnetic

9. (b) Shape of O_2F_2 is similar to that of H_2O_2 because both of them are peroxides.

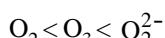
10. (d) In NO_2^+ nitrogen is in sp hybridised state. So, the molecule is linear. So ONO angle is 180° which is maximum among all other molecules.

11. (d) In all compounds, Xe will have same no. of lone pair (one only)

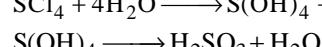
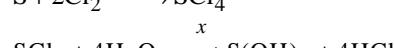
12. (a) Square Planar Structure : XeF_4 and $[\text{PtCl}_4]^{2-}$

13. (c) In one – C \equiv N, No. of π bonds = 2
So in $[\text{Ag}(\text{CN}_2)]^-$, No. of π bonds = $2 \times 2 = 4$

14. (a) Bond length is inversely proportional to bond order. Bond orders of O_2 , O_3 and O_2^{2-} are 2, 1.5 and 1 respectively. Hence the correct sequence of bond lengths is

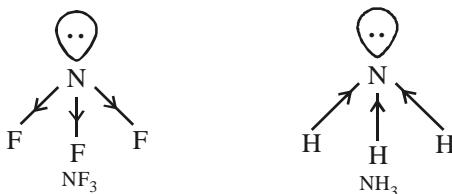


15. (c) $\text{S} + 2\text{Cl}_2 \longrightarrow \text{SCl}_4$



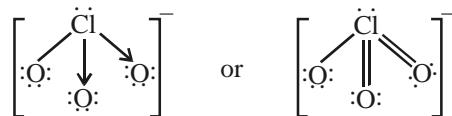
The anion of y is SO_3^{2-} in which S is sp^3 hybridised with one lone pair of electrons on S, giving SO_3^{2-} pyramidal shape.

16. (c) BF_3 and B_2H_6 being non-polar molecules do not show dipole moment. In NF_3 , the electronegative F pulls the electron toward itself due to which bond moments of the three N–F bonds is opposite to that of lone pair while in NH_3 bond moments of the N–H bonds are in same direction to that of lone pair.



Hence, bond moments add up in NH_3 resulting in highest dipole moment among the given options.

17. (b) Hybridisation is sp^3 and shape pyramidal

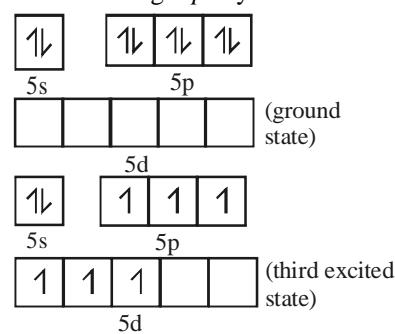


18. (d) N_2^+ is paramagnetic
 $\sigma 1s^2, \sigma^*1s^2, \sigma^*2s^2, \pi 2p_x^2 = \pi 2p_y^2, \sigma 2p_z^1$

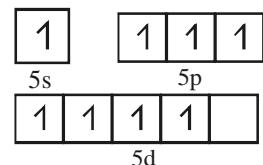
19. (b) List I List II

Compound	Structure
(A) ClF_3	T-shaped
(B) PCl_5	Trigonal bipyramidal
(C) IF_5	Square pyramidal
(D) CCl_4	Tetrahedral
(E) XeF_4	Square planar

20. (c) Xenon undergo sp^3 hybridization.



In the fourth excited state xenon atom, has 8 unpaired electrons



One s and three p orbital undergo sp^3 hybridization. Four sp^3 hybrid orbitals form four σ bonds with oxygen atoms. They are $\sigma sp^3 - p$. Four $p\pi - d\pi$ bonds are also formed with oxygen atoms by the unpaired electrons.

21. (c) M.O. electronic configuration of CN^- is $\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$

$$\therefore \text{B.O.} = \frac{10-4}{2} = 3$$

M.O. electronic configuration of O_2^- is $\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$

$$\pi 2p_y^2 \pi^*2p_x^2 \pi^*2p_y^1$$

$$\therefore \text{B.O.} = \frac{10-7}{2} = 1.5$$

M.O. electronic configuration of CN^+ is $\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^1$

$$\therefore \text{B.O.} = \frac{9-4}{2} = 2.5$$

M.O. electronic configuration of NO^+ is $\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$

$$\therefore \text{B.O.} = \frac{10-4}{2} = 3$$

$\therefore \text{CN}^-$ and NO^+ have bond order equal to 3
 According to Fajan's rule :

$$\text{Covalent character} \propto \frac{1}{\text{size of cation}} \\ \propto \text{size of anion}$$

Among the given species order of size of cations

$$\text{N}^{3+} < \text{O}^{2+} < \text{Pb}^{2+} < \text{Ba}^{2+}$$

order of size of anions $\text{O}^{2-} > \text{Cl}^-$.

Hence the order of covalent character is

$$\text{NCl}_3 > \text{Cl}_2\text{O} > \text{PbCl}_2 > \text{BaCl}_2$$

BaCl_2 is least covalent in nature.

Type B : Assertion Reason Questions

23. (b) Water is liquid but H_2S is gas due to hydrogen bond in water. Oxygen is paramagnetic.

24. (a)

25. (c) Sigma (σ) bond is formed by axial overlap of atomic orbitals while pi (π) bond is formed by lateral overlap. Since axial overlapping takes place to a greater extent than the

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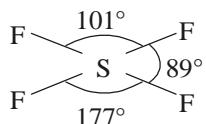
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lateral overlapping, former (σ) bond is stronger than pi bond. Atoms attached to doubly bonded atom can't rotate freely around the double bond.

26. (d) H_2O_2 is a covalent compound. In O_2F_2 , O–O bond is shorter than in H_2O_2 due to higher electronegativity of F.

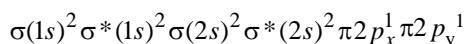
27. (d) SF_4 has see-saw type structure in which bond angles are different between different S–F atoms. It has non-planar structure.



According to VSEPR theory $\ell\text{p} - \ell\text{p}$ repulsion $> \ell\text{p} - \text{bp} > \text{bp} - \text{bp}$ repulsion

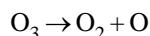
28. (c) SeCl_4 has distorted trigonal pyramidal geometry; here Se has only one lone pair of electrons hence it has sp^3d hybridisation.

29. (d) B_2 molecule has no of electrons = 10
Molecular orbital configuration



Due to unpaired electron, it is paramagnetic.
The highest occupied MO is of π -type.

30. (b) Ozone is a powerful oxidising agent because it is unstable and breaks into oxygen as it has higher energy content than oxygen.



It is also true that O_3 is diamagnetic, while O_2 is paramagnetic.

31. (a) Nitrogen molecule has triple bond, whereas oxygen has double bond. N–N Bond length of N_2 is shorter. Hence, it is difficult to break the triple bond of N_2 . Hence N_2 is less reactive. Both A and R are true.

32. (a) MO electronic configuration of F_2 molecule. $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_x^2$, $\pi 2p_y^2 \approx \pi 2p_z^2$, $\pi^* 2p_y^2 \approx \pi^* 2p_z^2$

Thus there are 10 electrons in bonding orbitals and 8 electrons in antibonding

orbitals. Thus, reason is true and it is also the correct explanation of assertion because

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 8}{2} = 1$$

33. (c) Assertion is true but Reason is false.
As the size of the atom increases the influence of the electric dipole also increases.
34. (c) Bond angle of H_2S (92°) $<$ H_2O ($104^\circ 31$). As the electronegativity of the central atom decreases, bond angle decreases. In the present case, S is less electronegative than oxygen. Thus bond pairs in H_2S are more away from the central atom than in H_2O and thus repulsive forces between bond pairs are smaller producing smaller bond angle.

35. (c) Bond angle of H_2S (92°) $<$ H_2O ($104^\circ 31$). As the electronegativity of the central atom decreases, bond angle decreases. In the present case, S is less electronegative than oxygen. Thus bond pairs in H_2S are more away from the central atom than in H_2O and thus repulsive forces between bond pairs are smaller producing smaller bond angle.

36. (c) LiCl is a covalent compound. Due to the large size of the anion (Cl^-) its effective nuclear charge lessens and its valence shell is held less tightly towards its nucleus. Here, assertion is correct but reason is incorrect.

37. (d)
38. (a) While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions.
Hence (b) is the correct option.

Chapter

5

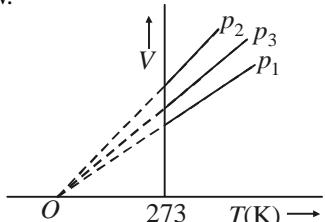
States of Matter

TYPE A : MULTIPLE CHOICE QUESTIONS

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13. The volume-temperature graphs of a given mass of an ideal gas at constant pressure are shown below. [2008]



- What is the correct order of pressures ?
- $p_1 > p_3 > p_2$
 - $p_1 > p_2 > p_3$
 - $p_2 > p_3 > p_1$
 - $p_2 > p_1 > p_3$
14. The inversion temperature T_i (K) of hydrogen is (given van der Waal's constants a and b are 0.244 atm L² mol⁻² and 0.027 L mol⁻¹ respectively)
- 440
 - 220
 - 110
 - 330
15. Amongst the following statements, the correct one is : [2011]
- The gas can not be compressed below the critical temperature.
 - Below critical temperature, thermal motion of the molecules is slow enough for the intermolecular forces to come into play leading to condensation of the gas.
 - At critical temperature liquid and gaseous phase can be distinguished.
 - An ideal gas has a characteristic critical temperature.
16. X ml of H₂ gas effuse through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is [2012]
- 10 seconds : He
 - 20 seconds : O₂
 - 25 seconds : CO
 - 55 seconds : CO₂
17. The rate of diffusion of SO₂, CO₂, PCl₃ and SO₃ are in the following order [2013]
- PCl₃ > SO₃ > SO₂ > CO₂
 - CO₂ > SO₂ > PCl₃ > SO₃
 - SO₂ > SO₃ > PCl₃ > CO₂
 - CO₂ > SO₂ > SO₃ > PCl₃

18. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be [2014]

- at the centre of the tube.
- near the hydrogen chloride bottle.
- near the ammonia bottle.
- throughout the length of the tube.

19. The gas with the highest critical temperature is [2014]

- H₂
- He
- N₂
- CO₂

20. Cyclopropane and oxygen at partial pressures 170 torr and 570 torr respectively are mixed in a gas cylinder. What is the ratio of the number of moles of cyclopropane to the number of moles of oxygen (nC_3H_6/nO_2)? [2015]

- $\frac{170 \times 42}{570 \times 32} = 0.39$
- $\frac{170}{42} / \left(\frac{170 + 570}{42 + 32} \right) \approx 0.19$
- $\frac{170}{740} = 0.23$
- $\frac{170}{570} = 0.30$

21. When a sample of gas is compressed at constant temperature from 15 atm to 60 atm, its volume changes from 76 cm³ to 20.5 cm³. Which of the following statements are possible explanations of this behaviour?

- The gas behaves non-ideally
 - The gas dimerises
 - The gas is adsorbed into the vessel walls
- [2016]

- 1, 2 and 3
- 1 and 2 only
- 2 and 3 only
- 1 only

22. Pure hydrogen sulphide is stored in a tank of 100 litre capacity at 20°C and 2 atm pressure. The mass of the gas will be [2017]

- 34 g
- 340 g
- 282.68 g
- 28.24 g

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 23-28) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

23. **Assertion :** Ice melts faster at high altitude.

Reason : At high altitude, atmospheric pressure is high. [1997]

24. **Assertion :** Gases do not settle to the bottom of container.

Reason : Gases have high kinetic energy [1997]

25. **Assertion :** Wet air is heavier than dry air.

Reason : The density of dry air is more than density of water. [1999]

26. **Assertion :** Use of pressure cooker reduces cooking time.

Reason : At higher pressure cooking occurs faster. [2000]

27. **Assertion :** All molecules in a gas have same speed.

Reason : Gas contains molecules of different size and shape. [2001]

28. **Assertion :** Compressibility factor for hydrogen varies with pressure with positive slope at all pressures.

Reason : Even at low pressure, repulsive forces dominate hydrogen gas. [2005]

Directions for (Qs.29-33) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.

- (c) If Assertion is correct but Reason is incorrect.

- (d) If both the Assertion and Reason are incorrect.

29. **Assertion :** The molecules of the dissolved gas present in a liquid gain kinetic energy as temperature is raised.

Reason : Gases tends to be more soluble in liquids as the temperature is raised. [2009]

30. **Assertion :** Greater the value of van der Waal's constant 'a' greater is the liquefaction of gas.

Reason : 'a' indirectly measures the magnitude of attractive forces between the molecules.

[2014]

31. **Assertion :** Compressibility factor (Z) for non-ideal gases can be greater than 1. [2015]

Reason : Non-ideal gases always exert higher pressure than expected.

32. **Assertion :** Gases do not liquefy above their critical temperature, even on applying high pressure.

Reason : Above critical temperature, the molecular speed is high and intermolecular attractions cannot hold the molecules together because they escape because of high speed.

[2016]

33. **Assertion :** At critical temperature liquid passes into gaseous state imperceptibly and continuously.

Reason : The density of liquid and gaseous phase is equal to critical temperature.

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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (b) From $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{V_1 \times 640}{(273+47)} = \frac{620 \times 300}{(273+27)}$$

$$V_1 = \frac{620 \times 300 \times 320}{640 \times 300} = 310 \text{ cc}$$

2. (c) Compressibility factor (Z) is a convenient method of showing deviation of real gases from an ideal gas

$$Z = \frac{PV}{nRT}$$

For ideal gas, $PV = nRT$; $\therefore Z = 1$

For real gases, $PV \neq nRT$; $\therefore Z \neq 1$

When, $Z > 1$, it refers positive deviation i.e., gas is less compressible than ideal gas. $Z < 1$, it refers negative deviation, i.e., gas is more compressible than ideal gas.

3. (b) From Charle's law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{12}{(273+27)} = \frac{14.9}{T_2}$$

$$T_2 = \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

$$= 372.5 - 273 = 99.5^\circ\text{C}$$

4. (b) Van der Waal's equation is applicable for real (non-ideal) gases.

5. (a) According to Graham's law of diffusion or effusion "under similar conditions of temperature and pressure, rate of diffusion is inversely proportional to square root of molecular weight" $r \propto \frac{1}{\sqrt{M}}$.

6. (a) Diffusion is the process by which matter is transported in small quantities.

7. (b) Let the wt. of each gas mixed = x g

$$\therefore \text{mole of } \text{SO}_2 = \frac{x}{64}$$

$$\text{mole of } \text{CH}_4 = \frac{x}{16}$$

$$\text{mole of } \text{O}_2 = \frac{x}{32}$$

Total number of moles of the three gases

$$= \frac{x}{64} + \frac{x}{16} + \frac{x}{32} = \frac{7x}{64}$$

Partial pressure exerted by a gas in the mixture of non-reacting gases (p) is given by

$$p = \frac{\text{moles of that gas}}{\text{total moles}} \times \text{Total pressure}$$

$$\therefore p_{\text{CH}_4} = \frac{x}{16} \times \frac{64}{7x} \times 2.1 = 1.2 \text{ atm}$$

8. (c) $\left(P + \frac{a}{V^2} \right) (V - nb) = RT$ is

Berthelot equation. The volume correction is same as in van der Waal's equation, but the pressure correction is different. He introduced the pressure correction as $\frac{a}{TV^2}$ in place of $\frac{a}{V^2}$

9. (a) $P \propto \frac{1}{V}$ and $\frac{m}{V} = \rho$; $\frac{1}{V} = \frac{\rho}{m}$

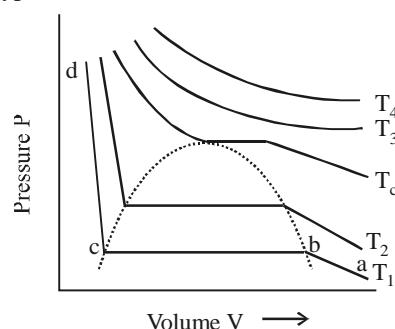
$$\text{So, } P \propto \frac{\rho}{m} \text{ i.e. Pressure} \propto \rho$$

10. (b) Repulsive force will decrease the compressibility factor i.e. so, value of $Z > 1$ as

$$Z = \frac{PV}{RT}$$

Due to repulsion value of PV will be greater than RT so $Z > 1$.

11. (c) Generally most of real gases show the same type of isotherm.



ab represents the gaseous state, line bc which is horizontal line shows liquid and vapour equilibrium. Pressure corresponding to the line bc is known as vapour pressure of liquid. Line cd represents liquid state.

12. (a) Critical temperature of a gas is given by

$$T_C = \frac{8a}{27Rb} \quad \text{P} \quad a \propto T_C$$

where a is measure of vander Waal's forces of attraction. Higher the critical temperature of a gas greater the intermolecular forces of attraction between the molecules of gas and easily the gas can be liquefied. Hence gas A whose critical temperature (25°C) is highest among all the given options will be liquefied more easily.

13. (a) From the graph we can see the correct order of pressures $p_1 > p_3 > p_2$

14. (b) Gases become cooler during Joule Thomson's expansion only if they are below a certain temperature known as inversion temperature (T_i). The inversion temperature is characteristic of each gas and is given by

$$T_i = \frac{2a}{bR}$$

where R is gas constant

Given $a = 0.244 \text{ atm L}^2 \text{ mol}^{-2}$

$$b = 0.027 \text{ L mol}^{-1}$$

$$R = 0.0821 \text{ L atm deg}^{-1} \text{ mol}^{-1}$$

$$\therefore T_i = \frac{2 \times 0.244}{0.027 \times 0.0821} = 220 \text{ K}$$

15. (b)

16. (b) For effusion of same volume,

$$\frac{t_1}{t_2} = \sqrt{\frac{M_1}{M_2}} \Rightarrow \frac{t_1}{\sqrt{M_1}} = \frac{t_2}{\sqrt{M_2}}$$

This is clearly seen from the options that

the ratio of $\frac{t}{\sqrt{M}}$ is same for H_2 and O_2 .

$$\left(\frac{5}{\sqrt{2}} = \frac{20}{\sqrt{32}} = \frac{5}{\sqrt{2}} \right)$$

17. (d) Rate $\propto \sqrt{\frac{1}{M}}$. The smaller the value of M the more is the rate of diffusion

18. (b) Rate of diffusion $\propto \sqrt{\frac{1}{\text{Molecular mass}}}$

\therefore Molecular mass of HCl > Molecular mass of NH_3

\therefore HCl diffuses at slower rate and white ammonium chloride is first formed near HCl bottle.

19. (d) CO_2 has highest critical temperature of 304.2 K

20. (d) By ideal gas equation

$$P_1 V = n_1 R T$$

$$n_1 \propto P_1 \text{ and } n_2 \propto P_2$$

$$\frac{n_1}{n_2} = \frac{P_1}{P_2} \Rightarrow \frac{n_1}{n_2} = \frac{170}{570} = 0.30$$

21. (d) Given, $P_1 = 15 \text{ atm}$, $P_2 = 60 \text{ atm}$

$$V_1 = 76 \text{ cm}^3, V_2 = 20.5 \text{ cm}^3.$$

If the gas is an ideal gas, then according to Boyle's law, it must follow the equation,

$$P_1 V_1 = P_2 V_2$$

$$P_1 \times V_1 = 15 \times 76 = 1140$$

$$P_2 \times V_2 = 60 \times 20.5 = 1230$$

$$\therefore P_1 V_1 \neq P_2 V_2$$

\therefore The gas behaves non-ideally.

The given information is not sufficient to comment on other statements.

$$22. (c) n = \frac{PV}{RT} = \frac{m}{M}$$

$$m = \frac{MPV}{RT} = \frac{34 \times 2 \times 100}{0.082 \times 293} = 282.68 \text{ gm}$$

Type B : Assertion Reason Questions

23. (d) Ice does not melt faster at high altitude because melting is favoured at high pressure, whereas atmospheric pressure decreases as we go higher. So, assertion and reason both are false.

24. (a) Gases do not settle to the bottom because of its kinetic energy. They are always in motion. Because of small mass, the effect of gravity on them is negative.

25. (e) Wet air is lighter than dry air because density of air is more than water.

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26. (a) Use of pressure cooker reduces cooking time because increase of pressure increases b.p and so cooking occurs faster.
27. (d) All molecules of a gas are identical in shape and size, but have different energies due to which they have different speeds.
28. (a) In case of hydrogen, Z increases with pressure. At $273K$, $Z > 1$. which shows that it is difficult to compress the gas as compared to ideal gas. In this case repulsive forces dominate.
29. (c) When the temperature is raised, the molecules of the dissolved gas present in a liquid gain kinetic energy. Higher kinetic energy of the gas molecules make them to escape from its solution. That is why, gases

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tend to be less soluble in liquids at higher temperature.

30. (a) Both assertion and reason are true and reason is the correct explanation of assertion. Considering the attractive force pressure in ideal gas equation ($PV = nRT$) is corrected

by introducing a factor of $\frac{an^2}{V^2}$ where a is van der waal constant.

31. (c) Z can be greater than 1 or less than 1. Non - ideal gases exert less pressure than expected due to backward pull by other molecules.

32. (a)

33. (a)

Chapter

6

Thermodynamics

TYPE A : MULTIPLE CHOICE QUESTIONS

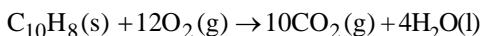
1. The enthalpy change of a reaction does not depend on : **[1997]**
 - (a) initial and final enthalpy change of reaction
 - (b) state of reactants and products
 - (c) different intermediate reactions
 - (d) nature of reactants and products
2. $S + O_2 \rightarrow SO_2 + x \text{ kcal}$ (1)
 $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 + y \text{ kcal}$ (2)
- The heat of formation of SO_3 in the above reaction is **[1997]**
 - (a) $(x+y)$
 - (b) $(x-y)$
 - (c) $(2x-y)$
 - (d) $(2x+y)$
3. At a constant volume the specific heat of a gas is 0.075 and its molecular weight is 40. The gas is: **[1998]**
 - (a) Monoatomic
 - (b) Diatomic
 - (c) Triatomic
 - (d) None of the above
4. The heat of combustion of yellow phosphorous is -9.91 kJ and of red phosphorous is -8.78 kJ . The heat of transition of yellow phosphorus to red phosphorus is : **[1998]**
 - (a) -9.91 kJ
 - (b) -8.78 kJ
 - (c) -9.34 kJ
 - (d) -1.13 kJ
5. Combustion of glucose takes place according to the equation:
 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$,
 $\Delta H = -72 \text{ k cal}$
The energy required for production of 1.6 g of glucose is [molecular mass of glucose is 180 g]
 - (a) 0.064 k cal
 - (b) 0.64 k cal **[1998]**
 - (c) 6.4 k cal
 - (d) 64 k cal
6. For a spontaneous process, entropy: **[1998]**
 - (a) Increases
 - (b) Decreases
 - (c) Unchanged
 - (d) Not clear
7. Internal energy does not include: **[1999]**
 - (a) Rotational energy
 - (b) Nuclear energy
 - (c) Vibrational energy
 - (d) Energy due to gravitational pull
8. A gas expands isothermally against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3 . It absorbs 300 J of thermal energy from its surrounding.
The ΔU is:
 - (a) -312 J
 - (b) $+123 \text{ J}$ **[1999]**
 - (c) -213 J
 - (d) $+231 \text{ J}$
9. During isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 273 K, the work done is [gas constant = 2] : **[2000]**
 - (a) -895.8 cal
 - (b) -1172.6 cal
 - (c) -1257.43 cal
 - (d) -1499.6 cal
10. One mole of an ideal gas for which $C_v = (3/2)R$ is heated reversibly at a constant pressure of 1 atm from 25°C to 100°C . The ΔH is: **[2000]**
 - (a) 3.775 cal
 - (b) 37.256 cal
 - (c) 372.56 cal
 - (d) 3725.6 cal
11. Enthalpy of neutralisation of CH_3COOH by $NaOH$ is -50.6 kJ/mol and the heat of neutralisation of a strong acid with $NaOH$ is -55.9 kJ/mol . The value of ΔH for the ionisation of CH_3COOH is: **[2000]**
 - (a) 3.5 kJ/mol
 - (b) 4.6 kJ/mol
 - (c) 5.3 kJ/mol
 - (d) 6.4 kJ/mol
12. The internal energy of a substance : **[2001]**
 - (a) increases with increase in temperature
 - (b) decreases with increase in temperature
 - (c) remains unaffected with temperature
 - (d) can be calculated by the reaction, $E = mc^2$

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13. The heat of reaction for :



at constant volume is -1228.2 kcal at 25°C . The heat of reaction at constant pressure and same temperature is : [2001]

- (a) -1228.2 kJ (b) -1229.3 kJ
 (c) -1232.9 kJ (d) -1242.6 kJ

14. Two moles of an ideal gas are compressed isothermally (100°C) and reversibly from a pressure of 10 atm to 25 atm , then the free energy change is : [2001]

- (a) $+15.482 \text{ kJ}$ (b) $+10.462 \text{ kJ}$
 (c) $+5.684 \text{ kJ}$ (d) $+3.364 \text{ kJ}$

15. In the exothermic reaction, the enthalpy of reaction is always : [2001]

- (a) zero (b) positive
 (c) negative (d) none of these

16. The heat of neutralization of a strong base and a strong acid is 57 kJ . The heat released when 0.5 moles of HNO_3 solution is added to 0.20 moles of NaOH solution, is [2002]

- (a) 11.4 kJ (b) 34.7 kJ
 (c) 23.5 kJ (d) 58.8 kJ

17. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter, the temperature of the calorimeter increases by 6.12 K . The heat capacity of the system is 1.23 kJ/g/deg . What is the molar heat of decomposition for NH_4NO_3 ? [2003]

- (a) -7.53 kJ/mol (b) -398.1 kJ/mol
 (c) -16.1 kJ/mol (d) -602 kJ/mol

18. Which one of the following has ΔS° greater than zero? [2003]

- (a) $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CaCO}_3(\text{s})$
 (b) $\text{NaCl}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{s})$
 (c) $\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
 (d) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

19. Which of the following is arranged in the increasing order of enthalpy of vaporisation? [2004]

- (a) $\text{NH}_3, \text{PH}_3, \text{AsH}_3$ (b) $\text{AsH}_3, \text{PH}_3, \text{NH}_3$
 (c) $\text{NH}_3, \text{AsH}_3, \text{PH}_3$ (d) $\text{PH}_3, \text{AsH}_3, \text{NH}_3$

20. How much energy is released when 6 moles of octane is burnt in air ? Given ΔH_f° for $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$ and $\text{C}_8\text{H}_{18}(\text{l})$ respectively are -490 , -240 and $+160 \text{ J/mol}$. [2004]

- (a) -6.2 kJ (b) -37.4 kJ
 (c) -35.5 kJ (d) -20.0 kJ

21. ΔH_f° (298K) of methanol is given by the chemical equation : [2005]

- (a) $\text{CH}_{4(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\text{g})}$
 (b) $\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\text{l})}$
 (c) $\text{C}(\text{diamond}) + \frac{1}{2}\text{O}_{2(\text{g})} + 2\text{H}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\text{l})}$
 (d) $\text{CO}_{(\text{g})} + 2\text{H}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\text{l})}$

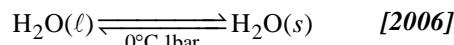
22. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w corresponds to [2005]

- (a) $\Delta U < 0, w = 0$ (b) $\Delta U < 0, w < 0$
 (c) $\Delta U > 0, w = 0$ (d) $\Delta U > 0, w > 0$

23. For a spontaneous process, the correct statement is : [2006]

- (a) Entropy of the system always increases
 (b) Free energy of the system always increases
 (c) Total entropy change is always negative
 (d) Total entropy change is always positive

24. For a phase change,



- (a) $\Delta G = 0$ (b) $\Delta S = 0$
 (c) $\Delta H = 0$ (d) $\Delta U = 0$

25. The enthalpy change (ΔH) for the reaction,

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ is -92.38 kJ at 298 K . The internal energy change ΔU at 298 K is [2006]

- (a) -92.38 kJ (b) -87.42 kJ
 (c) -97.34 kJ (d) -89.9 kJ

26. ΔS_{surr} for an exothermic reaction is [2007]

- (a) always positive
 (b) always negative
 (c) zero
 (d) may be positive or negative.

27. Calculate change in internal energy if [2007]

$\Delta H = -92.2 \text{ kJ}$, $P = 40 \text{ atm}$ and $\Delta H = -1\text{L}$.

- (a) -42 kJ (b) -88 kJ
 (c) $+88 \text{ kJ}$ (d) $+42 \text{ kJ}$.

28. ΔH_{fusion} of a substance is 'x' and ΔH_{vap} is 'y', then $\Delta H_{\text{sublimation}}$ will be [2007]
- (a) $x + y$ (b) $x - y$
 (c) x/y (d) y/x .
29. For a reaction to be spontaneous at all temperatures [2008]
- (a) $\Delta G - \text{ve}$, $\Delta H + \text{ve}$ and $\Delta S + \text{ve}$
 (b) $\Delta G + \text{ve}$, $\Delta H - \text{ve}$ and $\Delta S + \text{ve}$
 (c) $\Delta G - \text{ve}$, $\Delta H - \text{ve}$ and $\Delta S - \text{ve}$
 (d) $\Delta G - \text{ve}$, $\Delta H - \text{ve}$ and $\Delta S + \text{ve}$
30. What will be the heat of formation of methane, if the heat of combustion of carbon is ' $-x$ ' kJ, heat of formation of water is ' $-y$ ' kJ and heat of combustion of methane is ' z ' kJ? [2008]
- (a) $(-x - y + z)$ kJ (b) $(-z - x + 2y)$ kJ
 (c) $(-x - 2y - z)$ kJ (d) $(-x - 2y + z)$ kJ
31. When a solid melts reversibly [2009]
- (a) H decreases (b) G increases
 (c) E decreases (d) S increases
32. 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 litre to a volume of 10 litres at 27°C . What is the maximum work done? [2009]
- (a) 47 kJ (b) 100 kJ
 (c) 0 (d) 34.465 kJ
33. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are -241 , -3800 and -3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene. [2009]
- (a) -111 kJ/mol (b) -121 kJ/mol
 (c) -118 kJ/mol (d) -128 kJ/mol
34. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The value of ΔE for this process is ($R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$) [2010]
- (a) 163.7 cal (b) zero
 (c) 138.1 cal (d) 9 litre atm
35. For the reaction, $2\text{Cl(g)} \rightarrow \text{Cl}_2\text{(g)}$, the signs of ΔH and ΔS respectively, are: [2010]
- (a) $+, -$ (b) $+, +$
 (c) $-, -$ (d) $-, +$
36. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C . If the work done during the process is 3 kJ, then final temperature of the gas is ($C_v = 20 \text{ J/K}$) [2010]
- (a) 100 K (b) 150 K
 (c) 195 K (d) 255 K
37. Enthalpy of formation of HF and HCl are -161 kJ and -92 kJ respectively. Which of the following statements is incorrect? [2010]
- (a) HCl is more stable than HF
 (b) HF and HCl are exothermic compounds
 (c) The affinity of fluorine to hydrogen is greater than the affinity of chlorine to hydrogen
 (d) HF is more stable than HCl
38. Which of the following processes takes place with decrease of entropy? [2011]
- (a) Solid \rightarrow gas
 (b) sugar + water \rightarrow solution
 (c) $\text{NH}_3\text{(g)} + \text{HCl(g)} \rightarrow \text{NH}_4\text{Cl(s)}$
 (d) $\text{A(g)} + \text{B(g)} \rightarrow$ mixture
39. Enthalpy of combustion of CH_4 , C_2H_6 and C_3H_8 are -210.8 , -368.4 and -526.2 k cal mol^{-1} respectively. Enthalpy of combustion of hexane can be predicted as [2011]
- (a) -840 k cal mol^{-1} (b) -684 k cal mol^{-1}
 (c) -1000 k cal mol^{-1} (d) none of these
40. AB , A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2 , AB and B_2 are in the ratio $1:1:0.5$ and enthalpy of formation of AB from A_2 and B_2 is -100 kJ mol^{-1} . What is the bond energy of A_2 ? [2012]
- (a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
 (c) 300 kJ mol^{-1} (d) 400 kJ mol^{-1}
41. Which of the following condition favours the reduction of a metal oxide to metal? [2012]
- (a) $\Delta H = +\text{ve}$, $T\Delta S = +\text{ve}$ at low temperature
 (b) $\Delta H = +\text{ve}$, $T\Delta S = -\text{ve}$ at any temperature
 (c) $\Delta H = -\text{ve}$, $T\Delta S = -\text{ve}$ at high temperature
 (d) $\Delta H = -\text{ve}$, $T\Delta S = +\text{ve}$ at any temperature
42. The ΔH_f° for CO_2 (g), CO(g) and $\text{H}_2\text{O(g)}$ are -393.5 , -110.5 and -241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction [2013]
- $$\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{CO(g)} + \text{H}_2\text{O(g)}$$
- (a) 524.1 (b) 41.2
 (c) -262.5 (d) -41.2

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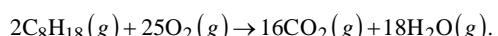
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- 43.** What is the enthalpy change for,

$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$ if heat of formation of $\text{H}_2\text{O}_2(l)$ and $\text{H}_2\text{O}(l)$ are -188 and -286 kJ/mol respectively? [2014]

- (a) -196 kJ/mol (b) $+948 \text{ kJ/mol}$
 (c) $+196 \text{ kJ/mol}$ (d) -948 kJ/mol

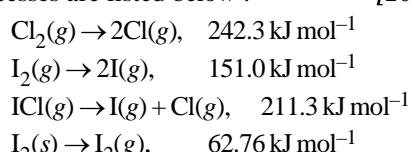
- 44.** Following reaction occurs in an automobile



The sign of ΔH , ΔS and ΔG would be [2015]

- (a) $+, -, +$ (b) $-, +, -$
 (c) $-+, +$ (d) $+, +, -$

- 45.** The enthalpy changes for the following processes are listed below : [2015]



Given that the standard states for iodine and chlorine are $\text{I}_2(s)$ and $\text{Cl}_2(g)$, the standard enthalpy of formation for $\text{ICl}(g)$ is:

- (a) $+16.8 \text{ kJ mol}^{-1}$ (b) $+244.8 \text{ kJ mol}^{-1}$
 (c) $-14.6 \text{ kJ mol}^{-1}$ (d) $-16.8 \text{ kJ mol}^{-1}$

- 46.** Choose the reaction in which ΔH is not equal to ΔU ? [2016]

- (a) $\text{C}_{(\text{graphite})} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
 (b) $\text{C}_{2\text{H}_{4(g)}} + \text{H}_{2(g)} \rightarrow \text{C}_{2\text{H}_{6(g)}}$
 (c) $2\text{C}_{(\text{graphite})} + \text{H}_{2(g)} \rightarrow \text{C}_{2\text{H}_{2(g)}}$
 (d) $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)}$

- 47.** The standard enthalpies of combustion of $\text{C}_{6\text{H}_{6(l)}}$, $\text{C}_{(\text{graphite})}$ and $\text{H}_{2(g)}$ are respectively $-3270 \text{ kJ mol}^{-1}$, -394 kJ mol^{-1} and -286 kJ mol^{-1} .

What is the standard enthalpy of formation of $\text{C}_{6\text{H}_{6(l)}}$ in kJ mol^{-1} ? [2016]

- (a) -48 (b) $+48$
 (c) -480 (d) $+480$

- 48.** The molar heat capacity of water at constant pressure is $75 \text{ JK}^{-1} \text{ mol}^{-1}$. When 1kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is [2017]

- (a) 6.6K (b) 1.2K
 (c) 2.4K (d) 4.8K

- 49.** The $\Delta_f H^\circ$ for $\text{CO}_2(g)$, $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ are -393.5 , -110.5 and -241.8 kJ/mol respectively, the standard enthalpy change (in kJ) for the reaction $\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$ is : [2017]
 (a) 524.1 (b) 41.2
 (c) -262.5 (d) -41.2

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 50-60) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.

- 50.** **Assertion :** Ionic reactions are not instantaneous.
Reason : Oppositely charged ions exert strong forces. [1997]

- 51.** **Assertion :** Entropy of ice is less than water.
Reason : Ice has cage like structure. [2000]

- 52.** **Assertion :** During an adiabatic process, heat energy is not exchanged between system and its surroundings.
Reason : The temperature of a gas increases when it undergoes an adiabatic expansion. [2002]

- 53.** **Assertion :** Mass and volume are extensive properties.
Reason : Mass / volume is also an extensive parameter. [2002]

- 54.** **Assertion :** Absolute values of internal energy of substances cannot be determined.
Reason : It is impossible to determine exact values of constituent energies of the substances. [2002]

- 55.** **Assertion :** The increase in internal energy (ΔE) for the vaporization of one mole of water at 1 atm and 373 K is zero.

- Reason :** For all isothermal processes, $\Delta E = 0$ [2003]

- 56.** **Assertion :** ΔH and ΔE are almost same for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
- Reason :** All reactants and products are gases. [2003]
- 57.** **Assertion :** Molar enthalpy of vaporisation of water is different from ethanol.
- Reason :** Water is more polar than ethanol. [2004]
- 58.** **Assertion :** Water in liquid state is more stable than ice at room temperature.
- Reason :** Water in liquid form has higher entropy than ice. [2006]
- 59.** **Assertion :** When a salt such as NaCl dissolves, the Na^+ and Cl^- ions leaving the crystal lattice acquire far greater freedom.
- Reason :** In thermodynamic terms, the formation of solution occurs with a favourable change in free energy, i.e., ΔH has a high positive value and $T\Delta S$ a low negative value. [2007]
- 60.** **Assertion :** For a reaction $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g); \Delta H > \Delta E$
- Reason :** Enthalpy change is always greater than internal energy change. [2008]
- Directions for (Qs.61-64) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- 61.** **Assertion :** For an isothermal reversible process $Q = -W$ i.e. work done by the system equals the heat absorbed by the system.
- Reason :** Enthalpy change (ΔH) is zero for isothermal process. [2011]
- 62.** **Assertion :** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
- Reason :** Entropy of the system increases with increase in temperature. [2012]
- 63.** **Assertion :** For an isothermal reversible process $Q = -W$ i.e. work done by the system equals the heat absorbed by the system. [2013]
- Reason :** Enthalpy change (ΔH) is zero for isothermal process.
- 64.** **Assertion :** For a reaction $2NH_3(g) \rightarrow N_2(g) + 3H_2(g); \Delta H > \Delta E$.
- Reason :** Enthalpy change is always greater than internal energy change. [2014]

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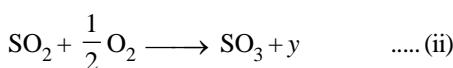
HINTS & SOLUTIONS

Type A : Multiple Choice Questions

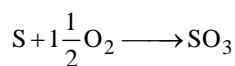
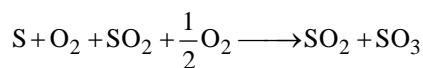
1. (c) Enthalpy change of a reaction does not depend upon different intermediate reactions.

$$\Delta H = H_p - H_r$$

2. (a) $S + O_2 \longrightarrow SO_2 + x$ (i)



Adding (i) and (ii), we have



So, heat of formation of SO_3 will be $(x + y)$.

3. (a) We know that,

Molar heat capacity at constant volume,

$C_v = \text{Specific heat at constant volume} \times \text{Mol. wt.}$

$$= 0.075 \times 40 = 3.0 \text{ cal}$$

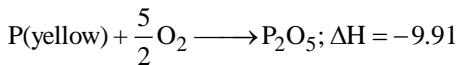
$$\therefore C_p - C_v = R$$

$$\text{or } C_p = R + C_v = 2 + 3 = 5$$

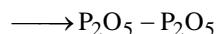
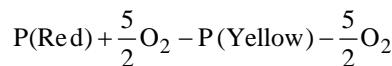
$$\text{Now, } \frac{C_p}{C_v} = \gamma; \therefore \gamma = \frac{5}{3} = 1.66$$

This value shows that the gas is monoatomic.

4. (d) $P(\text{red}) + \frac{5}{2}O_2 \longrightarrow P_2O_5; \Delta H = -8.78$



Subtracting



$$P(\text{Red}) - P(\text{Yellow}) = 0;$$

$$\Delta H = -8.78 + 9.91 = 1.113$$

$$P(\text{Red}) \rightarrow P(\text{Yellow}), \Delta H = 1.13$$

$$P(\text{Yellow}) \rightarrow P(\text{Red}), \Delta H = -1.13$$

5. (b) Formation of glucose will be the given by reaction taking place in reverse direction.



For production of 180 g of glucose, heat energy is 72 k cals.

So required heat for 1.6 g of glucose

$$= \frac{72}{180} \times 1.6 = 0.64 \text{ k cal}$$

6. (a) For a spontaneous process, the entropy should increase.

7. (d) Internal Energy of a gas consists of (i) kinetic energy of gas molecules (ii) potential energy of gas molecules due to intermolecular attractions. It does not include any other form of energy. So, potential energy due to gravitational pull is not included in it.

$$8. (c) W = - \int_{V_1}^{V_2} PdV = -P(V_2 - V_1)$$

$$W = -(1 \text{ atm}) (20 - 10) = -10 \text{ dm}^3 \text{ atm.}$$

$$= -10 \text{ dm}^3 \times \frac{8.314 \text{ J / K / mol}}{0.08206 \text{ dm}^3 / \text{K / mol}} = -1013 \text{ J}$$

According to Ist law of thermodynamics,

$$\Delta U = q + W = 800J + (-1013J) = -213J$$

9. (c) Work done in expansion of gas

$$= -2.303 nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 1 \times 2 \times 273 \log \frac{10}{1}$$

$$= -1257.43 \text{ cal.}$$

10. (c) $\Delta H = \Delta E + P\Delta V$ $\left[PV = RT; P\Delta V = R\Delta T \right]$

$$= \frac{3}{2}R \times 75 + R \times 75 = 75 \times \frac{5}{2}$$

$$= 372.56 \text{ cal}$$

11. (c) Enthalpy of neutralisation of CH_3COOH by $NaOH$ is -50.6 kJ/mol ; for strong acid and base this value is 55.9 kJ/mol . Heat evolved in the first case is less as some heat is used up in ionisation of CH_3COOH . So, ΔH for ionisation of $CH_3COOH = 55.9 - 50.6 = 5.3 \text{ kJ/mol}$.

12. (a) The internal energy of a substance increases with increase in temperature due to increase in rotational, translational and vibrational energy of the molecule.

13. (b) $\Delta E = -1228.2 \text{ k cal} = -1228.2 \times 10^3 \text{ cal}$

$$\begin{aligned}\Delta H &= \Delta E + \Delta nRT \\ &= -1228.2 \times 10^3 + (-2)(2)(298) \\ &= -1229392 \text{ cal} \\ &= -1229.392 \text{ kcal}\end{aligned}$$

14. (c) For isothermal reversible process,

$$\begin{aligned}W_{\text{rev}} &= -2.303 nRT \log \frac{P_1}{P_2} \\ &= -2.303 \times 2 \times 8.314 \times 373 \log \frac{10}{25} \\ &= +5684.1 \text{ J} = 5.684 \text{ kJ}\end{aligned}$$

15. (c) Enthalpy of reaction (ΔH) = $H_p - H_R$
For exothermic reactions, $H_p < H_R$
 $\therefore \Delta H$ is negative

16. (a) The chemical reaction between strong base and strong acid is a neutralisation reaction between H^+ ion and OH^- ion.



One mole of H^+ and one mole of OH^- give 57 kJ. When 0.5 moles of H^+ (from HNO_3) reacts with 0.2 mole of OH^- (from $NaOH$), 0.2 mole of H^+ is neutralised by 0.2 mole of OH^- and 0.3 mole of H^+ remains unreacted.



$$\text{Heat evolved will be } = \frac{57 \times 0.2}{1} = 11.4 \text{ kJ}$$

17. (d) Heat produced (Q) = $mC\Delta T$

$$= 1 \times 1.23 \times 6.12 \text{ kJ.}$$

Molecule weight of $NH_4NO_3 = 80 \text{ g}$

$$\text{Heat produced per mole} = 80 \times 1.23 \times 6.12 = 602 \text{ kJ/mol}$$

18. (c) Entropy (ΔS) of a reaction is positive if the products are in more random state as compared to reactants.

Order of randomness : Gas > Liquid > Solid

- (i) In (b), product $NaCl$ (solid) has lesser entropy as compared to $NaCl$ (aq) (Na^+ and Cl^-) in reactant.

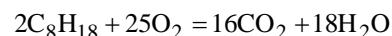
- (ii) In (a), product (solid) has lesser entropy as compared to reactants.

- (iii) In (d), both reactants and products are in gaseous state, but number of moles of products are decreasing.

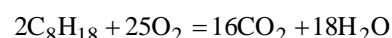
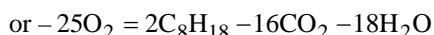
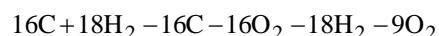
- (iv) In (c), products are in liquid state hence high entropy than reactant which is present in solid state.

19. (d) The order of heat of vaporisation or boiling point of the hydrides of VA group depend upon their molecular weight. Anomalous behaviour of NH_3 is due to H-bonding present in NH_3 . Thus the correct order is $NH_3 > AsH_3 > PH_3$

20. (c) $C + O_2 = CO_2 \quad \Delta H = -490 \text{ kJ/mol}$ (i)



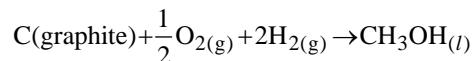
The required reaction can be obtained by $2 \times (\text{iii}) - 16(\text{i}) - 18(\text{ii})$



$$[\Delta H = 2 \times 160 - 16 \times -490 - 18 \times -240]$$

$\Delta H = -11840 \text{ J} = -11.840 \text{ kJ}$ for 2 moles of octane. Energy released for 6 moles of octane $= -11.840 \times 3 = -35.5 \text{ kJ}$

21. (b) Heat of formation is defined as the heat exchange when one mole of a compound is formed from its constituent elements at STP. In case of allotropes, most stable allotrope is taken into account. Among graphite and diamond, graphite is stable. Hence, heat of formation of CH_3OH is represented by the eqn.



22. (a) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

In bomb calorimeter, there is no expansion in volume, so, work done will be zero. This reaction is exothermic. So, some heat will be evolved which will result in lowering of internal energy. Hence,

$$\Delta U < 0 \text{ & } w = 0$$

- 36. (b)** Since the gas expands adiabatically (*i.e.*, no change in enthalpy) so the heat is totally converted into work.

For the gas, $C_V = 20 \text{ J/K}$. Thus, 20 J of heat is required for 1° change in temperature of the gas.

Heat change involved during the process *i.e.*, work done = 3 kJ = 3000 J.

$$\text{Change in temperature} = \frac{3000}{20} \text{ K} = 150 \text{ K}$$

Initial temperature = 300 K

Since, the gas expands so the temperature decreases and thus final temperature is

$$300 - 150 = 150 \text{ K}$$

- 37. (a)** More the enthalpy of formation less will be the stability of the compound.

- 38. (c)**

$$\Delta H_c(\text{C}_2\text{H}_6) - \Delta H_c(\text{CH}_4) \\ = -368.2 - (-210.8) = -157.4$$

$$\Delta H_c(\text{C}_3\text{H}_8) - \Delta H_c(\text{C}_2\text{H}_6) \\ = -526.2 - (-368.4) = -157.8$$

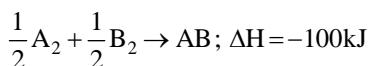
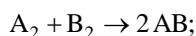
Thus, average

$$\Delta H_c(-\text{CH}_2) = -\frac{157.4 + 157.8}{2} \\ = -157.6 \text{ kcal mol}^{-1}$$

Then,

$$\Delta H_c(\text{C}_6\text{H}_{14}) = \Delta H_c(\text{C}_3\text{H}_8) + 3\Delta H_c(-\text{CH}_2) \\ = -526.2 + 3(-157.6) = -999 \text{ k cal mol}^{-1}$$

- 40. (d)** Let bond energy of A_2 be x then bond energy of AB is also x and bond energy of B_2 is $x/2$.
Enthalpy of formation of AB is -100 kJ/mole :



$$\text{or } -100 = \left(\frac{1x}{2} + \frac{x}{4} \right) - x$$

$$\therefore -100 = \frac{2x + x - 4x}{4} \quad \therefore x = 400 \text{ kJ mol}^{-1}$$

- 41. (d)**

$$\text{42. (b)} \quad \Delta H = H^\circ_f(\text{products}) - H^\circ_f(\text{reactants}) \\ = -110.5 + (-241.8) - (-393.5 + 0) = 41.2 \text{ kJ}$$

- 43. (a)** $2\text{H}_2\text{O}_2(l) \xrightarrow{\text{3/4 300 K}} 2\text{H}_2\text{O}(l) + \text{O}_2(g) \quad \Delta H = ?$

$$\Delta H = [2 \times \Delta H_f \text{ of } \text{H}_2\text{O}(l) + (\Delta H_f \text{ of } \text{O}_2) \\ - (2 \times \Delta H_f \text{ of } \text{H}_2\text{O}_2(l))] \\ = [(2 \times -286) + (0) - (2 \times -188)] \\ = [-572 + 376] = -196 \text{ kJ/mol}$$

- 44. (b)** For combustion reaction, ΔH is negative, $\Delta n = (16+18) - (25+2) = +7$, so ΔS is +ve, reaction is spontaneous, hence ΔG is -ve.

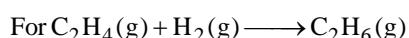
$$\text{45. (a)} \quad \text{I}_2(s) + \text{Cl}_2(g) \longrightarrow 2\text{ICl}(g) \\ \Delta_f H = [\Delta H(\text{I}_2(s) \rightarrow \text{I}_2(g)) + \Delta H_{\text{I}-\text{I}} \\ + \Delta H_{\text{Cl}-\text{Cl}}] - [\Delta H_{\text{I}-\text{Cl}}] \\ = 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46 \\ \Delta_f H^\circ(\text{ICl}) = \frac{33.46}{2} = 16.73 \text{ kJ/mol}$$

- 46. (b)** ΔH is given by

$$\Delta H = \Delta U + \Delta n_g RT$$

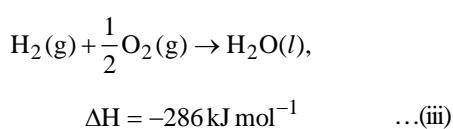
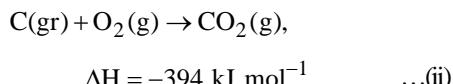
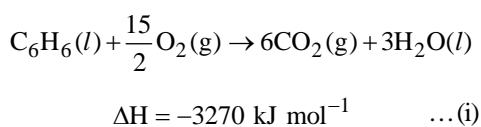
When $\Delta n_g = 0$, $\Delta H = \Delta U$

When $\Delta n_g \neq 0$, $\Delta H \neq \Delta U$



$$\Delta n_g = 1 - 2 = -1$$

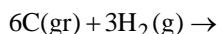
- 47. (b)** We are given,



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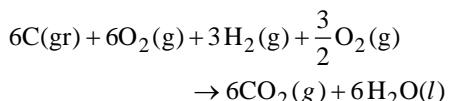
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Formation of C_6H_6 

$$C_6H_6(l); \Delta H = ? \quad \dots \text{(iv)}$$

By multiplying eq. (ii) with 6 and eq. (iii) with 3 and adding we get,

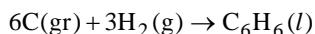


$$\Delta H = 6(-394) + 3(-286)$$

$$= (-2364) + (-858)$$

$$= -3222 \text{ kJ/mol}$$

Now, by subtracting eq. (i) from (v) we get



$$\Delta H = -3222 - (-3270) = +48 \text{ kJ/mol}$$

48. (c) Given $C_p = 75 \text{ JK}^{-1} \text{ mol}^{-1}$

$$n = \frac{100}{18} \text{ mole}, Q = 1000 \text{ J} \quad \Delta T = ?$$

$$Q = nC_p \Delta T \Rightarrow \Delta T = \frac{1000 \times 18}{100 \times 75} = 2.4 \text{ K}$$

49. (b) $\Delta H = \sum [\Delta H_f^\circ \text{ products}]$

$$- \sum [\Delta H_f^\circ \text{ reactants}]$$

$$\Delta H^\circ = [\Delta H_f^\circ (\text{CO})(\text{g}) + \Delta H_f^\circ (\text{H}_2\text{O})(\text{g})] -$$

$$[\Delta H_f^\circ (\text{CO}_2)(\text{g}) + \Delta H_f^\circ (\text{H}_2)(\text{g})]$$

$$= [-110.5 + (-241.8)] - [-393.5 + 0]$$

$$= 41.2 \text{ kJ}$$

Type B : Assertion Reason Questions

50. (e) Ionic reactions are spontaneous as oppositely charged ions exert stronger forces and combine immediately.

51. (b) Entropy is defined as the extent of randomness in a system. When a substance is heated, its randomness and hence entropy increases. Thus entropy of ice is less than water because of lesser molecular motion in ice. It is also true that ice has an open cage like structure.

52. (c) The temperature of a gas decreases when it undergoes adiabatic expansion.

53. (c) The properties of a system which depend upon quantity of matter contained in it are called extensive properties, e.g., mass, volume, heat capacity etc. But mass / volume = density is an intensive property as density does not depend upon quantity of matter in a system.

54. (a) Absolute values of internal energy of substance can not be determined because it is impossible to determine exact values of constituent energies of the substances.

55. (a) For all isothermal process change in internal energy is zero.

$$56. (c) \Delta H = \Delta E + (RT)^{\Delta n}$$

If there is no change in the moles of reactants (gaseous) and products (gaseous) $\Delta n = 0$

$$\therefore \Delta H = \Delta E$$

57. (b) Molar heat of vaporisation of water is more than ethanol because of presence of stronger H-bonding in water as compared to ethanol. It is also true that water is more polar than ethanol.

58. (a) At room temperature water is more stable because ice will tend to melt at room temperature. So, A is true. But water will have larger entropy than ice because ice absorbs heat to be converted into water.

$$\Delta S = \frac{\Delta H}{T}$$

We know that greater the entropy, greater the stability. Hence, water is more stable than ice. Both A and R is true and R explains A.

59. (c) In NaCl crystal Na^+ and Cl^- are strongly bonded due to electrostatic attraction. As it is dissolved in solvent, Na^+ and Cl^- acquire greater freedom. In thermodynamic terms formation of solution occurs with a favourable change in ΔG . $T\Delta S$ is largely $-ve$ which overcomes the small $+ve$ value of ΔH . Thus ΔG is negative for dissolution of salt. Hence assertion is true but reason is false.

- 60. (c)** For given reaction $\Delta H > \Delta E$ because $\{\Delta H = \Delta E + \Delta nRT\}$. In this reaction $\Delta n_{(g)}$ is $[(3+1)-2=+2]$ so $\Delta H > \Delta E$. Thus, assertion is true.
In some cases, the enthalpy change may be less than internal energy change (in these cases $\Delta n_{(g)}$ is negative), so the reason is false.
- 61. (b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).
 \therefore According to first law of thermodynamics
 $\because Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)
 If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.
- 62. (b)** The factor $T\Delta S$ increases with increase in temperature.
- 63. (b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).
 \therefore According to first law of thermodynamics
 $\because Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)
 If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.
- 64. (c)** Assertion is true but reason is false.
 $\Delta H = \Delta E + n_g RT$
 $\Delta n_g = (1+3)-2 \quad \Delta H > \Delta E$.
 If the value of Δn_g is less than one then $\Delta H < \Delta E$.

Chapter

7

Equilibrium

TYPE A : MULTIPLE CHOICE QUESTIONS

- 1.** In the reaction $I_2 + I^- \longrightarrow I_3^-$, the Lewis base is : **[1997]**

 - I_3^-
 - I_2
 - I^-
 - none of the above

2. The equilibrium constant for the following reaction will be : $3A + 2B \longrightarrow C$ **[1997]**

 - $\frac{[3A][2B]}{[C]}$
 - $\frac{[C]}{[3A][2B]}$
 - $\frac{[C]}{[A]^2[B]^2}$
 - $\frac{[C]}{[A]^3[B]^2}$

3. Which is Lewis acid ? **[1998]**

 - C_2H_5OH
 - BF_3
 - Cl^-
 - NH_3

4. The pH value of ordinary water is: **[1998]**

 - 7
 - 6.5
 - 5.3
 - 7.8

5. The value of K_p for the reaction:

$$2H_2S_{(g)} = 2H_{2(g)} + S_{2(g)}$$

is 1.2×10^{-2} at $1065^\circ C$. The value for K_C is: **[1999]**

 - $<1.2 \times 10^{-2}$
 - $>1.2 \times 10^{-2}$
 - 1.2×10^{-2}
 - 0.12×10^{-2}

6. One mole of CH_3COOH and one mole of C_2H_5OH reacts to produce $\frac{2}{3}$ mole of $CH_3COOC_2H_5$. The equilibrium constant is : **[1999]**

 - 2
 - +2
 - 4
 - +4

7. The pH of a solution having the H^+ ion concentration of 1×10^{-4} ions/litre is **[1999]**

 - 2
 - 3
 - 4
 - 5

8. D was 1.5 times that of A , but the equilibrium concentration of A and B are found to be equal. The equilibrium constant for the reaction is: **[2000]**

 - 4
 - 8
 - 12
 - 16

9. pK_a value of four acids are given below. The strongest acid is: **[2000]**

 - 4.0
 - 3.5
 - 2.5
 - 2

10. Ostwald's dilution law is applicable on: **[2000]**

 - Strong electrolytes
 - Weak electrolytes
 - Both strong and weak electrolytes
 - None of them

11. The pH value of N/10 NaOH is : **[2001]**

 - 9
 - 10
 - 12
 - 13

12. A solution having hydrogen ion concentration is 0.0005 g eqvt./litre, its pOH is: **[2001]**

 - 8.2798
 - 10.6990
 - 12.7854
 - 13.3344

13. The pH of solution containing 0.10 M sodium acetate and 0.03 M acetic acid is **[2002]**

$$(pK_a \text{ for } CH_3COOH = 4.57)$$
 - 4.09
 - 6.09
 - 5.09
 - 7.09

14. The solubility of $CuBr$ is 2×10^{-4} mol/L at $25^\circ C$. The K_{sp} value of $CuBr$ is **[2002]**

 - $4 \times 10^{-8} \text{ mol}^2 L^{-2}$
 - $4 \times 10^{-4} \text{ mol}^2 L^{-2}$
 - $4 \times 10^{-11} \text{ mol}^2 L^{-2}$
 - $4 \times 10^{-15} \text{ mol}^2 L^{-2}$

15. At $80^\circ C$, distilled water (H_3O^+) has concentration equal to 1×10^{-6} mole/litre. The value of K_w , at this temperature will be **[2002]**

 - 1×10^{-6}
 - 1×10^{-12}
 - 1×10^{-9}
 - 1×10^{-15}

16. Which one of the following is NOT a buffer solution? **[2003]**

 - $0.8 \text{ M } H_2S + 0.8 \text{ M } KHS$
 - $2MC_6H_5NH_2 + 2MC_6H_5N^+H_3Br^-$
 - $3MH_2CO_3 + 3MKHCO_3$
 - $0.05 \text{ M } KClO_4 + 0.05 \text{ M } HClO_4$

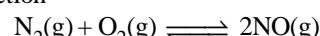
17. In which of the following acid-base titration, pH is greater than 8 at equivalence point. [2003]
- Acetic acid versus ammonia
 - Acetic acid versus sodium hydroxide
 - Hydrochloric acid versus ammonia
 - Hydrochloric acid versus sodium hydroxide
18. What is the pH of 0.01 M glycine solution ? For glycine, $K_{a_1} = 4.5 \times 10^{-3}$ and
- $$K_{a_2} = 1.7 \times 10^{-10} \text{ at } 298 \text{ K?} \quad [2004]$$
- 3.0
 - 10.0
 - 6.1
 - 7.1
19. Of the following which change will shift the reaction towards the product?
- $$I_2(g) \rightleftharpoons 2I(g), \Delta H_r^0 (298 \text{ K}) = +150 \text{ kJ}$$
- Increase in concentration of I_2 [2004]
 - Decrease in concentration of I_2
 - Increase in temperature
 - Increase in total pressure
20. For the equilibrium
- $$H_2O(l) \rightleftharpoons H_2O(g) \text{ at } 1 \text{ atm and } 298 \text{ K:} \quad [2004]$$
- standard free energy change is equal to zero ($\Delta G^\circ = 0$)
 - free energy change is less than zero ($\Delta G < 0$)
 - standard free energy change is less than zero ($\Delta G^\circ < 0$)
 - standard free energy change is greater than zero ($\Delta G^\circ > 0$)
21. When 10 mL of 0.1 M acetic acid ($pK_a = 5.0$), is titrated against 10 mL of 0.1 M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at pH : [2005]
- 5.0
 - 6.0
 - 7.0
 - 9.0
22. For reaction, $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$; K_c at 427°C is $3 \times 10^{-6} \text{ L mol}^{-1}$. The value of K_p is nearly : [2005]
- 7.50×10^{-5}
 - 2.50×10^{-5}
 - 2.50×10^{-4}
 - 1.75×10^{-4}
23. 40 mL of 0.1 M ammonia solution is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution is 4.74). [2006]
- 4.74
 - 2.26
 - 9.26
 - 5.00
24. During titration of acetic acid with aq. NaOH solution, the neutralisation graph has a vertical line. This line indicates [2007]
-
- (a) alkaline nature of equivalence
(b) acidic nature of equivalence
(c) neutral nature of equivalence
(d) depends on experimental proceeding.
25. The pH of the solution obtained on neutralisation of 40 mL 0.1 M NaOH with 40 mL 0.1 M CH_3COOH is [2007]
- 7
 - 8
 - 6
 - 3
26. What is the pH value of 0.1 M H_2SO_4 ? [2008]
- 0
 - 0.213
 - 2
 - 0.3010
27. In which of the following reactions, the concentration of the product is higher than the concentration of reactant at equilibrium ? (K = equilibrium constant) [2008]
- $A \rightleftharpoons B; K = 0.001$
 - $M \rightleftharpoons N; K = 10$
 - $X \rightleftharpoons Y; K = 0.005$
 - $R \rightleftharpoons P; K = 0.01$
28. On adding 0.1 M solution each of $[Ag^+]$, $[Ba^{2+}]$, $[Ca^{2+}]$ in a Na_2SO_4 solution, species first precipitated is [2008]
 $[K_{sp} BaSO_4 = 10^{-11}, K_{sp} CaSO_4 = 10^{-6}, K_{sp} Ag_2SO_4 = 10^{-5}]$
- Ag_2SO_4
 - $BaSO_4$
 - $CaSO_4$
 - All of these
29. A weak acid, HA is found to be 10% ionized in 0.01 M aqueous solution. Calculate the pH of a solution which is 0.1 M in HA and 0.05 M in NaA . [2009]
- 5.365
 - 6.355
 - 3.653
 - 6.593

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- 30.** The solubility of PbF_2 in water at 25°C is $\sim 10^{-3}$ M. What is its solubility in 0.05 M NaF solution? Assume the latter to be fully ionised. [2009]
- (a) $1.6 \times 10^{-6}\text{ M}$ (b) $1.2 \times 10^{-6}\text{ M}$
 (c) $1.2 \times 10^{-5}\text{ M}$ (d) $1.6 \times 10^{-4}\text{ M}$

- 31.** Air containing 79% of nitrogen and 21% of oxygen by volume is heated at 2200 K and 1 atm until equilibrium is established according to the reaction



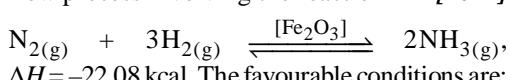
If the K_p of the reaction is 1.1×10^{-3} , calculate the amount of nitric oxide produced in terms of volume percent. [2009]

- (a) 1.33 (b) 1.12
 (c) 1.02 (d) 1.44

- 32.** Solubility product of a salt AB is 1×10^{-8} in a solution in which the concentration of A^+ ions is 10^{-3} M . The salt will precipitate when the concentration of B^- ions is kept [2010]

- (a) between 10^{-8} M to 10^{-7} M
 (b) between 10^{-7} M to 10^{-8} M
 (c) $> 10^{-5}\text{ M}$
 (d) $< 10^{-8}\text{ M}$

- 33.** In the manufacture of NH_3 in Haber's continuous flow process involving the reaction [2011]



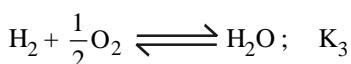
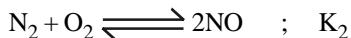
The favourable conditions are:

(a) High pressure and low temperature due to low activation energy (E_a).
 (b) Low pressure and low temperature due to low E_a .
 (c) High pressure and elevated optimum temperature due to high E_a .
 (d) None of these

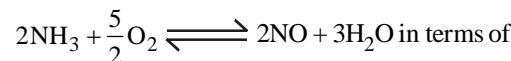
- 34.** In which of the following cases, pH is greater than 7? [2011]

- (a) 50 ml of 0.1 M HCl + 50 ml of 0.1 M NaCl
 (b) 50 ml of $0.1\text{ M H}_2\text{SO}_4$ + 50 ml of 0.2 M NaOH
 (c) 50 ml of $0.1\text{ M CH}_3\text{COOH}$ + 50 ml of 0.1 M KOH
 (d) 50 ml of 0.1 M HNO_3 + 50 ml of 0.1 M NH_3

- 35.** The following equilibria are given: [2012]



The equilibrium constant of the reaction

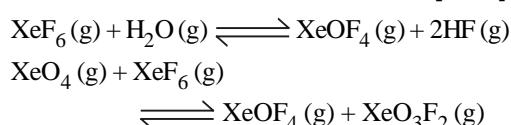


K_1 , K_2 and K_3 is

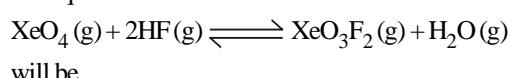
- (a) $\frac{K_1 K_2}{K_3}$ (b) $\frac{K_1 K_3^2}{K_2}$
 (c) $\frac{K_2 K_3^3}{K_1}$ (d) $K_1 K_2 K_3$

- 36.** The pH of blood does not appreciably change by a small addition of acid or a base because blood
- (a) contains serum protein which acts as buffer
 (b) contains iron as a part of the molecule
 (c) can be easily coagulated
 (d) is body fluid [2012]

- 37.** If K_1 and K_2 are respective equilibrium constants for the two reactions [2013]

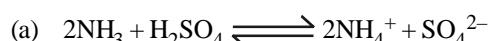


the equilibrium constant for the reaction



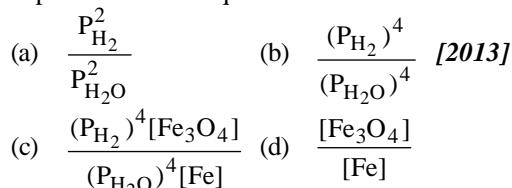
- (a) $\frac{K_1}{K_2^2}$ (b) $K_1 K_2$
 (c) $\frac{K_1}{K_2}$ (d) $\frac{K_2}{K_1}$

- 38.** Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition? [2013]



- (b) $\text{NH}_3 + \text{CH}_3\text{COOH} \rightleftharpoons \text{NH}_4^+ + \text{CH}_3\text{COO}^-$
 (c) $\text{H}_2\text{O} + \text{CH}_3\text{COOH} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$
 (d) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+} + 4\text{H}_2\text{O}$

- 39.** Steam reacts with iron at high temperature to give hydrogen gas and Fe_3O_4 (s). The correct expression for the equilibrium constant is



- 40.** Why only As^{3+} gets precipitated as As_2S_3 and not Zn^{2+} as ZnS when H_2S is passed through an acidic solution containing As^{3+} and Zn^{2+} ?

- (a) Solubility product of As_2S_3 is less than that of ZnS [2013]
 (b) Enough As^{3+} are present in acidic medium
 (c) Zinc salt does not ionise in acidic medium
 (d) Solubility product changes in presence of an acid

- 41.** K_{sp} of M(OH)_2 is 3.2×10^{-11} . The pH of saturated solution in water is [2014]

- (a) 3.40 (b) 10.30
 (c) 10.60 (d) 3.70

- 42.** Which of the following equilibria will shift to right side on increasing the temperature? [2014]

- (a) $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
 (b) $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$
 (c) $\text{H}_2\text{O(g)} \rightleftharpoons \text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$
 (d) $4\text{HCl(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{O(g)} + 2\text{Cl}_2\text{(g)}$

- 43.** The reaction $2\text{A(g)} + \text{B(g)} \rightleftharpoons 3\text{C(g)} + \text{D(g)}$ is began with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression [2015]

- (a) $[(0.75)^3 (0.25)] \div [(0.75)^2 (0.25)]$
 (b) $[(0.75)^3 (0.25)] \div [(1.00)^2 (1.00)]$
 (c) $[(0.75)^3 (0.25)] \div [(0.50)^2 (0.75)]$
 (d) $[(0.75)^3 (0.25)] \div [(0.50)^2 (0.25)]$

- 44.** The solubility product (K_{sp}) of the following compounds are given at 25°C.

Compound	K_{sp}
AgCl	1.1×10^{-10}
AgI	1.0×10^{-16}
PbCrO_4	4.0×10^{-14}
Ag_2CO_3	8.0×10^{-12}

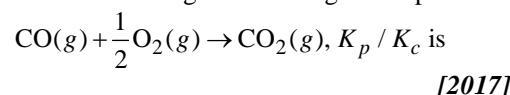
The most soluble and least soluble compounds are respectively. [2016]

- (a) AgCl and PbCrO_4
 (b) AgI and Ag_2CO_3
 (c) AgCl and Ag_2CO_3
 (d) Ag_2CO_3 and AgI

- 45.** Two equilibria, $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$ and $\text{AB} + \text{B}^- \rightleftharpoons \text{AB}_2^-$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. The ratio of $[\text{A}^+]$ to $[\text{AB}_2^-]$ in the solution is [2016]

- (a) directly proportional to $[\text{B}^-]$
 (b) inversely proportional to $[\text{B}^-]$
 (c) directly proportional to the square of $[\text{B}^-]$
 (d) inversely proportional to the square of $[\text{B}^-]$

- 46.** For the following reaction in gaseous phase



- (a) $(RT)^{1/2}$ (b) $(RT)^{-1/2}$
 (c) (RT) (d) $(RT)^{-1}$

- 47.** At 25°C, the solubility product of Mg(OH)_2 is 1.0×10^{-11} . At which pH, will Mg^{2+} ions start precipitating in the form of Mg(OH)_2 from a solution of 0.001 M Mg^{2+} ions? [2017]

- (a) 9 (b) 10
 (c) 11 (d) 8

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 48-53) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.

- 48. Assertion:** The aqueous solution of FeCl_3 is basic in nature.

Reason: FeCl_3 hydrolyses in water. [1998]

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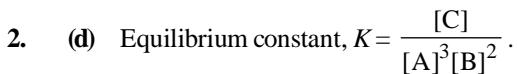
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- 49.** **Assertion :** Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl
Reason : K_{sp} of AgCl < K_{sp} of AgBr [2004]
- 50.** **Assertion :** Addition of NH_4OH to an aqueous solution of BaCl_2 in the presence of NH_4Cl (excess) precipitates $\text{Ba}(\text{OH})_2$.
Reason : $\text{Ba}(\text{OH})_2$ is insoluble in water [2005]
- 51.** **Assertion :** Mixture of CH_3COOH and $\text{CH}_3\text{COONH}_4$ is an example of acidic buffer.
Reason : Acidic buffer contains equimolar mixture of a weak acid and its salt with weak base. [2007]
- 52.** **Assertion :** The equilibrium constant is fixed and a characteristic for any given chemical reaction at a specified temperature.
Reason : The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants. [2007]
- 53.** **Assertion :** For reaction
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- Unit of $K_C = \text{L}^2\text{mol}^{-2}$
- Reason :** For the reaction
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- Equilibrium constant, $K_C = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ [2008]
- Directions for (Qs.54-59) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- 54.** **Assertion :** In a titration of weak acid and NaOH, the pH at half equivalence point is pK_a .
Reason : At half equivalence point, it forms an acidic buffer and the buffer capacity is maximum where $[\text{acid}] = [\text{salt}]$ [2009]
- 55.** **Assertion :** $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is a stronger acid than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$.
Reason : Size of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is smaller than $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ and possesses more effective nuclear charge. [2008, 2010]
- 56.** **Assertion :** Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.
Reason : If Q_c (reaction quotient) < K_C (equilibrium constant) reaction moves in direction of reactants. [2011]
- 57.** **Assertion :** KOH is more soluble in water than NaOH.
Reason : NaOH is a stronger base than KOH. [2011]
- 58.** **Assertion :** Buffer system of carbonic acid and sodium bicarbonate is used for the precipitation of hydroxides of third group elements. [2015]
Reason : It maintains the pH to a constant value, about 7.4.
- 59.** **Assertion :** Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl.
Reason : K_{sp} of AgCl > K_{sp} of AgBr. [2016]

HINTS & SOLUTIONS

Type A : Multiple Choice Questions

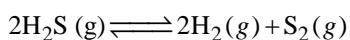
1. (c) Here I^- is Lewis base as it is giving electron to I_2 molecule.



3. (b) In BF_3 , B is electron deficient because it has incomplete octet and thus can accept electron pair (Lewis acid).

4. (c) pH value of ordinary water is about 5.3 because some CO_2 from atmosphere dissolves in pure water to form H_2CO_3 (carbonic acid), thus making water slightly acidic.

5. (a) For the given reaction,

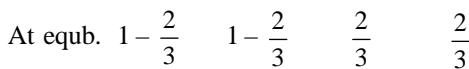
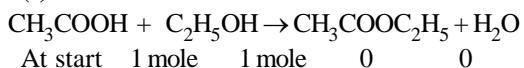


$$\Delta n = 3 - 2 = 1$$

$$K_c = \frac{K_p}{(RT)^n} = \frac{1.2 \times 10^{-2}}{(RT)^1}$$

$$\therefore K_c < K_p \text{ or } K_c < 1.2 \times 10^{-2}$$

6. (d)



Let the total volume = V L

$$\therefore [CH_3OOH] = \frac{1}{3}V \text{ mol/L}$$

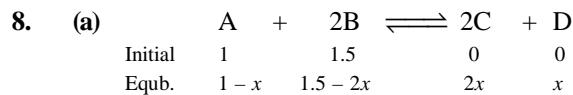
$$[C_2H_5OH] = \frac{1}{3}V \text{ mol/L}$$

$$[CH_3COOC_2H_5] = \frac{2}{3}V \text{ mol/L}$$

$$[H_2O] = \frac{2}{3}V \text{ mol/L}$$

$$\therefore K = \frac{\frac{2}{3}V \times \frac{2}{3}V}{\frac{1}{3}V \times \frac{1}{3}V} = 4$$

7. (c) $pH = -\log [H^+]$
 $= -\log 10^{-4}$
 $= -(-4) \log 10$
 $= 4$



At equilibrium, $[A] = [B]$

$$1 - x = 1.5 - 2x$$

$$x = 0.5$$

$$\therefore K_c = \frac{[C]^2[D]}{[A][B]^2}$$

$$= \frac{(2x)^2(x)}{(1-x)(1.5-2x)^2}$$

$$= \frac{1 \times 1 \times 0.5}{0.5 \times 0.5 \times 0.5} = 4$$

9. (d) Strength of acid $\propto K_a$

or $\propto \frac{1}{pK_a}$

Hence acid with lowest pK_a value (2.0) will be strongest.

10. (b) Ostwald's dilution law is applicable for weak electrolytes because strong electrolytes are 100% ionised at all concentrations while ionisation of weak electrolytes increases with increase in dilution.

11. (d) $0.1 \text{ N NaOH} \rightleftharpoons Na^+ + OH^-$

Normality of NaOH = Molarity of NaOH

$$= \frac{M}{10}$$

$$[OH^-] = 10^{-1}$$

$$[H^+] [OH^-] = 10^{-14}$$

$$[H^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

$$\therefore pH = -\log 10^{-13}$$

$$\therefore pH = 13$$

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12. (b) $\text{pH} = -\log [\text{H}^+] = -\log [5 \times 10^{-4}]$
 $= 4 - \log 5 = 4 - [\log 10 - \log 2]$
 $= 3 + \log 2 = 3.3010$

- pOH = 14 - pH = 14 - 3.3 = 10.7.
13. (c) According to Henderson equation, pH of acidic buffer is given as

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log \frac{\text{Salt}}{\text{Acid}} \\ &= 4.57 + \log \frac{0.10}{0.03} \\ &= 4.57 + [\log 10 - \log 3] \\ &= 4.57 + \log 3.33 \\ &= 4.57 + 0.52 = 5.09\end{aligned}$$

14. (a) $\text{CuBr} \rightleftharpoons \text{Cu}^+ + \text{Br}^-$
[CuBr will be fully dissociated]

$$\therefore [\text{Cu}^+] = 2 \times 10^{-4}$$

$$\text{and } [\text{Br}^-] = 2 \times 10^{-4}$$

$$\begin{aligned}[\text{Cu}^+] [\text{Br}^-] &= 2 \times 10^{-4} \times 2 \times 10^{-4} \\ &= 4 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}\end{aligned}$$

15. (b) $[\text{H}_3\text{O}^+] = [\text{H}^+] = 10^{-6}$
 $K_w = [\text{H}^+] [\text{OH}^-]$
In pure water, $[\text{H}^+] = [\text{OH}^-]$
So, $[\text{OH}^-] = [\text{H}^+] = [\text{H}_3\text{O}^+] = 10^{-6}$
 $K_w = [10^{-6}] [10^{-6}] = 10^{-12}$.
Remember that K_w increases with increase in temperature.

16. (d) Buffer solution contains weak base + salt of weak base with strong acid or weak acid + salt of weak acid with strong base.
In option (d) the acid used is HClO_4 which is strong acid and KClO_4 is salt of this acid with strong base. So it is not an example of buffer solution.

17. (b) Acetic acid is a weak acid and sodium hydroxide is strong base. Salt of the two will hydrolyse to give basic solution. So at neutral point pH of the solution will be greater than 8.

18. (d) For glycine solution ;

$$\begin{aligned}K &= K_{a1} \times K_{a2} \\ &= 4.5 \times 10^{-13} \times 1.7 \times 10^{-10} \\ &= 7.65 \times 10^{-13}\end{aligned}$$

$$\begin{aligned}[\text{H}^+] &= \sqrt{K_c} \\ &= \sqrt{7.65 \times 10^{-13} \times 0.01} = 8.7 \times 10^{-8}\end{aligned}$$

$$\text{Hence, pH} = -\log [\text{H}^+]$$

$$\begin{aligned}&= -\log [8.7 \times 10^{-8}] \\ &= -(\log 10^{-8} + \log 8.7) \\ &= 8 - 0.93 = 7.07 \approx 7.1\end{aligned}$$

19. (c) The given reaction is endothermic. If we increase the temp. forward reaction will be promoted so that heat is absorbed to decrease the temp.

20. (b) The process, $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(g)$, is an endothermic process, ($\Delta H = +\text{ve}$) and entropy increases during this change ($\Delta S = +\text{ve}$). Hence this process is spontaneous at all temperatures above 0°C ($T\Delta S > \Delta H$, so ΔG is negative, $\Delta G = \Delta H - T\Delta S$). Thus free energy change (ΔG) will be less than zero (negative) at 1 atm and 298 K.

21. (c) $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O}$
For salt of weak base & weak acid

$$\begin{aligned}\text{pH} &= -\frac{1}{2} [\log K_a + \log K_w - \log K_b] \\ &= -\frac{1}{2} [-pK_a + \log K_w + pK_b] \\ &= -\frac{1}{2} [-5 + \log 10^{-14} + 5] \\ &= -\frac{1}{2} [-5 - 14 + 5] \\ &= 7\end{aligned}$$

22. (d) $K_p = K_c [\text{RT}]^{\Delta n}$
 $= 3 \times 10^{-6} \times (0.082 \times 700)^1$
 $= 3 \times 10^{-6} \times 0.082 \times 7 \times 10^2 = 1.75 \times 10^{-4}$

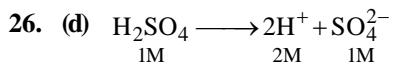
23. (c) $\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$
 $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$pOH = 4.74 + \log \frac{0.1/60}{0.1/60}$$

$$pOH = 4.74 + 0 = 4.74$$

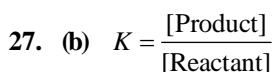
$$pH = 14 - 4.74 = 9.26$$

24. (a) In the titration of weak acid (CH_3COOH) with a strong base (NaOH), there is a change in the pH value at the end point. But it is not sharp due to weak ionisation of CH_3COOH . Due to the excess of free base beyond the equivalence point, there is steep rise in pH which is indicated by vertical line. Hence, the vertical line in the graph indicates alkaline nature of equivalence.
25. (b) As NaOH is a strong base and CH_3COOH is a weak acid. So on neutralisation of 40 mL 0.1 M NaOH with 40 mL 0.1 M CH_3COOH , we obtain a basic solution of $pH > 7$. Hence, option (b) is correct.



$$[\text{H}^+] = 2$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] = -\log 2 \\ &= -0.3010 \quad [\because \log 2 = 0.3010] \end{aligned}$$



Hence, $[\text{Product}] = K[\text{Reactant}]$

$\therefore [\text{Product}] > \text{Reactant}$, when $K > 1$

28. (b) The species having minimum value of K_{sp} will get precipitated first of all because ionic product will exceed the solubility product of such a species.
The K_{sp} value is minimum for $\text{BaSO}_4(10^{-11})$, so, BaSO_4 will get precipitated first of all.

29. (c) $\alpha = 0.1$,

$$K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{(0.1)^2 \times (0.01)}{(1-0.1)} = 1.11 \times 10^{-4}$$

$$\text{Now } pK_a = -\log 1.11 \times 10^{-4} = 3.9542$$

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 3.9542 + \log \left[\frac{0.05}{0.10} \right] = 3.653$$

30. (a) Solubility of $\text{PbF}_2 \approx 10^{-3}$ M
 $\therefore K_{sp} = 4S^3 = 4 \times 10^{-9}$

In 0.05 M NaF we have 0.05 M of F^- ion contributed by NaF . If the solubility of PbF_2

in this solution is S M, then

$$\text{total } [\text{F}^-] = [2S + 0.05] \text{ M.}$$

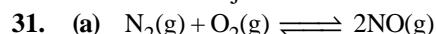
$$\therefore S[2S + 0.05]^2 = 4 \times 10^{-9}$$

Assuming $2S \ll 0.05$,

$$S \times 25 \times 10^{-4} = 4 \times 10^{-9}$$

$$\therefore S = 0.16 \times 10^{-5} \text{ M} \Rightarrow 1.6 \times 10^{-6} \text{ M}$$

We observe that our approximation that $2S \ll 0.05$ is justified.



At equilibrium, we have $[\text{N}_2] = 0.79(1-\alpha)$; $[\text{O}_2] = 0.21(1-\alpha)$; $[\text{NO}] = 2\alpha$

Total number of moles

$$= 0.79(1-\alpha) + 0.21(1-\alpha) + 2\alpha = 1 + \alpha$$

$$p_{\text{N}_2} = \frac{0.79(1-\alpha)}{1+\alpha} \times 1;$$

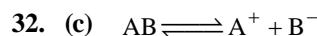
$$p_{\text{O}_2} = \frac{0.21(1-\alpha)}{1+\alpha} \times 1; \quad p_{\text{NO}} = \frac{2\alpha}{1+\alpha} \times 1$$

$$K_p = \frac{p_{\text{NO}}^2}{p_{\text{N}_2} \cdot p_{\text{O}_2}}$$

$$1.1 \times 10^{-3} = \frac{4\alpha^2}{0.79 \times 0.21(1-\alpha)^2}$$

$$\text{or } \alpha = 0.0067$$

$$\Rightarrow \text{vol \% of NO} = 2\alpha \times 100 \\ = 2 \times 0.0067 \times 100 = 1.33 \%$$



$$K_{sp} = [\text{A}^+][\text{B}^-]$$

Salt will precipitate if ionic conc. $> K_{sp}$
 $[\text{A}^+][\text{B}^-] > 1 \times 10^{-8}$

$$(1 \times 10^{-3})[\text{B}^-] > 1 \times 10^{-8}$$

$$[\text{B}^-] > \frac{1 \times 10^{-8}}{1 \times 10^{-3}} \text{ or } 1 \times 10^{-5}$$

33. (c) The reaction is exothermic and takes place with a decrease in number of molecules of gaseous species. Obviously high pressure and low temperature are the favourable conditions for the shift of equilibrium to products side. However, in continuous flow process, optimum elevated temperature is required to have more NH_3 due to high activation energy of the reaction.

34. (c) (a) $[\text{H}_3\text{O}^+] = \frac{0.1}{2} = 0.05$;

$$\text{pH} = -\log 0.05 = 1.301$$

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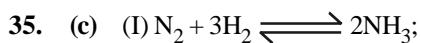
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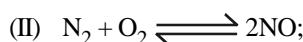
- (b) Complete neutralization of strong acid and strong base, pH = 7.

- (c) Hydrolysis of the salt CH_3COOK , pH > 7 (salt of weak acid with strong base)

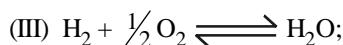
- (d) Hydrolysis of the salt NH_4NO_3 , pH < 7 (salt of strong acid with weak base)



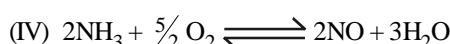
$$K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$



$$K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$



$$K_3 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{\frac{1}{2}}}$$



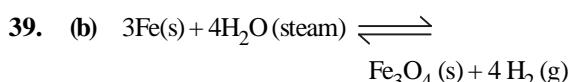
$$K_c = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{\frac{5}{2}}} = \frac{K_2 K_3^3}{K_1}$$

36. (a) Blood contains serum protein which acts as buffer.

37. (d) Reaction (II) and reverse of reaction (I) gives the desired reaction hence

$$K = K_2 \times \frac{1}{K_1} = \frac{K_2}{K_1}.$$

38. (d) $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+} + 4\text{H}_2\text{O}$ involves loss and gain of electrons. H_2O is coordinated to Cu by donating electrons (LHS). It is then removed by withdrawing electrons.



$$K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4} \text{ only gaseous products and reactants.}$$

40. (a) K_{sp} of As_2S_3 is less than ZnS . In acid medium ionisation of H_2S is suppressed (common ion effect) and K_{sp} of ZnS does not exceed.

41. (c) $K_{\text{sp}} = 4\text{S}^3 = 3.2 \times 10^{-11} \therefore \text{S} = 2 \times 10^{-4} \text{ M}$

$$[\text{OH}^-] = 2\text{S} = 2 \times 2 \times 10^{-4} \text{ M}$$

$$\therefore \text{pH} = 14 - \text{pOH}$$

$$= 14 + \log 4 \times 10^{-4} = 10.60$$

42. (c) Reaction (c) is endothermic. Electrolysis or decomposition of H_2O is endothermic in nature.

43. (c) $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 3\text{C}(\text{g}) + \text{D}(\text{g})$

Mole ratio	2	1	3	1
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Molar conc.	1	1	0	0
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at t=0				
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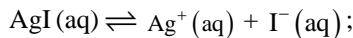
Equilibrium	1–0.5	1–0.25	0.75	0.25
-------------	-------	--------	------	------

molar				
-------	--	--	--	--

Concentration	= 0.50	= 0.75		
---------------	--------	--------	--	--

$$K_c = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}$$

44. (d) The solubility equilibrium for AgI is



$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

Let solubility of AgI be S moles per litre,

$$[\text{Ag}^+] = S, [\text{I}^-] = S$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$

$$1 \times 10^{-16} = (S) \times (S) = S^2$$

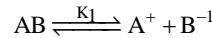
$$S = (1 \times 10^{-16})^{\frac{1}{2}} = 1 \times 10^{-8}$$

On calculating solubility of all given compounds

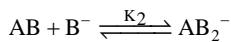
Compound	Solubility
AgCl	1×10^{-5}
AgI	1×10^{-8}
PbCrO_4	2×10^{-7}
Ag_2CO_3	1.26×10^{-4}

$\therefore \text{Ag}_2\text{CO}_3$ is most soluble and AgI is least soluble.

45. (d) Given,



$$K_1 = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$



$$K_2 = \frac{[AB_2^-]}{[AB][B^-]}$$

Dividing K_1 and K_2 we get

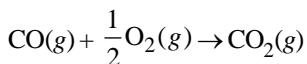
$$K = \frac{K_1}{K_2} = \frac{[A^+][B^-]^2}{[AB_2^-]}$$

$$\therefore \frac{[A^+]}{[AB_2^-]} = \frac{K}{[B^-]^2}$$

- 46. (b)** For a gaseous phase reaction K_p and K_c are related as

$$K_p = K_c (RT)^{\Delta n_g}$$

For the given reaction,



$$\Delta n_g = 1 - (1 + 0.5) = -0.5 \text{ or } -\frac{1}{2}$$

$$\therefore K_p = K_c (RT)^{-\frac{1}{2}}$$

$$\text{or } \frac{K_p}{K_c} = (RT)^{-\frac{1}{2}}$$

- 47. (b)** $Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$

$$K_{sp} = [Mg^{++}][OH^-]^2$$

$$1.0 \times 10^{-11} = 10^{-3} \times [OH^-]^2$$

$$[OH^-] = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

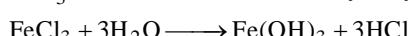
$$\therefore pOH = 4$$

$$\therefore pH + pOH = 14$$

$$\therefore pH = 10$$

Type B : Assertion Reason Questions

- 48. (e)** $FeCl_3$ is acidic in nature due to hydrolysis.



- 49. (c)** K_{sp} of $AgCl > K_{sp}$ of $AgBr$

- 50. (e)** Presence of NH_4Cl suppresses the dissociation of NH_4OH , hence, concentration of OH^- is reduced to

minimum. Further, $Ba(OH)_2$ is soluble in water.

- 51. (d)** Acidic buffer is the solution of a mixture of weak acid and a salt of this weak acid with a strong base.

CH_3COOH is weak acid and CH_3COONH_4 is a salt of CH_3COOH with weak base. So the mixture of CH_3COOH and CH_3COONH_4 is not an example of acidic buffer. Hence, both assertion and reason are false.

- 52. (c)** The equilibrium constant has a fixed value for every reaction at a particular temperature. However composition of final equilibrium mixture at a particular temperature does not depend upon the starting amount of reactant.

Hence, assertion is true but reason is false.

- 53. (a)** For the reaction

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{mol^2 \times L \times L^3}{L^2 \times mol \times mol^3} = L^2 mol^{-2}$$

So, the units for K_c are $L^2 mol^{-2}$

The assertion and reason, both are true and reason is correct explanation of assertion.

- 54. (a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

- 55. (a)** The size of $[Al(H_2O)_6]^{3+}$ is smaller than $[Mg(H_2O)_6]^{2+}$. Also, the former possesses more effective nuclear charge and thus, attracts electron pair from donor more effectively. This gives rise to relatively strong acidic nature of $[Al(H_2O)_6]^{3+}$.

- 56. (c)** $aA + bB \rightleftharpoons cC + dD, Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

If $Q_c > K_c$, reaction will proceed in the direction of reactants

If $Q_c < K_c$, reaction will move in direction of products.

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If $Q_c = K_c$, the reaction mixture is already at equilibrium.

- 57. (c) NaOH is a weaker base than KOH.
- 58. (d) In biological systems buffer system of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value of about 7.4.
- 59. (a) Ionic product of AgBr is greater than that of AgCl in comparison with there solubility product AgBr will precipitate first rather than that of AgCl.

Chapter

8

Redox Reactions

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Oxidation is : [1999]
 - (a) Gain of electrons
 - (b) Loss of neutrons
 - (c) Loss of electrons
 - (d) Decrease in positive valency
2. Oxidation number of Os in OsO_4 : [1999]
 - (a) +2
 - (b) +4
 - (c) +8
 - (d) +10
3. The oxidation number of sulphur in $\text{H}_2\text{S}_2\text{O}_7$ is: [2000]
 - (a) +2
 - (b) +6
 - (c) +4
 - (d) +8
4. In the following chemical reaction:

$$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Ag} + 2\text{OH}^- \quad [2000]$$
 - (a) Hydrogen is reduced
 - (b) Electrons are reduced
 - (c) Water is oxidised
 - (d) Silver is oxidised
5. Both oxidation and reduction takes place in :
 - (a) $\text{NaBr} + \text{HCl} \rightarrow \text{NaCl} + \text{HBr}$ [2001]
 - (b) $\text{HBr} + \text{AgNO}_3 \rightarrow \text{AgBr} + \text{HNO}_3$
 - (c) $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$
 - (d) $\text{CaO} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
6. The oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ is :
 - (a) +3
 - (b) -3 [1997, 2001]
 - (c) +6
 - (d) -6
7. Oxidation state of Fe in Fe_3O_4 is [2002]
 - (a) $\frac{3}{2}$
 - (b) $\frac{5}{4}$
 - (c) $\frac{4}{5}$
 - (d) $\frac{8}{3}$
8. MnO_4^{2-} (1 mole) in neutral aqueous medium disproportionates to [2003]
 - (a) 2/3 mole of MnO_4^- and 1/3 mole of MnO_2
 - (b) 1/3 mole of MnO_4^- and 2/3 mole of MnO_2
 - (c) 1/3 mole of Mn_2O_7 and 1/3 mole of MnO_2
 - (d) 2/3 mole of Mn_2O_7 and 1/3 mole of MnO_2
9. For decolourisation of 1 mole of KMnO_4 , the moles of H_2O_2 required is: [2004]
 - (a) 1/2
 - (b) 3/2
 - (c) 5/2
 - (d) 7/2
10. In the balanced chemical reaction,

$$\text{IO}_3^- + a\text{I}^- + b\text{H}^+ \rightarrow c\text{H}_2\text{O} + d\text{I}_2$$
 - a, b, c and d respectively corresponds to :
 - (a) 5, 6, 3, 3
 - (b) 5, 2, 6, 3 [2005]
 - (c) 3, 5, 3, 6
 - (d) 5, 6, 5, 5
11. The oxidation states of iodine in HIO_4 , H_3IO_5 and H_5IO_6 are respectively [2008]
 - (a) +1, +3, +7
 - (b) +7, +7, +3
 - (c) +7, +7, +7
 - (d) +7, +5, +3
12. Which of the following molecules can act as an oxidizing as well as a reducing agent ? [2008]
 - (a) H_2S
 - (b) SO_3
 - (c) H_2O_2
 - (d) F_2
13. The oxidation states of sulphur in S_8 , S_2F_2 , H_2S respectively, are [2010, 12]
 - (a) 0, +1 and -2
 - (b) +2, +1 and -2
 - (c) 0, +1 and +2
 - (d) -2, +1 and -2
14. The strength of an aqueous solution of I_2 can be determined by titrating the solution with standard solution of: [2012]
 - (a) Oxalic acid
 - (b) Sodium thiosulphate
 - (c) Sodium hydroxide
 - (d) Mohr's salt

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- 15.** Which of the following is a redox reaction ?
 (a) H_2SO_4 with NaOH [2013]
 (b) In atmosphere, O_3 from O_2 by lightening
 (c) Nitrogen oxides from nitrogen and oxygen by lightening
 (d) Evaporation of H_2O
- 16.** Which of the following involves transfer of five electrons ? [2014]
 (a) $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
 (b) $\text{CrO}_4^{2-} \rightarrow \text{Cr}^{3+}$
 (c) $\text{MnO}_4^{2-} \rightarrow \text{MnO}_2$
 (d) $\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$
- 17.** Oxidation numbers of P in PO_4^{3-} , of S in SO_4^{2-} and that of Cr in $\text{Cr}_2\text{O}_7^{2-}$ are respectively [2015]
- (a) +3, +6 and +5 (b) +5, +3 and +6
 (c) -3, +6 and +6 (d) +5, +6 and +6
- 18.** Which of the following species can function both as oxidizing as well as reducing agent ? [2016]
 (a) Cl^- (b) ClO_4^-
 (c) ClO^- (d) MnO_4^-
- 19.** Consider the following reaction occurring in basic medium [2017]

$$2\text{MnO}_4^-(\text{aq}) + \text{Br}^-(\text{aq}) \longrightarrow 2\text{MnO}_2(\text{s}) + \text{BrO}_3^-(\text{aq})$$
- How the above reaction can be balanced further?
 (a) By adding 2 OH^- ions on right side
 (b) By adding one H_2O molecule to left side
 (c) By adding 2H^+ ions on right side
 (d) Both (a) and (b)

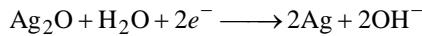
HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (c) Oxidation involves loss of electrons.
 2. (c) Oxidation No. of Os in OsO_4 is +8.
 3. (b) Oxidation no. of sulphur in $\text{H}_2\text{S}_2\text{O}_7$ can be calculated as follows : $2 + 2x - 14 = 0$
 $2x = 14 - 2 = 12$

$$x = \frac{12}{2} = 6$$

4. (c) In the given reaction, water is being oxidised because it is accepting oxygen from Ag_2O , while Ag^+ is reduced.



5. (c) In the reaction :



Oxidation number of H in H_2 is zero whereas its value is +1 in HBr ; similarly oxidation number of Br in Br_2 is zero whereas its value is -1 in HBr . So, here H is oxidised and Br reduced. In all other reactions, there is no change in the oxidation number of any element.

6. (c) Oxidation no of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$
 $= 2 + 2 \times x - 7 \times 2 = 0$

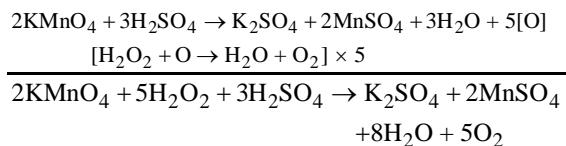
$$x = \frac{14 - 2}{2} = +6$$

7. (d) Oxidation state of Fe in Fe_3O_4

$$3x - 8 = 0; x = \frac{8}{3}$$

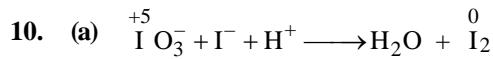
8. (a) $3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{MnO}_4^- + 4\text{OH}^-$
 or $\text{MnO}_4^{2-} + \frac{2}{3}\text{H}_2\text{O} \rightarrow \frac{1}{3}\text{MnO}_2 + \frac{2}{3}\text{MnO}_4^- + \frac{4}{3}\text{OH}^-$

9. (c)



2 mol of KMnO_4 oxidise 5 mol of H_2O_2

1 mol of KMnO_4 will oxidise $\frac{5}{2}$ mol of H_2O_2



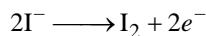
(A) Oxidation half cell



(i) Balancing the number of atoms



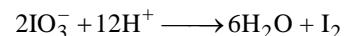
(ii) Balancing charge



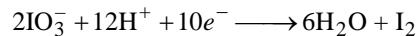
(B) Reduction half reaction



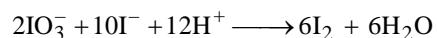
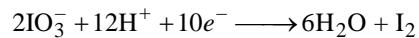
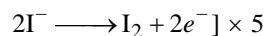
(i) Balancing number of atoms



(ii) Balancing the charge

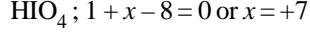
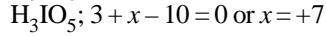
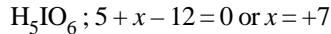


Multiplying the balanced oxidation half reaction by 5 and adding it to balanced reduction half reaction



Hence $a = 5$, $b = 6$, $c = 3$ and $d = 3$

11. (c) Calculating the oxidation states of I, we get



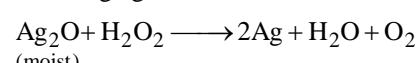
Thus, the correct answer is +7, +7, +7

12. (c) H_2O_2 can act both as an oxidising as well as a reducing agent.

Oxidising agent



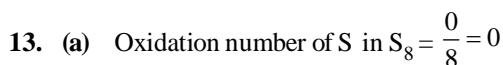
Reducing agent



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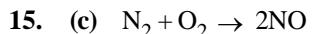
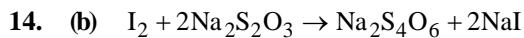
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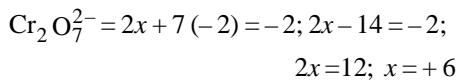
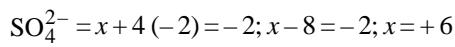
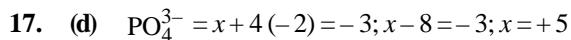
Let oxidation number of S in S_2F_2 be x
 $2x + 2(-1) = 0$
 $2x - 2 = 0$
 $2x = 2; x = +1$

Let oxidation number of S in H_2S be x .
 $2(+1) + x = 0$
 $2 + x = 0$
 $x = -2$



O.N. of N changes from 0 to +2 (oxidation) and O.N. of O changes from 0 to -2 (reduction).

16. (a) O.N. of Mn in MnO_4^- is +7 and in Mn^{2+} it is +2. The difference is of 5 electrons.



18. (c) Species

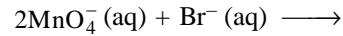
Species	O.N.
Cl^-	-1
$\underline{Cl}O_4^-$	+7
$\underline{Cl}O^-$	+1
$\underline{Mn}O_4^-$	+7
$\underline{N}O_3^-$	+5

In $\underline{Cl}O^-$ chlorine is in +1 oxidation state which can be increased or decreased thus it acts as an oxidising or reducing agent.

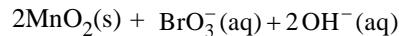
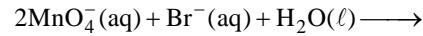
In other given species the underlined elements are either in their minimum or maximum oxidation state.

19. (d)

Since reaction is occurring in basic medium therefore $2OH^-$ are added on right side.



Now, hydrogen atoms can be balanced by adding one H_2O molecule to the left side



Chapter

9

Hydrogen

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Hydrogen is not more reactive at ordinary temperature, because at ordinary temperature it is in its: [1997]
 - (a) gaseous state
 - (b) liquid state
 - (c) molecular state
 - (d) atomic state
2. Hydrogen has high ionization energy than alkali metals because it has : [1999]
 - (a) Ionic bond
 - (b) Covalent bond
 - (c) Large size
 - (d) Small size
3. Which of the following statement is not correct regarding hydrogen atom? [2000]
 - (a) It resembles with halogens in some properties
 - (b) It resembles with alkali metals in some properties.
 - (c) It cannot be placed in first group of periodic table.
 - (d) It is the lightest element
4. Which of the following reaction produces hydrogen? [2002]
 - (a) $Mg + H_2O$
 - (b) $H_2S_2O_8 + H_2O$
 - (c) $BaO_2 + HCl$
 - (d) $Na_2O_2 + 2HCl$
5. Consider the following statements : [2012]
 1. Atomic hydrogen is obtained by passing hydrogen through an electric arc.
 2. Hydrogen gas will not reduce heated aluminium oxide.
 3. Finely divided palladium adsorbs large volume of hydrogen gas
 4. Pure nascent hydrogen is best obtained by reacting Na with C_2H_5OH

Which of the above statements is/are correct ?

 - (a) 1 alone
 - (b) 2 alone
 - (c) 1, 2 and 3
 - (d) 2, 3 and 4
6. Which of the following statement is not correct about Ellingham diagram? [2012]
 - (a) ΔG increases with an increase in temperature
 - (b) It consists of plots of $\Delta_f G^\circ$ vs T for formation of oxides
 - (c) a coupling reaction can be well expressed by this diagram
 - (d) It express the kinetics of the reduction process
7. The alkali metals form salt-like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders ? [2015]
 - (a) $CsH > RbH > KH > NaH > LiH$
 - (b) $KH > NaH > LiH > CsH > RbH$
 - (c) $NaH > LiH > KH > RbH > CsH$
 - (d) $LiH > NaH > KH > RbH > CsH$
8. Which of the following statements is incorrect?
 - (a) Ionic hydrides are stoichiometric compounds of dihydrogen formed with most of s-block elements [2016]
 - (b) Ionic hydrides are crystalline, non-volatile and non-conducting in solid state.
 - (c) Melts of ionic hydrides conduct electricity and liberate dihydrogen gas at cathode.
 - (d) Both (a) and (c)
9. When zeolite (hydrated sodium aluminium silicate) is treated with hard water the sodium ions are exchanged with [2017]
 - (a) H^+ ions
 - (b) Ca^{2+} ions
 - (c) SO_4^{2-} ions
 - (d) OH^- ions

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 10-11) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

10. Assertion : HOF bond angle in HFO is higher than HOCl bond angle in HClO.

Reason : Oxygen is more electronegative than halogens. [2014]

11. Assertion : Hydrogen combines with other elements by losing, gaining or sharing of electrons. [2015]

Reason : Hydrogen forms electrovalent and covalent bonds with other elements.

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Type A : Multiple Choice Questions

1. (c) Hydrogen is not reactive at ordinary temperature because it is in molecular state i.e., as H₂ with its complete duplet which makes it stable and lesser reactive. At very high temperature, hydrogen exists in atomic form having one electron i.e., incomplete duplet which makes it less stable and highly reactive.
2. (d) Hydrogen has high ionisation energy in comparison with alkali metals because it has only one orbital i.e. smaller size. Due to smaller size, hold of nucleus on outermost electron is greater in case of hydrogen.
3. (c) Actually hydrogen is in the first group of periodic table due to its much resemblance with alkali metals
4. (a) Mg reacts with hot water to produce H₂ because it is more electropositive than hydrogen.



All other reactions are used for manufacture of H₂O₂.



5. (c) Pure hydrogen is evolved by reacting absolute alcohol and Na

$$\text{C}_2\text{H}_5\text{OH} + \text{Na} \rightarrow \text{C}_2\text{H}_5\text{ONa} + \frac{1}{2}\text{H}_2$$
 other statements are correct.
6. (d) Ellingham diagrams are based on thermodynamic concepts. It does not tell anything about the kinetics of the reduction process.
7. (d) The stability of alkali metal hydrides decreases from Li to Cs. It is due to the fact that M–H bonds become weaker with increase in size of alkali metals as we move down the group from Li to Cs. Thus the order of stability of hydrides is

$$\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$$
 i.e. option (d) is correct answer.
8. (c) Melts of ionic hydrides conduct electricity and liberate dihydrogen gas at anode.
9. (b) $\text{Na zeolite} + \text{CaCl}_2 \rightarrow \text{Ca zeolite} + 2\text{NaCl}$

Type B : Assertion Reason Questions

10. (d) *Both assertion and reason are false.*
 HOF bond angle in HFO is lesser than that of HOCl bond angle in HClO. Oxygen is more electronegative than all halogens except fluorine.
11. (a)

Chapter

10

The s-Block Elements

TYPE A : MULTIPLE CHOICE QUESTIONS

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Directions for (Qs.29-37) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- 29. Assertion :** We feel cold on touching the ice.
Reason : Ice is a solid form of water. [2009]
- 30. Assertion :** s-Block elements do not occur free in nature.
Reason : s-Block elements are highly electropositive in nature. [2009]
- 31. Assertion :** Both Be and Al can form complexes such as BeF_4^{2-} and AlF_6^{3-} respectively, BeF_6^{3-} is not formed.
Reason : In case of Be, no vacant d-orbitals are present in its outermost shell. [2009]

- 32. Assertion :** In fused state, calcium chloride cannot be used to dry alcohol or NH_3 .
Reason : CaCl_2 is not a good dessicant. [2010]
- 33. Assertion :** LiCl is predominantly a covalent compound.
Reason : Electronegativity difference between Li and Cl is too small. [2012]
- 34. Assertion :** Of the various chlorides of alkaline earth metals BeCl_2 is covalent in nature, whereas MgCl_2 and CaCl_2 are ionic compounds.
Reason : Be is the first member of group 2. [2012]
- 35. Assertion :** Best diagonal relationship is shown between Be and Al.
Reason : Ionization energy of Be is almost the same as that of Al. [2013]
- 36. Assertion :** K, Rb and Cs (all belonging to group 1) can also form superoxides.
Reason : The ionic radii of K, Rb and Cs show the following trend $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+$. [2014]
- 37. Assertion :** Lithium carbonate is not so stable to heat.
Reason : Lithium being very small in size polarizes large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2 [2017]

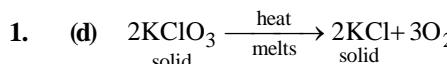
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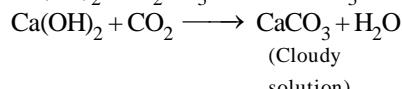
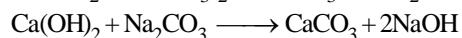
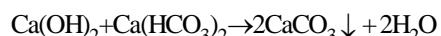
Type A : Multiple Choice Questions



2. (b) Sodium carbonate ionises in aqueous solution. It is soluble in water because of low lattice energy. Low lattice energy helps in solubility. For substances which do not ionise

$$\text{Solubility} \propto \frac{1}{\text{Molecular mass}}$$

3. (d) $\text{Ca}(\text{OH})_2$ is used to remove temporary hardness of water.



4. (c) Sodium on heating with moist air produces Na_2O .



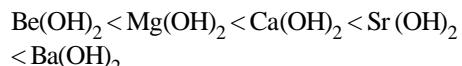
5. (b) Nitrolim is $\text{CaCN}_2 + \text{C}$. It is used as fertilizer since it reacts with H_2O to form NH_3 .



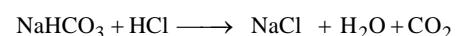
7. (c) In hydroxides of alkaline earth metals, hydration energy does not alter very much while lattice energy decreases down the group due to increase in size.

The overall effects of the two factors is that ΔH solution of the hydroxides

(ΔH solution = $\Delta H_{\text{lattice}} - \Delta H_{\text{hydration}}$) becomes more negative from Be to Ba and hence solubility increases from top to bottom.



8. (b) $\text{Na}_2\text{CO}_3 + 2\text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$



$$\text{Mole of Na}_2\text{CO}_3 = \frac{0.5}{106} = 0.0047$$

$$\text{Mole of NaHCO}_3 = \frac{0.5}{84} = 0.0059$$

$$0.0047 \text{ mole of Na}_2\text{CO}_3 \\ \equiv 0.0047 \times 2 \text{ mole of HCl} \\ = 0.0094 \text{ mole of HCl}$$

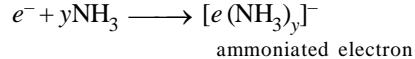
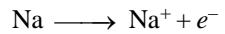
$$0.0059 \text{ mole of NaHCO}_3 \\ \equiv 0.0059 \text{ mole of HCl}$$

Total mole required = 0.0153 moles of HCl

If V be the volumes in litre of HCl required then mole of HCl required = $V \times 0.1$

$$V = \frac{0.0153}{0.1} = 0.153 \text{ litre} \\ = 153 \text{ ml}$$

9. (d) Sodium dissolves in liquid ammonia to form blue solution which is good conductor of electricity. The blue colour of the solution is due to formation of ammoniated electrons.



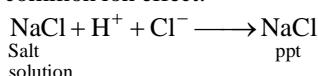
Due to presence of unpaired electron liquid ammonia become paramagnetic.

10. (a) NaHCO_3 is used in medicine to neutralise the acidity in the stomach. $\text{Mg}(\text{OH})_2$ is basic in nature and dissolves in acids forming corresponding salts. So both are used in antacid medicinal preparations.

11. (b) Radii of atoms increase as we go down the group due to the addition of extra energy shell. Nuclear charge also increases on moving down the group but the influence of addition of energy shell predominates. This predomination is larger in case when we move from Na to K among all the options given.

12. (b) Composition of cement depends upon its type. Portland cement is most common kind and contains 51% tricalcium silicate, 24% of dicalcium silicate and 6% of tricalcium aluminate.

13. (b) The common table salt is prepared by passing HCl gas through a saturated solution of salt. The precipitation is due to common ion effect.



14. (a) In alkaline medium Na_2CO_3 reacts with SO_2 to form Na_2SO_3 (sodium sulphite).

On reaction with caustic alkalies SO_2 forms two types of salts – bisulphites and sulphites. In alkaline medium, it forms Na_2SO_3 .

15. (b) The ionic character and hence the m.pt. increases as the size of cation increases.

16. (d) Be shows diagonal relationship with Al

17. (c) The property of sodium atom to emit photons in yellow region of visible spectrum, due to electrically stimulated electron transitions is used in street lights.

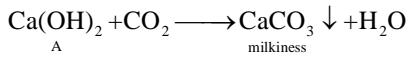
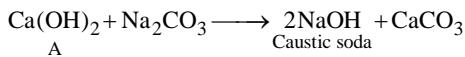
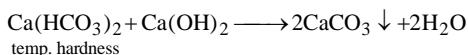
18. (b) BaCO_3 forms a yellow ppt of barium chromate. BaCO_3 forms a white precipitate of BaSO_4 . BaCl_2 is soluble in water.

19. (a) As the size of the anion increases from, F^- to I^- the covalent character increase and hence the solubility in non-polar solvent increases.



20. (b)

21. (c)



22. (a) $(\text{Na}_2\text{O}_2 + \text{HCl})$ is commercially known as oxone and is used for bleaching of delicate fibres.

23. (a) Lithium does not form peroxide.

Type B : Assertion Reason Questions

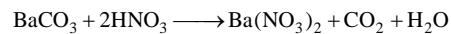
24. (c) Magnesium continues to burn in nitric oxide because the heat evolved decomposes NO to give N_2 and O_2 and Mg burns readily in the atmosphere of N_2 and O_2 .

25. (a) Potassium and Cesium are electropositive elements with very low ionisation potential so they emit electrons on exposure to light.

26. (b) Both the assertion and reason are correct. The reason is not the explanation of the assertion.

Note that alkaline earth metals are bivalent, i.e. have an oxidation state of +2.

27. (a) Barium carbonate is more soluble in HNO_3 than in water because carbonate is a weak base and reacts with the H^+ ion of HNO_3 causing the barium salt to dissociate.



28. (e) Calcium is present in the enamel but Mg is an essential element for biological functions of human.

29. (b) It is correct that on touching the ice we feel cold because ice absorbs heat from our hand.

30. (a) The s-block elements are highly electropositive in nature. So, these are very reactive. That is why these elements do not occur free in nature. Usually, the s-group elements occur in nature as halides, carbonates and sulphates. These metals are obtained from their molten halides by electrolytic reduction.

31. (a) Both assertion and reason are correct and reason is correct explanation of assertion.

32. (c) Assertion is true but Reason is false. CaCl_2 forms addition products with alcohol and ammonia.

33. (c) LiCl is a covalent compound. Due to the large size of the anion (Cl^-) its effective nuclear charge lessens and its valence shell is held less tightly towards its nucleus. Here, assertion is correct but reason is incorrect.

34. (b) Both assertion and reason are true but reason is not the correct explanation of assertion. The ionic nature of MgCl_2 and CaCl_2 is due to the large difference in electronegativity values of Mg, Ca to that of chlorine.

35. (a) Reason is the correct explanation of Assertion.

36. (c) Assertion is correct. Reason is incorrect.

37. (a) Lithium carbonate is unstable to heat; lithium being very small in size polarises a large CO_3^{2-} ion leading to the formation of more stable Li_2O and CO_2 .

Chapter

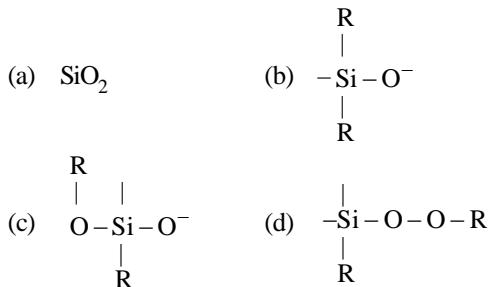
11

The p-Block Elements

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The approximate percentage of silica in cement is: [1998]
 - (a) 5–10%
 - (b) 15–20%
 - (c) 20–25%
 - (d) 25–30%
2. The most abundant metal in the earth crust is: [1998]
 - (a) Pb
 - (b) Cu
 - (c) Al
 - (d) Mg
3. Bell metal is an alloy of: [1999]
 - (a) Sn and Pb
 - (b) Cu and Pb
 - (c) Sn and Cu
 - (d) In, Sn and Cu
4. Al_2O_3 on heating with carbon in an atmosphere of N_2 at high temperature produces : [1999]
 - (a) $\text{Al} + \text{CO}_2$
 - (b) $\text{Al} + \text{CO}_2 + \text{NO}$
 - (c) $\text{Al}_4\text{C}_3 + \text{CO}_2$
 - (d) $\text{AlN} + \text{CO}$
5. Producer gas is a mixture of: [1998, 2000]
 - (a) $\text{CO} + \text{H}_2$
 - (b) $\text{H}_2 + \text{CH}_4$
 - (c) $\text{CO} + \text{N}_2$
 - (d) $\text{CO} + \text{H}_2\text{O}$
6. Solid CO_2 is known as dry ice:
 - (a) It melts at 0°C
 - (b) Its B.P. is more than 199°C
 - (c) It evaporates at -78°C without melting
 - (d) None of the above
7. Water glass is : [2001]
 - (a) Na_2SiO_3
 - (b) Mg_2Si
 - (c) SiCl_4
 - (d) $\text{Ca}(\text{H}_2\text{PO}_4)_2$
8. Water gas is produced by : [2001]
 - (a) passing steam over red hot coke
 - (b) passing steam and air over red hot coke
 - (c) burning coke in excess of air
 - (d) burning coke in limited supply of air
9. In lake test of Al^{3+} ion, there is formation of coloured floating. It is due to : [2001]
 - (a) adsorption of litmus by H_2O
 - (b) adsorption of litmus by Al(OH)_3
 - (c) adsorption of litmus by Al(OH)_4^-
 - (d) none of these
10. In diamond crystal, each carbon atom is linked with carbon atoms? The number of carbon atoms linked is : [2001]
 - (a) 2
 - (b) 4
 - (c) 3
 - (d) 1
11. The electrical conductivity of semiconductors :
 - (a) decreases with temperature [2001]
 - (b) increases with temperature
 - (c) remains constant on heating
 - (d) none of the above
12. Which of the following is only acidic in nature?
 - (a) $\text{Be}(\text{OH})_2$
 - (b) $\text{Mg}(\text{OH})_2$ [2004]
 - (c) $\text{B}(\text{OH})_3$
 - (d) $\text{Al}(\text{OH})_3$
13. The liquefied metal expanding on solidification is : [2004]
 - (a) Ga
 - (b) Al
 - (c) Zn
 - (d) Cl
14. In diborane, the two H–B–H angles are nearly :
 - (a) $60^\circ, 120^\circ$
 - (b) $95^\circ, 120^\circ$ [2005]
 - (c) $95^\circ, 150^\circ$
 - (d) $120^\circ, 180^\circ$
15. The pair of amphoteric hydroxides is [2005]
 - (a) $\text{Al}(\text{OH})_3, \text{LiOH}$
 - (b) $\text{Be}(\text{OH})_2, \text{Mg}(\text{OH})_2$
 - (c) $\text{B}(\text{OH})_3, \text{Be}(\text{OH})_2$
 - (d) $\text{Zn}(\text{OH})_2, \text{Be}(\text{OH})_2$
16. Borax is used as cleansing agent because on dissolving in water it gives [2006]
 - (a) Alkaline solution
 - (b) Acidic solution
 - (c) Bleaching solution
 - (d) Colloidal solution
17. The energy gaps (E_g) between valence band and conduction band, for diamond, silicon and germanium are in the order: [2006]
 - (a) $E_g(\text{diamond}) > E_g(\text{silicon}) > E_g(\text{germanium})$
 - (b) $E_g(\text{diamond}) < E_g(\text{silicon}) < E_g(\text{germanium})$
 - (c) $E_g(\text{diamond}) = E_g(\text{silicon}) = E_g(\text{germanium})$
 - (d) $E_g(\text{diamond}) > E_g(\text{germanium}) > E_g(\text{silicon})$

18. The repeating unit in silicone is [2007]



19. Select correct statement(s). [2008]

- (a) Cyanamide ion (CN_2^{2-}) is isoelectronic with CO_2 and has the same linear structure
- (b) Mg_2C_3 reacts with water to form propyne
- (c) CaC_2 has NaCl type lattice
- (d) All of the above

20. Non-oxide ceramics can be [2008]

- (a) B_4C
- (b) SiC
- (c) Si_3N_4
- (d) All of these

21. The chemical formula of 'tear gas' is [2008]

- (a) COCl_2
- (b) CO_2
- (c) Cl_2
- (d) CCl_3NO_2

22. Thermodynamically, the most stable form of carbon is [2009]

- (a) Diamond
- (b) Graphite
- (c) Fullerenes
- (d) Coal

23. Which of the following product is formed when SiF_4 reacts with water? [2010]

- (a) SiF_3
- (b) H_4SiO_4
- (c) H_2SO_4
- (d) H_2SiF_4

24. BCl_3 does not exist as dimer but BH_3 exists as dimer (B_2H_6) because [2012]

- (a) Chlorine is more electronegative than hydrogen
- (b) there is $p\pi-p\pi$ back bonding in BCl_3 but BH_3 does not contain such multiple bonding
- (c) large sized chlorine atoms do not fit in between the small boron atoms whereas small sized hydrogen atoms get fitted in between boron atoms
- (d) none of the above

25. Ge(II)compounds are powerful reducing agents whereas Pb(IV)compounds are strong oxidants. It can be due to [2012]

- (a) Pb is more electropositive than Ge
- (b) Ionization potential of lead is less than that of Ge

- (c) Ionic radii of Pb^{2+} and Pb^{4+} are larger than those of Ge^{2+} and Ge^{4+}
- (d) More pronounced inert pair effect in lead than in Ge

26. Carbon cannot be used to produce magnesium by chemical reduction of MgO because: [2014]

- (a) Carbon is not a powerful reducing agent
- (b) Magnesium reacts with carbon to form carbides
- (c) Carbon does not react with magnesium
- (d) Carbon is a non-metal

27. Carborundum is obtained when silica is heated at high temperature with [2014]

- (a) carbon
- (b) carbon monoxide
- (c) carbon dioxide
- (d) calcium carbonate

28. An inorganic salt (A) is decomposed on heating to give two products (B) and (C). Compound (C) is a liquid at room temperature and is neutral to litmus while the compound (B) is a colourless neutral gas. Compounds (A), (B) and (C) are [2014]

- (a) $\text{NH}_4\text{NO}_3, \text{N}_2\text{O}, \text{H}_2\text{O}$
- (b) $\text{NH}_4\text{NO}_2, \text{NO}, \text{H}_2\text{O}$
- (c) $\text{CaO}, \text{H}_2\text{O}, \text{CaCl}_2$
- (d) $\text{Ba}(\text{NO}_3)_2, \text{H}_2\text{O}, \text{NO}_2$

29. Which of the following oxides is strongly basic?

- (a) B_2O_3
- (b) Al_2O_3 [2015]
- (c) Ga_2O_3
- (d) Tl_2O_3

30. Chemically borax is [2015]

- (a) Sodium metaborate
- (b) Sodium orthoborate
- (c) Sodium tetraborate
- (d) Sodium tetraborate decahydrate

31. Match List – I with List – II for the compositions of substances and select the correct answer using the code given below the lists : [2015]

List - I

Substances

- (A) Plaster of paris
- (B) Epsomite
- (C) Kieserite
- (D) Gypsum

List - II

Composition

- (i) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- (ii) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
- (iii) $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- (iv) $\text{MgSO}_4 \cdot \text{H}_2\text{O}$
- (v) CaSO_4

Code :

- | | | | |
|-----------|-------|-------|------|
| (A) | (B) | (C) | (D) |
| (a) (iii) | (iv) | (i) | (ii) |
| (b) (ii) | (iii) | (iv) | (i) |
| (c) (i) | (ii) | (iii) | (v) |
| (d) (iv) | (iii) | (ii) | (i) |

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32. The liquefied metal which expands on solidification is : [2016]
 (a) Ga (b) Al
 (c) Zn (d) In
33. A neutral molecule XF_3 has a zero dipole moment. The element X is most likely [2016]
 (a) chlorine (b) boron
 (c) nitrogen (d) carbon
34. The correct formula of borax is [2016]
 (a) $Na_2[B_4O_4(OH)_3] \cdot 9 H_2O$
 (b) $Na_2[B_4O_5(OH)_4] \cdot 8 H_2O$
 (c) $Na_2[B_4O_6(OH)_5] \cdot 7 H_2O$
 (d) $Na_2[B_4O_7(OH)_6] \cdot 6 H_2O$
40. **Assertion :** PbI_4 is a stable compound.
Reason : Iodide stabilizes higher oxidation state [2003]
41. **Assertion :** SiF_6^{2-} is known but $SiCl_6^{2-}$ is not
Reason : Size of fluorine is small and its lone pair of electrons interacts with *d*-orbitals of Si strongly. [2005]
42. **Assertion :** Silicones are hydrophobic in nature.
Reason : Si-O-Si linkages are moisture sensitive. [2006]
43. **Assertion :** $PbCl_2$ is more stable than $PbCl_4$.
Reason : $PbCl_4$ is powerful oxidising agent. [2008]

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 35-43) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.

35. **Assertion :** $Al(OH)_3$ is insoluble in NH_4OH but soluble in $NaOH$.

Reason : $NaOH$ is strong alkali. [1997]

36. **Assertion :** Boron is metalloid.

Reason : Boron shows metallic nature. [1997]

37. **Assertion :** NH_3 is absorbed more readily over activated charcoal than CO_2 .

Reason : NH_3 is non-polar. [2000]

38. **Assertion :** Stannous chloride gives grey precipitate with mercuric chloride, but stannic chloride does not do so.

Reason : Stannous chloride is a powerful oxidising agent which oxidises mercuric chloride to metallic mercury. [2002]

39. **Assertion :** Diamond is a bad conductor.

Reason : Graphite is a good conductor. [2002]

Directions for (Qs.44-47) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 (c) If Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
44. **Assertion :** Coloured cations can be identified by borax bead test.

Reason : Transparent bead ($NaBO_2 + B_2O_3$) forms coloured bead with coloured cation. [2009]

45. **Assertion :** Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

Reason : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to ‘inert pair effect’.

[2014]

46. **Assertion :** Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.

Reason : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to ‘inert pair effect’.

[2016]

47. **Assertion :** Atomic radius of gallium is higher than that of aluminium [2017]

Reason : The presence of additional *d*-electron offer poor screening effect for the outer electrons from increased nuclear charge.

[2017]

HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (c) The approximate composition of cement is :

Lime (CaO) = 50–60%

Silica (SiO_2) = 20–25 %

Alumina (Al_2O_3) = 5–10 %

Magnesia (MgO) = 2–3 %

Ferric oxide (Fe_2O_3) = 2–3 %

2. (c)

3. (d) Bell metal is an alloy of Cu and Sn.

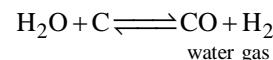
4. (d) $\text{Al}_2\text{O}_3 + \text{N}_2 + 3\text{C} \longrightarrow 2\text{AlN} + 3\text{CO}$

5. (c) Producer gas is a mixture of CO and N_2 .

6. (c) Solid CO_2 is known as dry ice because it evaporates at -78°C without melting.

7. (a) Sodium silicate (Na_2SiO_3) is known as water glass. It is soluble in water. Just as plants grow in the soil, coloured crystals grow in the water glass.

8. (a) Water gas is produced by passing steam over hot coke.



9. (b) In lake test of Al^{3+} , a coloured floating lake is formed as $\text{Al}(\text{OH})_3$ which being a solid surface (suspension), adsorbs litmus colour, resulting in coloured floating lake appearance.

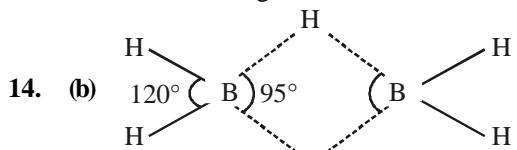
10. (b) In diamond crystal, carbon atom is in sp^3 hybridised state so each carbon is linked with four other carbons by σ – bond.

11. (b) With the increase in temperature, more number of covalent bonds are broken, resulting large increase in current carrier concentration (i.e. electrons and holes). Due to which the conductivity of semiconductor increases.

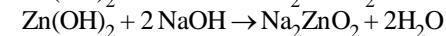
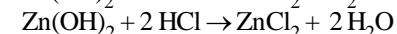
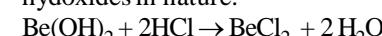
12. (c) $\text{B}(\text{OH})_3$ is actually H_3BO_3 which is an acid (boric acid): It is a monobasic acid. It is not a proton donor (Bronsted acid), but behaves as Lewis acid. It can accept a lone pair of electrons from OH^- ion.



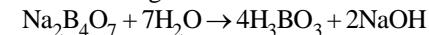
13. (a) Gallium (Ga) is soft, silvery metal. Its melting point is 30°C . This metal expands by 3.1% when it solidifies and hence, it should not be stored in glass or metal containers.



14. (b) $\text{Be}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$ are amphoteric hydroxides in nature.



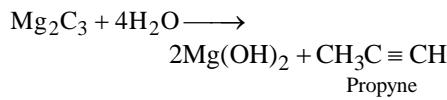
15. (a) Borax is $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$. It gives alkaline solution on dissolution in water as it is a salt of strong base and weak acid.



16. (a) In diamond, it is highest (6 eV), for silicon, it is 1.1 eV and for germanium, it is 0.72 eV.

17. (a) Polymeric organosilicon compounds containing Si–O–Si bonds are called silicones. Silicones have general formula $(\text{R}_2\text{SiO})_n$. Hence repeating unit of silicone is R_2SiO^- .

18. (b) In CO_2 we have $22(6+8+8=22)$ electrons. In $(\text{CN}_2)^{2-}$, we have $22(6+7+7+2=22)$ electrons. Both CO_2 and $(\text{CN}_2)^{2-}$ have linear structures. Thus, statement (a) is correct.



i.e., statement (b) is also correct .

The structure of CaC_2 is of NaCl type

i.e., statement (c) is also correct.

20. (d) Ceramics are inorganic, non-metallic, solid minerals. They come in a variety of forms, including silicates (silica, SiO_2 with metal oxides), oxides (oxygen and metals), carbides (carbon and metals), aluminates (alumina, Al_2O_3 with metal oxides) and nitrides.

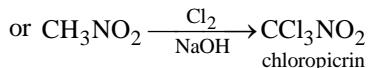
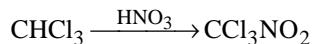
The given ceramics are B_4C (carbides), SiC (carbides), Si_3N_4 (nitrides) and thus, none of these is an oxide . All of these are non-oxide ceramics.

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21. (d) "Tear gas" is the name given to the compound, CCl_3NO_2 . It is also called **chloropicrin**.

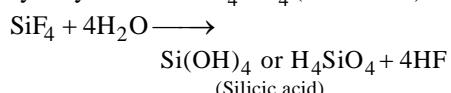


22. (b) Graphite is thermodynamically, the most stable allotrope of carbon. That is why $\Delta_f H^\circ$ (graphite) is taken as zero.

$$\Delta_f H^\circ (\text{diamond}) = + 1.90 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{fullerene}) = + 38.1 \text{ kJ mol}^{-1}$$

23. (b) In reaction with water, SiF_4 (like SiCl_4) gets hydrolysed to form H_4SiO_4 (silicic acid).

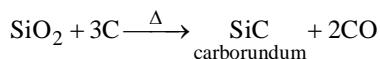


24. (c)

25. (d) Ge(II) tends to acquire Ge (IV) state by loss of electrons. Hence it is reducing in nature. Pb (IV) tends to acquire Pb (II) O.S. by gain of electrons. Hence it is oxidising in nature. This is due to inert pair effect.

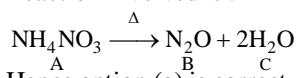
26. (b)

27. (a) Silica on heating with carbon at elevated temperature, gives carborundum (silicon carbide)



Carborundum is a very hard substance.

28. (a) Reaction involved is :



Hence option (a) is correct.

29. (d) The correct sequence of increasing basic strength is



30. (d) Chemically borax is sodium tetraborate decahydrate and it has the formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

31. (b) (A) Plaster of paris = $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

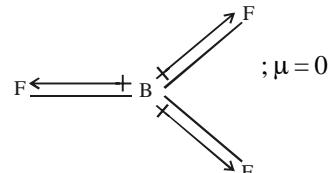
(B) Epsomite = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

(C) Kieserite = $\text{MgSO}_4 \cdot \text{H}_2\text{O}$

(D) Gypsum = $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

32. (a) Gallium (Ga) is soft, silvery metal. Its melting point is 30°C. This metal expands by 3.1% when it solidifies and hence, it should not be stored in glass or metal containers.

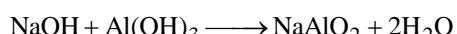
33. (b) BF_3 has planar and symmetrical structure thus as a result the resultant of two bond moments, being equal and opposite to the third, cancels out and hence molecule possess zero dipole moment.



34. (b) Borax is sodium tetraborate decahydrate i.e. $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$

Type B : Assertion Reason Questions

35. (a) **Assertion**: Al(OH)_3 is soluble in strong alkali like NaOH because of formation of meta-aluminate ion

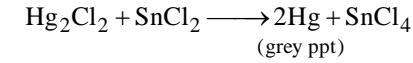


- Reason**: Boron is a metalloid. Thus, assertion is true. Metalloids possess metallic as well as non-metallic nature. Hence, reason is false.

37. (c) **Assertion**: It is correct that NH_3 is absorbed more readily over activated charcoal than CO_2 because of its polar nature.

- Reason**: Sn^{4+} is more stable than Sn^{2+} .

So, Sn^{2+} is oxidised to Sn^{4+} by losing 2 electrons when it reacts with mercuric chloride, i.e., SnCl_2 is a reducing agent.



So assertion is correct but reason is wrong. Hence correct option is (c).

39. (b) **Assertion**: Diamond is a bad conductor because of lack of free electrons in its lattice. Graphite is a good conductor of electricity because of free electron in its lattice.

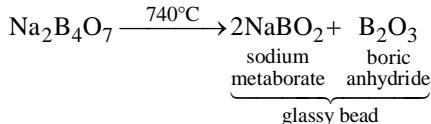
So both assertion and reason are correct but reason is not correct explanation of assertion.

40. (d) As we move down the group IVA, +2 oxidation state becomes more stable. Thus Pb^{4+} is not possible, i.e., PbI_4 is highly unstable. I_2 is a weak oxidising agent so it cannot oxidise Pb to Pb^{4+} oxidation state. So assertion and reason both are wrong.

41. (a) **Assertion**: SiF_6^{2-} is known because F has small size and thus the ion is quite stable unlike SiCl_6^{2-} in which size of Cl atom is large which destabilise it.

- 42.** (c) Silicons are hydrophobic in nature i.e. it is water repellent because most of the groups which form bulky silicon molecule are organic in nature so they are water repellent. Thus assertion is true. The Si–O–Si linkages are stable, so these are moisture resistant. Hence reason is false.
- 43.** (b) Pb^{2+} is more stable than Pb^{4+} due to inert pair effect. Due to this reason, PbCl_4 decomposes readily into PbCl_2 and Cl_2 .

$$\text{PbCl}_4 \rightarrow \text{PbCl}_2 + \text{Cl}_2$$
 Thus Pb^{4+} salts are better oxidising agents
- 44.** (a) Borax ($\text{Na}_2\text{B}_4\text{O}_7$) when heated at about 740°C , forms a glassy bead which gives different colour beads with different cations.
 Hence, it is used to identify cations in qualitative analysis. This test is called borax bead test.



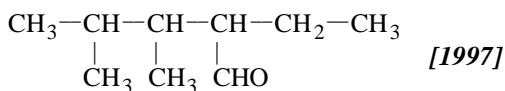
- 45.** (c) Assertion is true because lower oxidation state becomes more & more stable for heavier elements in *p*-block due to inert pair effect. Hence Reason is false.
- 46.** (c) Assertion is true because lower oxidation state becomes more & more stable for heavier elements in *p*-block due to inert pair effect. Hence Reason is false.
- 47.** (c) Atomic radius of gallium is less than that of aluminium.

Chapter
12

Organic Chemistry—Some Basic Principles and Techniques

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The IUPAC name of following compound is



- (a) 2-ethyl-3, 4-dimethylpentanal
- (b) 2, 3-dimethyl-4-aldohexane
- (c) 3-Aldo-4, 5-dimethylhexane
- (d) 1, 3, 4, 5-tetraethylbutanal

2. The number of enantiomers of the compound



- (a) 2
- (b) 3
- (c) 4
- (d) 6

3. The process of decomposition of organic compound by the application of heat is : [1999]

- (a) pyrolysis
- (b) evaporation
- (c) sublimation
- (d) condensation

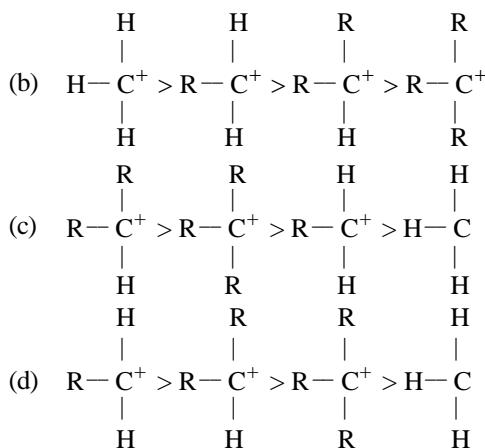
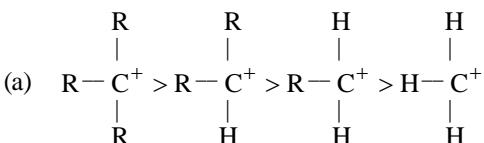
4. Turpentine oil can be purified by: [1999]

- (a) Steam distillation
- (b) Sublimation
- (c) Vacuum distillation
- (d) Fractional distillation

5. Which pairs have same percentage of carbon?

- (a) CH_3COOH and $\text{C}_6\text{H}_{12}\text{O}_6$ [2000]
- (b) CH_3COOH and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- (c) CH_3COOH and $\text{C}_2\text{H}_5\text{OH}$
- (d) $\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

6. The decreasing order of stability of alkyl carbonium ion is in the order of: [2001]



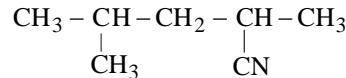
7. The number of sigma electrons in toluene are [2001]

- (a) 6
- (b) 9
- (c) 15
- (d) 30

8. The most suitable method for removing water traces from ethanol is: [2001]

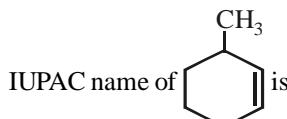
- (a) distillation
- (b) passing dry HCl
- (c) reacting it with Mg
- (d) heating with sodium metal

9. IUPAC name of



[2002]

- (a) 2-cyano-3-methylhexane
- (b) 2, 4-dimethylcyanopentane
- (c) 3-methyl-5-cyano hexane
- (d) 2-cyano-3-methylhexane



10. IUPAC name of [2003]

- (a) 3-methylcyclohexene
- (b) 1-methylcyclohex-2-ene
- (c) 6-methylcyclohexene
- (d) 1-methylcyclohex-5-ene

- 11.** The most reactive nucleophile among the following is : [2003]
- (a) CH_3O^- (b) $\text{C}_6\text{H}_5\text{O}^-$
 (c) $(\text{CH}_3)_2\text{CHO}^-$ (d) $(\text{CH}_3)_3\text{CO}^-$
- 12.** The absolute configuration of the following : [2003]
- Cl— $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}—\text{C}—\text{Cl} \\ | \\ \text{C}_2\text{H}_5 \end{array}$ is [2003]
- (a) 2S, 3R (b) 2S, 3S
 (c) 2R, 3S (d) 2R, 3R
- 13.** Which of the following compound possesses the C—H bond with the lowest bond dissociation energy? [2003]
- (a) Toluene
 (b) Benzene
 (c) *n*-pentane
 (d) 2, 2-dimethylpropane
- 14.** The dipole moment is the highest for : [2004]
- (a) *trans*-2-butene
 (b) 1, 3 -dimethylbenzene
 (c) acetophenone
 (d) ethanol
- 15.** The geometrical isomerism is shown by [2004]
- (a)
 (b)
 (c)
 (d)
- 16.** Among the following, the strongest nucleophile is : [2005]
- (a) $\text{C}_2\text{H}_5\text{SH}$ (b) CH_3COO^-
 (c) CH_3NH_2 (d) NCCH_2^-
- 17.** Among the following the most stable compound is : [2005]
- (a) *cis*-1, 2-cyclohexanediol
 (b) *trans*-1, 2-cyclohexanediol
 (c) *cis*-1,3-cyclohexanediol
 (d) *trans*-1, 3-cyclohexanediol
- 18.** Correct configuration of the following is [2005]
-
- (a) 1S, 2S (b) 1S, 2R
 (c) 1R, 2R (d) 1R, 2S
- 19.** Among the following, L-serine is : [2006]
- (a)
 (b)
 (c)
 (d)
- 20.** Methyl- α - D-glucoside and methyl- β -D-glucoside are: [2006]
- (a) Epimers
 (b) Anomers
 (c) Enantiomers
 (d) Conformational diastereomers
- 21.** Chain transfer reagent is [2007]
- (a) CCl_4 (b) CH_4
 (c) O_2 (d) H_2
- 22.** The correct structure of 4-bromo-3-methylbut-1-ene is [2008]
- (a) $\text{Br}-\text{CH}=\text{C}(\text{CH}_3)_2$
 (b) $\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{Br}$
 (c) $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$
 (d) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CHCH}_2-\text{Br}$

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23. Spin isomerism is shown by [2008] 29. The incorrect IUPAC name is [2012]
- (a) dichlorobenzene (b) hydrogen
 - (c) dibasic acid (d) *n*-butane
24. The correct stability order of following species is – [2009]
-
- (a) $x > y > w > z$ (b) $y > x > w > z$
 (c) $x > w > z > y$ (d) $z > x > y > w$
25. Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions? [2010]
- (a) Methyl acetate (b) Acetonitrile
 - (c) Diethyl ether (d) Acetamide
26. The correct IUPAC name for [2011]
-
- (a) 5-methyl-4-(1'-2'-dimethylpropyl) heptane
 (b) 3-methyl-4-(1',2'-dimethylpropyl) heptane
 (c) 2,3,5-trimethyl-4-propylheptane
 (d) 4-propyl-2,3,5-trimethylheptane
27. Which of the cations in more stable? [2011]
- (a) $\text{R}'-\overset{\text{H}}{\underset{|}{\text{C}}}^+ - \text{OR}$
- (b) $\text{R}'-\overset{\text{H}}{\underset{|}{\text{C}}}=\overset{+}{\text{OR}}$
- (c) both equal
 (d) both are unstable
28. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because [2012]
- (a) Silver halides are soluble in HNO_3
 - (b) Na_2S and NaCN are decomposed by HNO_3
 - (c) Ag_2S is soluble in HNO_3
 - (d) AgCN is soluble in HNO_3
29. The incorrect IUPAC name is [2012]
- (a) $\text{CH}_3-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{CH}-\text{CH}_3$
 $\text{O} \quad \text{CH}_3$
 2-methyl-3-butanone
 - (b) $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CH}_3$
 2, 3 -dimethylpentane
 - (c) $\text{CH}_3-\text{C}\equiv\text{CCH}(\text{CH}_3)_2$
 4-methyl-2-pentyne
 - (d) $\text{CH}_3-\overset{\text{Cl}}{\underset{|}{\text{CH}}}-\overset{\text{Br}}{\underset{|}{\text{CH}}}-\text{CH}_3$
 3-chloro-2-bromobutane
30. Among the following compounds (I-III), the correct order of reactivity towards electrophilic substitution reaction is [2012]
-
- I II III
 (a) II > III > I (b) III < I < II
 (c) I > II > III (d) I = II > III
31. The most stable carbanion among the following is [2012, 2013]
-
- (a) $\text{CH}_2-\text{CH}_2^-$
 (b) CH_2^-
 (c) CH_2^-
 (d) CH_2^-
32. Which one of the statements about $\text{HOH}_2\text{CCH}(\text{OH})\text{CHO}$ is not correct? It [2013]
- (a) is an isomer of 1, 3-dihydroxypropanone
 - (b) contains a tertiary alcoholic group
 - (c) has the same empirical formula as glucose
 - (d) can show optical isomerism

33. Which is the correct order of stability of the following three carbonium ions? [2014]

$\text{CH}_2 = \text{CH}^+ \text{CH}_3$ I $\text{CH}_2 = \text{C}(\text{CH}_3)^+ \text{CH}_2$ II $\text{CH}_3\text{CH} = \text{CH}^+ \text{CH}_2$ III

(a) I > II > III
 (b) II > I > III
 (c) I ≈ III > II
 (d) All are equally stable

34. The molecular formula of diphenyl methane, is $\text{C}_{13}\text{H}_{12}$. How many structural isomers are possible when one of the hydrogens is replaced by a chlorine atom? [2014]

(a) 6 (b) 4
 (c) 8 (d) 7

35. The compound $\text{CHCl} = \text{CHCHOHCOOH}$ with molecular formula $\text{C}_4\text{H}_5\text{O}_3\text{Cl}$ can exhibit [2014]

(a) geometric, optical position and functional isomerism
 (b) geometric, optical and functional isomerism only
 (c) position and functional isomerism only
 (d) geometric and optical isomerism only

36. Tautomerism is exhibited by – [2015]

(1)
 (2)
 (3)
 (4)

(a) (1), (3) and (4) (b) (2), (3), and (4)
 (c) All of these (d) None of these

37. Name of the compound given below is [2013, 2015]

(a) 3- methyl -4- ethyloctane (b) 2, 3- diethylheptane
 (c) 5- ethyl - 6- methyloctane (d) 4- ethyl- 3- methyloctane

38. Which of the following represents the given mode of hybridisation $sp^2-sp^2-sp-sp$ from left to right? [2015]

(a) $\text{H}_2\text{C} = \text{CH}-\text{C}\equiv\text{N}$
 (b) $\text{CH}\equiv\text{C}-\text{C}\equiv\text{CH}$
 (c) $\text{H}_2\text{C}=\text{C}=\text{C}=\text{CH}_2$
 (d)

39. In Lassaigne's test for the detection of halogens, the sodium fusion extract is first boiled with concentrated nitric acid. This is [2016]

(a) to remove silver halides
 (b) to decompose Na_2S and NaCN , if present
 (c) to dissolve Ag_2S
 (d) to dissolve AgCN , if formed

40. Which one among the following cannot exhibit enantiomerism? [2016]

(a) Diphenyl methanol
 (b) 1-Bromo-2-chlorobutane
 (c) 2-Butanol
 (d) Tartaric acid

41. The IUPAC name of the following compound is [2016]

$(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_3$

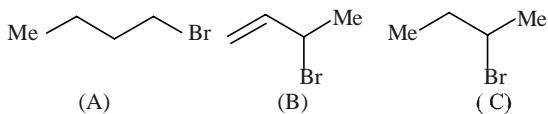
(a) 1,1,7,7-tetramethyl-2,5-octadiene
 (b) 2,8-dimethyl-3,6-decadiene
 (c) 1,5-di-iso-propyl-1,4-hexadiene
 (d) 2,8-dimethyl-4,6-decadiene

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42. Consider the following bromides :



The correct order of S_N1 reactivity is

[2016]

- (a) B > C > A (b) B > A > C
 (c) C > B > A (d) A > B > C

43. The strongest ortho - para and strongest meta - directing groups respectively are [2017]

- (a) $-NO_2$ and $-NH_2$
 (b) $-CONH_2$ and $-NH_2$
 (c) $-NH_2$ and $-CONH_2$
 (d) $-NH_2$ and $-NO_2$

44. Hybridisation states of C in CH_3^+ and CH_4 are

[2017]

- (a) sp^2 & sp^3 (b) sp^3 & sp^2
 (c) sp^2 & sp^2 (d) sp^3 & sp^3

45. The increasing order of stability of the following free radicals is [2017]

- (a) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$
 (b) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
 (c) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$
 (d) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs.46-48) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 (c) If Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

46. **Assertion :** In the third group of qualitative analysis, NH_4Cl is added to NH_4OH medium.

Reason : This is to convert the ions of group into their respective chlorides. [2014]

47. **Assertion :** Carbanions like ammonia have pyramidal shape. [2015]

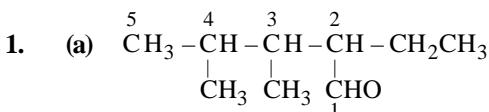
Reason : The carbon atom carrying negative charge has an octet of electrons.

48. **Assertion :** NF_3 is a weaker ligand than $N(CH_3)_3$. [2017]

Reason : NF_3 ionizes to give F^- ions in aqueous solution.

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Type A : Multiple Choice Questions



2. (c) No. of asymmetric carbon = 2

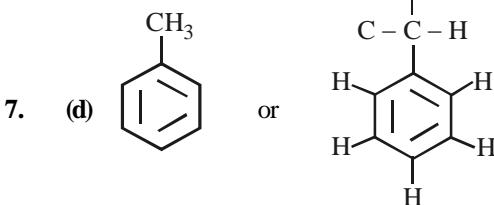
No. of enantiomers = $2^2 = 4$.

3. (a) Pyrolysis is the process of decomposition of organic compound by the application of heat.

4. (a) Turpentine oil is volatile and is insoluble in water. Therefore, it can be purified by steam distillation.

5. (a) Molecular formula of $\text{CH}_3\text{COOH} = \text{C}_2\text{H}_4\text{O}_2$
Both the compounds given have same empirical formula that is CH_2O . So, percentage of carbon in both of them will be same.

6. (a) Tertiary carbonium ion has highest stability followed by secondary and then primary carbonium ion. So, option (a) is correct.

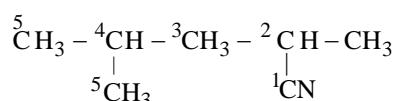


There are 15σ bonds in toluene, so 30σ -electrons.

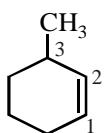
8. (c) Magnesium reacts only with H_2O to form insoluble $\text{Mg}(\text{OH})_2$ and not with alcohol.



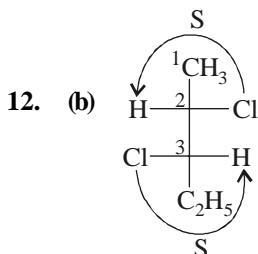
9. (b) 2, 4-Dimethylcyanopentane



10. (a) The IUPAC name is 3-methylcyclohexene.

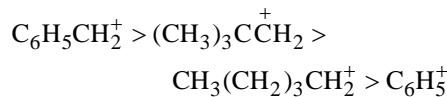


11. (d) The most reactive nucleophile will be $(\text{CH}_3)_3-\text{CO}^-$ due to +I effect of three $-\text{CH}_3$ groups.



So compound is (2S, 3S)

13. (a) Among the carbonium ions formed by the cleavage of the C—H bond, the order of stability is :



As $\text{C}_6\text{H}_5\text{CH}_2^+$ is most stable so, in $\text{C}_6\text{H}_5\text{CH}_2$ —H, C—H bond energy will be lowest.

14. (c) Dipole moment will be highest in case of acetophenone as it has strong electron withdrawing group.

15. (d) Geometrical isomerism is observed when different groups are attached to each of the doubly bonded carbon atom.

16. (a) Strongest nucleophile is $\text{C}_2\text{H}_5\text{SH}$.

In this compound S is electron pair donor.
Since S is least electronegative, hence, its tendency to donate electron pair is highest.

17. (d) Among 1, 2- and 1, 3- configurations, 1, 3- is more stable due to less repulsion.

Further among *cis* and *trans* isomers, *trans* is more stable due to less crowding.

18. (a)

19. (c)

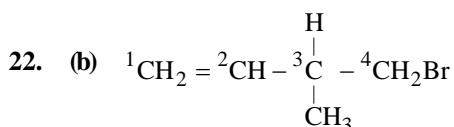
20. (b) In α -D glucoside $-\text{OCH}_3$ group at C_1 is towards right while in β -D glucose, it is towards left at C_1 . Such pairs which differ around only C_1 in configuration are called *anomers*.

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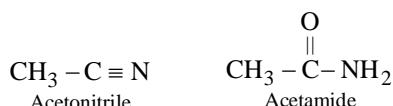
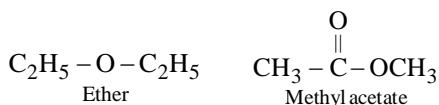
21. (a) Some molecules react with main growing chain to interrupt further growth of the original chain. This leads to lowering of average molecular mass of the polymer. Such reagents are called chain transfer agents. CCl_4 is the only chain transfer agent among the given options.



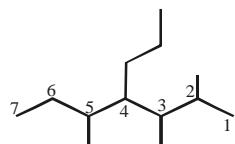
23. (b) Spin isomerism is shown by hydrogen. In *ortho-hydrogen*, the spin of nuclei of two atoms of the molecule are in same direction whereas in case of *para hydrogen*, the spin of nuclei of two atoms are in opposite direction.

24. (c) x is a conjugated diene system, w is an isolated diene system, z is a cumulated diene system, y is antiaromatic system.

25. (c) Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_3$) is resistant to nucleophilic attack because it does not have an electron deficient carbon.



26. (c) In case two or more chains are of equal length, then the chain with greater number of side chains is selected as the principal chain.

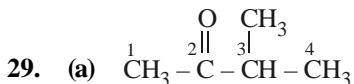
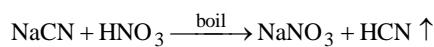
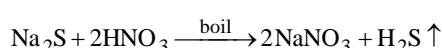
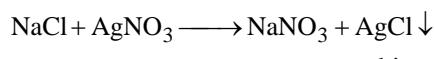
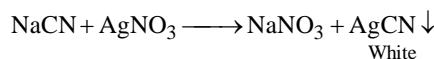
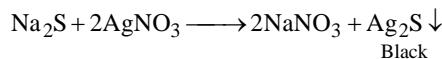


2, 3, 5-Trimethyl-4-propylheptane

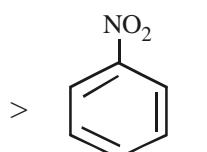
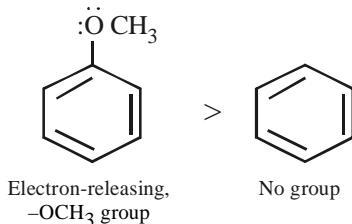
27. (b) Although (b) has positive charge on O (an electronegative element), it is more stable because here every atom has octet of electrons.

28. (b) Na_2S and NaCN , formed during fusion with metallic sodium, must be removed before adding AgNO_3 , otherwise black ppt. due

to Na_2S or white precipitate due to AgCN will be formed and thus white precipitate of AgCl will not be identified easily.



30. (c)

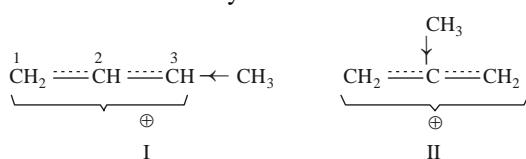


Electron-withdrawing,
 NO_2 group
hence deactivating

31. (d) $-\text{NO}_2$ group, being strong electron-withdrawing, disperses the negative charge, hence stabilizes the concerned carbanion.

32. (b) It has 1° and 2° alcoholic group, but not 3°

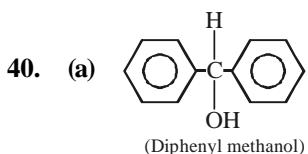
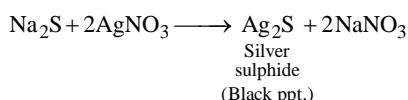
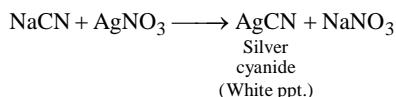
33. (c) Let us first write the resonance hybrid of the three allyl carbonium ions.



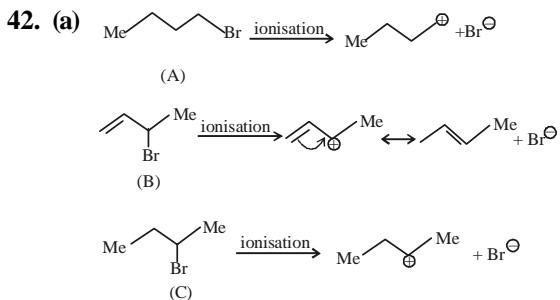
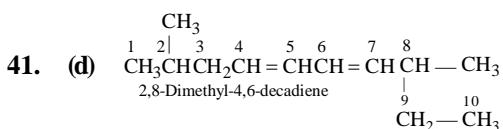
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It does not contain any chiral carbon atom.



Since $\text{S}_{\text{N}}1$ reactions involve the formation of carbocation as intermediate in the rate

determining step, more is the stability of carbocation higher will be the reactivity of alkyl halides towards $\text{S}_{\text{N}}1$ route. Now we know that stability of carbocations follows the order : $3^\circ > 2^\circ > 1^\circ$, so $\text{S}_{\text{N}}1$ reactivity should also follow the same order.

$3^\circ > 2^\circ > 1^\circ >$ Methyl (**$\text{S}_{\text{N}}1$ reactivity**)

43. (d)
 44. (a) Hybridisation of carbon in CH_3^+ is sp^2 and in CH_4 its hybridisation is sp^3
 45. (b) The order of stability of free radicals
 $(\text{C}_6\text{H}_5)_3\dot{\text{C}} > (\text{C}_6\text{H}_5)_2\dot{\text{CH}} > (\text{CH}_3)_3\dot{\text{C}} > (\text{CH}_3)_2\dot{\text{CH}}$

The stabilisation of first two is due to resonance and last two is due to inductive effect.

Type B : Assertion Reason Questions

46. (c) Assertion is true but reason is false. NH_4Cl suppresses the ionisation of NH_4OH due to common ion effect and so ions of third group get precipitated as their hydroxides.
 47. (b)
 48. (c) It is correct statement that NF_3 is a weaker ligand than $\text{N}(\text{CH}_3)_3$, the reason is that fluorine is highly electronegative therefore, it with draw electrons from nitrogen atom. Hence, the lone pair of nitrogen atom cannot be ligated. While $\text{N}(\text{CH}_3)_3$ is a strong ligand because CH_3 is electron releasing group.

Chapter

13

Hydrocarbons

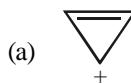
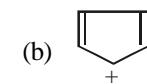
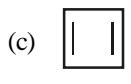
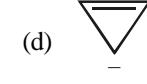
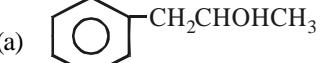
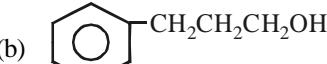
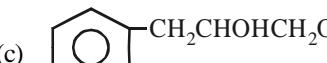
TYPE A : MULTIPLE CHOICE QUESTIONS

1. Which is not aromatic compound ? [1997]
 - (a) Cyclohexane
 - (b) Trinitrotoluene
 - (c) Picric acid
 - (d) Xylene
2. 1-Butyne and cold alkaline KMnO_4 react to produce : [1997]
 - (a) $\text{CH}_3\text{CH}_2\text{COOH}$
 - (b) $\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2$
 - (c) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$
 - (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
3. Which is used as antiknock in petrol ? [1997]
 - (a) Tetraethyl lead
 - (b) Tetramethyl lead
 - (c) Tetrapropyl lead
 - (d) Tetrabutyl lead
4. In the following reaction, Z is identified as

$$\text{CH} \equiv \text{CH} \xrightarrow{\text{Z}} \text{CH}_3\text{CHO}$$
 [1997]
 - (a) concentrated H_2SO_4
 - (b) CH_3COCl
 - (c) 20 % $\text{H}_2\text{SO}_4 + \text{HgSO}_4$
 - (d) CH_3OH
5. The number of σ and π bonds present in ethene is : [1997]
 - (a) 6σ
 - (b) 3σ
 - (c) $4\sigma, 2\pi$
 - (d) $5\sigma, 1\pi$
6. Glycerol contains [1997]
 - (a) one primary and two secondary alcoholic groups
 - (b) two primary and one secondary alcoholic groups
 - (c) one primary, one secondary and one tertiary alcoholic groups
 - (d) one secondary and two tertiary alcoholic groups
7. Prestone is a mixture of: [1998]
 - (a) Glycol + H_2O
 - (b) Glycerol + H_2O
 - (c) Acetone + H_2O
 - (d) propanal + H_2O
8. $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$
Benzene Methyl chloride Toluene
The above reaction is: [1998]
 - (a) Wurtz Fittig reaction
 - (b) Grignard reaction
 - (c) Friedel-Craft's reaction
 - (d) Ullmann reaction
9. Geometrical isomerism is possible in case of : [1999]
 - (a) tartaric acid
 - (b) 1-butene
 - (c) 2-butene
 - (d) propene
10. Alkynes usually show which type of reaction? [1999]
 - (a) Substitution
 - (b) Elimination
 - (c) Addition
 - (d) Replacement
11. The product obtained by treating benzene with chlorine in presence of ultraviolet light is: [1999]
 - (a) CCl_4
 - (b) $\text{C}_6\text{H}_5\text{Cl}$
 - (c) $\text{C}_6\text{H}_6\text{Cl}_6$
 - (d) C_6Cl_6
12. The natural gas mainly contains : [1999]
 - (a) methane
 - (b) propane
 - (c) butane
 - (d) pentane
13. Which compound can be sulphonated easily ? [1999]
 - (a) benzene
 - (b) toluene
 - (c) nitrobenzene
 - (d) chlorobenzene
14. With ammonical cuprous chloride solution, a reddish brown precipitate is obtained on treating with :
 - (a) CH_4
 - (b) C_2H_4
 - (c) C_2H_2
 - (d) C_3H_6
15. The boiling points of four saturated hydrocarbons are given below. Which boiling point suggests maximum number of carbon atoms in its molecule : [2001]
 - (a) -162°C
 - (b) -88.6°C
 - (c) -0.5°C
 - (d) -42.2°C

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16. The size of C – C bond in benzene is [2002]
 (a) 1.22 Å (b) 1.54 Å
 (c) 1.39 Å (d) 1.56 Å
17. Thermite is a mixture of iron oxide and [2002]
 (a) zinc powder
 (b) potassium metal
 (c) sodium shavings
 (d) aluminium powder
18. The treatment of benzene with isobutene in the presence of sulphuric acid gives : [2003]
 (a) iso-butylbenzene (b) tert-butylbenzene
 (c) n-butylbenzene (d) no reaction
19. The compound having only primary hydrogen atoms is : [2004]
 (a) isobutene (b) 2, 3-dimethylbutene-1
 (c) cyclohexane (d) propane
20. Among the following, the aromatic compound is :
 (a)  (b)  [2004]
 (c)  (d) 
21. Which of the following gives propyne on hydrolysis? [2005]
 (a) Al_4C_3 (b) Mg_2C_3
 (c) B_4C (d) La_4C_3
22. The major product obtained on treatment of $\text{CH}_3\text{CH}_2\text{CH}(\text{F})\text{CH}_3$ with $\text{CH}_3\text{O}^-/\text{CH}_3\text{OH}$ is : [2005]
 (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_3$ (b) $\text{CH}_3\text{CH}=\text{CHCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_3$
23. 3-Phenylpropene on reaction with HBr gives (as a major product) : [2005]
 (a) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$
 (b) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{OCH}_3$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
 (d) $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}=\text{CH}_2$
24. Below, some catalysts and corresponding processes/reactions are matched. The mismatch is :
 (a) $[\text{RhCl}(\text{PPh}_3)_2]$: Hydrogenation [2006]
 (b) $\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$: Polymerization
 (c) V_2O_5 : Haber-Bosch process
 (d) Nickel-Hydrogenation
25. Which of the following sequence of reactions (reagents) can be used for the conversion of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ into $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$? [2006]
 (a) $\text{SOCl}_2 : \text{H}_2\text{O}$ (b) $\text{SO}_2\text{Cl}_2 : \text{alc KOH}$
 (c) $\text{Cl}_2 / h\nu : \text{H}_2\text{O}$ (d) $\text{SOCl}_2 : \text{alc KOH}$
26. Propene on hydroboration and oxidation produces [2007]
 (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (b) $\text{CH}_3\text{CHOHCH}_3$
 (c) $\text{CH}_3\text{CHOHCH}_2\text{OH}$
 (d) $\text{CH}_3\text{CH}_2\text{CHO}$.
27.  [2007]
 on mercuration and demercuration produces
 (a) 
 (b) 
 (c) 
 (d) none of these.
28. Which of the following species participate in sulphonation of benzene ring ? [2007]
 (a) H_2SO_4 (b) SO_3
 (c) HSO_3^- (d) SO_2^-
29. The most important method of preparation of hydrocarbons of lower carbon number is [2009]
 (a) Pyrolysis of higher carbon number of hydrocarbons
 (b) Electrolysis of salts of fatty acids
 (c) Sabatier and Senderen's reaction
 (d) Direct synthesis
30. The alkene $\text{R} - \text{CH} = \text{CH}_2$ reacts readily with B_2H_6 and formed the product B which on oxidation with alkaline hydrogen peroxide produces [2010]
 (a) $\text{R} - \text{CH}_2 - \text{CHO}$
 (b) $\text{R} - \text{CH}_2 - \text{CH}_2 - \text{OH}$
 (c) $\text{R} - \underset{\text{CH}_3}{\text{C}} = \text{O}$
 (d) $\text{R} - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}_2}$

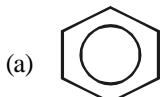
31. 1-Butyne can be distinguished most easily from 2-butyne by [2011]

(a) bromine water (b) ozonolysis
 (c) Tollen's reagent (d) KMnO_4 solution

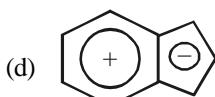
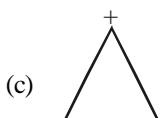
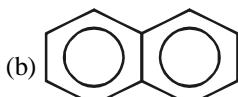
32. Compound X of molecular formula C_4H_6 takes up one equivalent of hydrogen in presence of Pt to form another compound Y which on ozonolysis gives only ethanoic acid. The compound X can be [2011]

(a) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
 (b) $\text{CH}_2 = \text{C} = \text{CHCH}_3$
 (c) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 (d) All the three

33. The chemical system that is non-aromatic is



[2012]



34. Consider the following statements : A hydrocarbon of molecular formula C_5H_{10} is a I. monosubstituted alkene II. disubstituted alkene III. trisubstituted alkene

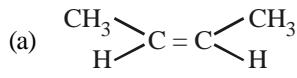
Which of the following statement(s) is(are) correct? [2012]

(a) I, II and III (b) I and II
 (c) II and III (d) I and III

35. Which one of the following cannot be prepared by Wurtz reaction ? [2012]

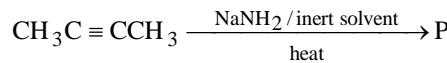
(a) CH_4 (b) C_2H_6
 (c) C_3H_8 (d) C_4H_{10}

36. Which of the following has the lowest dipole moment ? [2013]



(b) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 (d) $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$

37. Predict the nature of P in the following reaction



[2014]

(a) $\text{CH}_2 = \text{CHCH} = \text{CH}_2$
 (b) $\text{CH}_2 = \text{C} = \text{CHCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 (d) No reaction

38. Which of the following would not give 2-phenylbutane as the major product in a Friedel-Crafts alkylation reaction ? [2014]

(a) 1-butene + HF
 (b) 2-butanol + H_2SO_4
 (c) Butanoyl chloride + AlCl_3 then Zn, HCl
 (d) Butyl chloride + AlCl_3

39. Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds ? [2015]

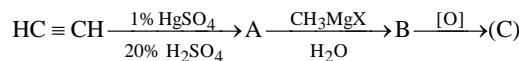
1. $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$
2. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
3. $\text{CH}_3 - \text{CH}_2\text{C} \equiv \text{CH}$
4. $\text{CH}_3 - \text{CH} = \text{CH}_2$.

(a) Bromine in carbon tetrachloride
 (b) Bromine in acetic acid
 (c) Alk KMnO_4
 (d) Ammonical silver nitrate.

40. The alkene that will give the same product with HBr in the absence as well as in the presence of peroxide is [2016]

(a) 2-butene (b) 1-butene
 (c) propene (d) 1-hexene

41. The end product (C) in the following sequence of reactions is [2017]



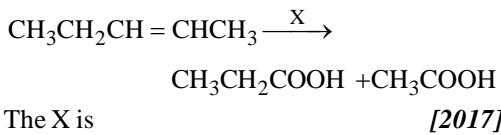
(a) acetic acid (b) isopropyl alcohol
 (c) acetone (d) ethanol

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42. In the given reaction



- (a) $\text{C}_2\text{H}_5\text{ONa}$
- (b) Conc. HCl + Anhy. ZnCl_2
- (c) Anh. AlCl_3
- (d) $\text{KMnO}_4/\text{OH}^-$

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 43-53) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

43. **Assertion :** CH_4 does not react with Cl_2 in dark.
Reason : Chlorination of CH_4 takes place in sunlight. [2001]

44. **Assertion :** Alkylbenzene is not prepared by Friedel-Craft alkylation of benzene.
Reason : Alkyl halides are less reactive than acyl halides. [2003]

45. **Assertion :** *trans*-2-Butene on reaction with Br_2 gives *meso*-2, 3-dibromobutane.
Reason : The reaction involves *syn*-addition of bromine. [2003]

46. **Assertion :** 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.
Reason : 1-Butene is more stable than 2-butene [2004]

According to Saytzeff's rule, 2-butene should be the product which is more branched or substituted compound and hence, more stable than butene-1

47. **Assertion :** Rates of nitration of benzene and hexadeuterobenzene are different.

Reason : C–H bond is stronger than C–D bond. [2005]

48. **Assertion :** Cyclopentadienyl anion is much more stable than allyl anion.

Reason : Cyclopentadienyl anion is aromatic in character. [2005]

49. **Assertion :** 1, 3-Butadiene is the monomer for natural rubber.

Reason : Natural rubber is formed through anionic addition polymerization. [2006]

50. **Assertion :** Addition of HBr on 2-butene gives two isomeric products.

Reason : Addition of HBr on 2-butene follows Markovnikov rule. [2006]

51. **Assertion :** *trans*-butene-2 on reaction with bromine forms racemic mixture.

Reason : *trans*-Compound in *trans* addition forms two types of stereoisomers. [2007]

52. **Assertion :** Acetylene on reacting with sodamide gives sodium acetylide and ammonia.

Reason : *sp* hybridised carbon atoms of acetylene are considerably electronegative. [2007]

53. **Assertion :** Friedel-Craft's reaction is used to introduce an alkyl or acyl group in benzene nucleus.

Reason : Benzene is a solvent for the Friedel-Craft's alkylation of bromobenzene. [2008]

Directions for (Qs.54-61) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.

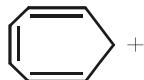
- (c) If Assertion is correct but Reason is incorrect.

- (d) If both the Assertion and Reason are incorrect.

54. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.

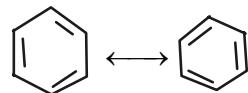
Reason : It involves the free radical mechanism. [2009]

55. **Assertion :** Benzene removes a butter stain from a table cloth.
Reason : Butter has an affinity towards benzene. [2010]
56. **Assertion :** Trans-2-butene on reaction with Br₂ gives meso-2, 3-dibromobutane.
Reason : The reaction involves syn-addition of bromine. [2009, 2014]
57. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Reason : It involves the formation of a primary radical. [2015]
58. **Assertion :** Nitrating mixture used for carrying out nitration of benzene consists of conc. HNO₃ + conc. H₂SO₄.
Reason : In presence of H₂SO₄, HNO₃ acts as a base and produces NO₂⁺ ions. [2015]
59. **Assertion :** Energy of resonance hybrid is equal to the average of energies of all canonical forms.
Reason : Resonance hybrid cannot be presented by a single structure. [2016]
60. **Assertion :** Tropylium cation is aromatic in nature



Reason : The only property that determines its aromatic behaviour is its planar structure. [2014, 2016]

61. **Assertion :** Benzene exhibit two different bond lengths, due to C – C single and C = C double bonds. [2017]
- Reason :** Actual structure of benzene is a hybrid of following two structures.



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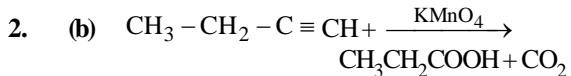
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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

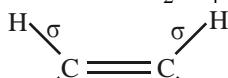
1. (a) Aromatic compounds are closed chain planar compounds with $(4n + 2)\pi$ electrons and show delocalization of π electrons. Cyclohexane does not coincide with this definition as it does not have benzene ring, while other three have benzene ring.



3. (a) Tetraethyl lead (TEL) is used as antiknock in petrol.

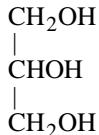


So, z is 20% $\text{H}_2\text{SO}_4 + \text{HgSO}_4$



5. (d) No. of σ bonds 5 and no. of π bond = 1

6. (b) The structure of glycerol is



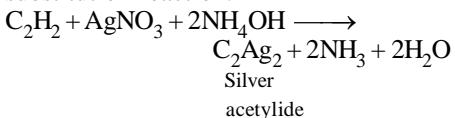
It contains two primary and one secondary alcoholic groups.

7. (a) Prestone is a mixture of glycol & H_2O . It has freezing point much below 0°C , hence it is used as an antifreeze for automobile radiators.

8. (c) The given reaction is known as Friedel-Crafts reaction.

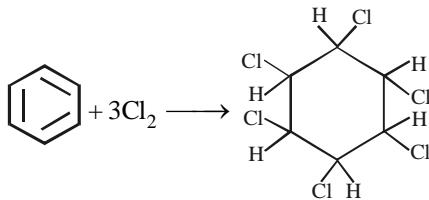
9. (c) Geometrical isomerism is shown by molecules containing double bond having unlike groups on each of the doubly bonded carbon atom.

10. (c) In most cases, alkynes show addition reactions as they contain two double bonds. In some cases, it undergoes substitution reaction.



This reaction occurs only in terminal alkynes.

11. (c) In presence of sunlight, benzene reacts with chlorine to form addition product.

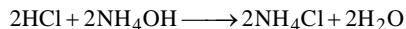


Benzene hexachloride

12. (a) Natural gas contains mainly methane

13. (b) Sulphonation is electrophilic substitution reaction of benzene. This reaction is facilitated by any group having +I effect (inductive effect). As CH_3 has +I effect, toluene facilitates this reaction most.

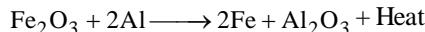
14. (c) Acetylene forms brown copper acetylid with ammonical cuprous chloride solution.



15. (c) The heavier the molecule, greater is the boiling point. So molecule with boiling point -0.5°C will have maximum number of carbon atoms.

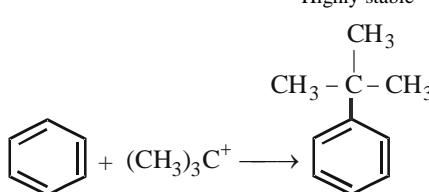
16. (c) The size of C – C bond in benzene is 1.39 \AA which lies between 1.34 \AA (bond length of C – C) and 1.54 \AA (bond length of C = C).

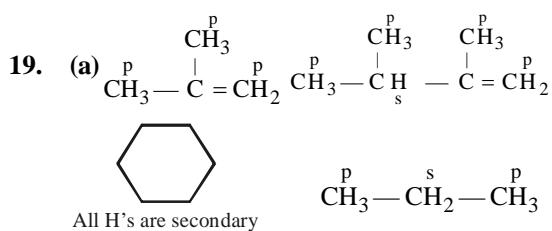
17. (d) Thermite is a mixture of iron oxide and Al powder. Al reduces iron oxide to iron giving out enormous heat.



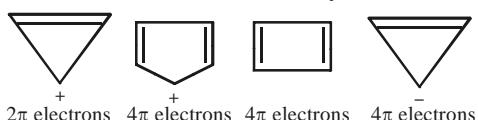
18. (b) $\text{CH}_2 = \text{C} - \text{CH}_3 + \text{H}^+ \longrightarrow \text{CH}_3 - \underset{\text{CH}_3}{\text{C}}^+ - \text{CH}_3$

Highly stable

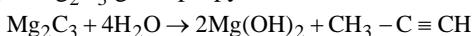




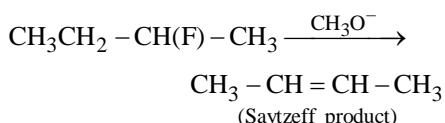
- 20. (a)** According to Huckel's rule, the cyclic planar conjugated system having $(4n + 2)\pi$ electrons show aromaticity.



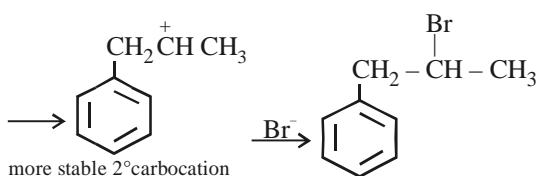
- 21. (b)** Mg_2C_3 gives propyne.



22. (b) $\text{CH}_3\text{CH}_2 - \text{CH}(\text{F}) - \text{CH}_3$ is a secondary halide. So, it will undergo dehydrohalogenation to form alkene.

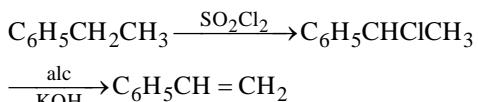


23. (a) 
3-Phenylpropene

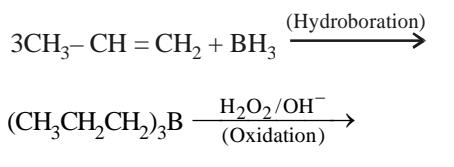


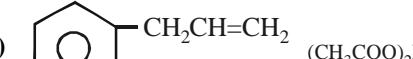
24. (c) V_2O_5 is used as a catalyst in contact process for the manufacture of SO_3 and hence H_2SO_4 . In Haber-Bosch process for the manufacture of NH_3 , finely divided Fe + molybdenum are used.

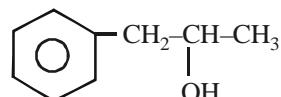
25. (b) SO_2Cl_2 causes free radical substitution at benzylic position.



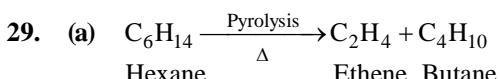
26. (a) Propene on hydroboration and oxidation produces propanol



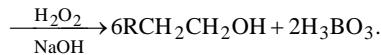
27. (a) 



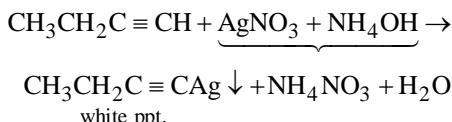
28. (b) SO_3 participates in sulphonation of benzene.



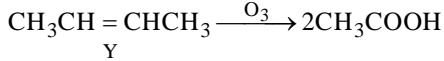
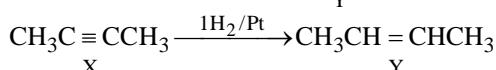
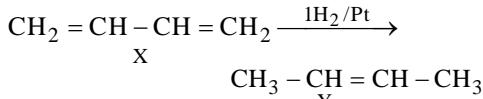
30. (b) $6R - CH = CH_2 \xrightarrow[\text{Ether, } 0^\circ C]{B_2H_6} 2(RCH_2CH_2)_3B$



31. (c) Tollen's reagent is ammonical silver nitrate which reacts with 1-alkynes to form white precipitate of silver alkynide.



32. (d) Formation of only CH_3COOH by ozonolysis indicates that the compound Y should be $\text{CH}_3\text{CH}=\text{CHCH}_3$ which can be formed by all of the three given compounds



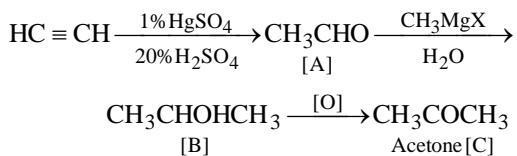
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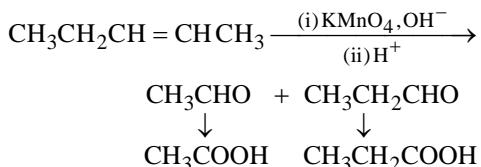
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33. (c) 34. (a)
 35. (a) CH_4 has only one carbon atom, hence it can't be prepared by Wurtz reaction, which involves two molecules of alkyl halide.
 36. (b) $\text{CH}_3\text{C} \equiv \text{CCH}_3$, being symmetrical, has the lowest dipole moment
 37. (c) When non-terminal alkynes are heated with NaNH_2 in an inert solvent, the triple bond migrates to the end carbon atom.
 38. (c) The Friedel-crafts alkylation reaction will give propyl phenyl ketone which further on Clemmenson's reduction will give butyl benzene
 39. (d) Br_2 in CCl_4 (a), Br_2 in CH_3COOH (b) and alk. KMnO_4 (c) will react with all unsaturated compounds, i.e., 1, 3 and 4 while ammonical AgNO_3 (d) reacts only with terminal alkynes, i.e., 3 and hence 3 can be distinguished from 1, 2 and 4 by ammonical AgNO_3 (d).
 40. (a) The addition of HBr takes place according to anti-Markovnikoff's rule in presence of peroxide for unsymmetrical alkenes.
 The addition of HBr to symmetrical alkenes is not affected by the presence or absence of peroxide.

41. (c)



42. (d) A doubly bonded carbon atom having an alkyl group is oxidised to aldehyde which is further oxidised to carboxylic acid.



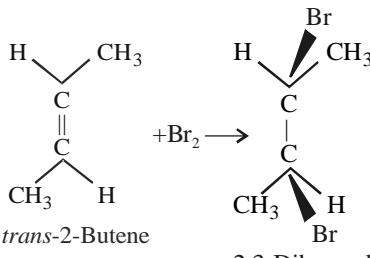
Type B : Assertion Reason Questions

43. (b) Chlorination of CH_4 takes place either in presence of light or at high temperature, and not in dark because in darkness, Cl free radicals are not produced.
 44. (b) Alkylbenzene is not prepared by Friedel-Crafts alkylation because monoalkyl product

undergoes alkylation to produce polyalkylated benzene. Further the reason that "acyl halides are more reactive than alkyl halides" although not correct explanation of the assertion it is true because acyl halides are more electron deficient than alkyl halides

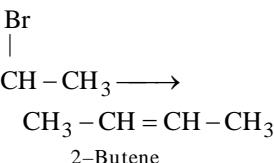


45. (c)



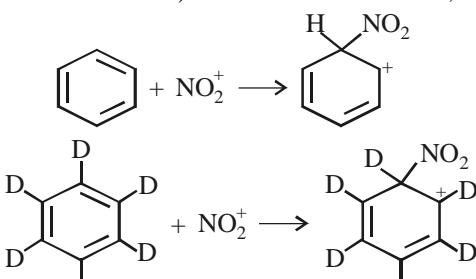
The reaction is *trans* addition of Br_2 and not *syn* addition.

46. (d)



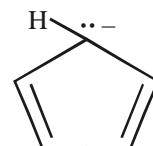
47. (d)

Rates of nitration of benzene and hexadeuterobenzene are same because the rate determining step (formation of carbocation) is same in both the cases, i.e.,



it does not involve the cleavage of C—H / C—D bond which takes in the second step.

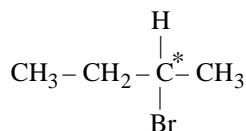
48. (a)



Cyclopentadienyl anion contains 6π electrons, so it is aromatic and stabilised

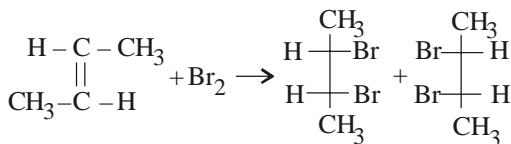
by resonance. Thus it is more stable than allyl anion which is not aromatic, although it is also stabilised by resonance.

49. (d) Natural rubber is polymer of isoprene. Thus assertion is false. Further the reason is also false because 1, 3- butadiene undergoes free radical polymerisation rather than anionic.
 50. (c) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ on reaction with HBr gives



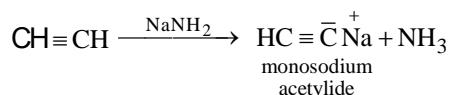
which contains one chiral carbon. So, it will give two optical isomers. Hence A is correct. Since 2-butene is symmetrical molecule so it will not follow Markownikov rule. Thus R is false.

51. (d) On *anti* addition of Br_2 to *trans*-butene-2, we get *meso* compounds



While *syn* addition gives a racemic mixture. Hence both assertion and reason are false.

52. (a) Acetylene on reaction with sodamide gives sodium acetylidyde and ammonia.



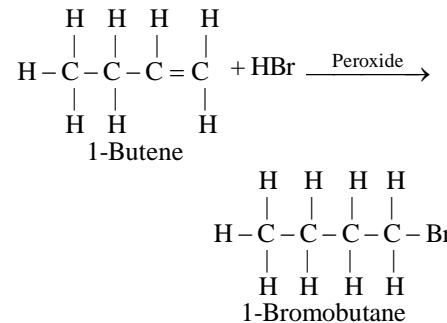
Here formation of sodium acetylidyde can be explained by *sp*-hybridisation of carbon atom. As we know that an electron in *s*-orbital is more tightly held than in a *p*-orbital. In *sp* hybridisation, *s*-character is 50% as compared to *sp*² (33%) or *sp*³ (25%). So, due to large *s*-character the carbon atom is quite electronegative and hence Na of NaNH_2 can replace H^+ of C–H bond.

Hence assertion and reason both are true and reason is the correct explanation of assertion.

53. (c) Yes, we use Friedel-Crafts reaction for introducing an alkyl or acyl group in benzene nucleus. Thus, assertion is true. However, the reason is not true because if benzene is used as a solvent, during

alkylation of bromobenzene, benzene will be alkylated in preference to bromobenzene because benzene is more reactive for S_E than bromobenzene.

54. (a) This reaction takes place against Markovnikoff's rule

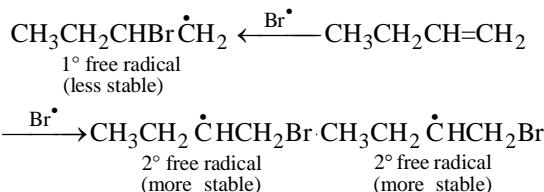


In this reaction *anti*-Markovnikoff's addition is explained on the basis of the fact that in the presence of peroxide the addition takes place via a free radical mechanism.

55. (b) Benzene is a non-polar solvent. Butter is composed of organic compounds of low polarity. So, it gets dissolved in benzene.

56. (c) The assertion that *trans*-2 butene reacts with Br_2 to product *meso*-2, 3-dibromobutane is correct but it does not involve *syn*-addition of Br_2 .

57. (c) Here assertion is correct but reasoning is incorrect. In presence of peroxide, addition of HBr on alkenes takes place via free radicals; here two free radical are formed, *2° free radical, being more stable, governs the product.*



58. (a) $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{HSO}_4^- + \text{NO}_2^+ + \text{H}_3\text{O}^+$

59. (d)

60. (c) $(4n + 2)\pi$ electrons and planar structure are the essential conditions for aromaticity.

61. (c) Benzene has a uniform C – C bond distance of 139 pm, a value intermediate between the C – C single. (154 pm) and C = C double (134 pm) bonds.

Chapter

14

Environmental Chemistry

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Nitrolium is; [1999]
 - (a) CaCN_2
 - (b) $\text{Ca}(\text{CN})_2$
 - (c) $\text{CaCN}_2 + \text{C}$
 - (d) $\text{Ca}(\text{NO}_3)_2$
2. Which one of the following is not a green house gas? [2001]
 - (a) CO_2
 - (b) H_2O
 - (c) N_2
 - (d) O_3
3. Which of the following is not a green house gas? [2003]
 - (a) Carbon dioxide
 - (b) Water vapour
 - (c) Oxygen
 - (d) Methane
4. Ozone in stratosphere is depleted by: [2004]
 - (a) CF_2Cl_2
 - (b) C_7F_{16}
 - (c) $\text{C}_6\text{H}_6\text{Cl}_6$
 - (d) C_6F_6
5. The secondary precursors of photochemical smog are [2014]
 - (a) SO_2 and NO_2
 - (b) SO_2 and hydrocarbons
 - (c) NO_2 and hydrocarbons
 - (d) O_3 and PAN
6. The irritant red haze in the traffic and congested places is due to presence of which of the following ?
 - (i) Oxides of sulphur
 - (ii) Oxides of nitrogen

(iii) Carbon dioxide

(iv) Mists, smoke and dust

(v) Smog

[2016]

(a) (i), (iv) and (v) (b) (iii) only

(c) (ii) only (d) (ii) and (v)

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs.7-8) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

7. **Assertion :** Photochemical smog is produced by nitrogen oxides.

Reason : Vehicular pollution is a major source of nitrogen oxides. [2003]

8. **Assertion :** Suspended particulate matter (SPM) is an important pollutant released by diesel vehicles. [2015]

Reason : Catalytic converters greatly reduce pollution caused by automobiles.

HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (c) Nitrolium is the name of a fertilizer which is chemically a mixture of $\text{CaCN}_2 + \text{C}$. It reacts with water to form ammonia, vital for plants.

$$\text{CaCN}_2 + 3\text{H}_2\text{O} \longrightarrow \text{CaCO}_3 + 2\text{NH}_3$$
2. (c) Most of the radiations of the sun falling on earth are radiated back in the space. However, certain atmospheric gases, like CO_2 , O_3 , water vapour, chlorofluorocarbons, oxides of nitrogen etc. trap these radiations. This is known as green house effect.
3. (c) **Greenhouse gases** (GHGs) are gaseous components of the atmosphere that contribute to the “greenhouse effect”. Although uncertainty exists about exactly how earth’s climate responds to these gases, global temperatures are rising. Some greenhouse gases occur naturally in the atmosphere, while others result from human activities. Naturally occurring greenhouse gases include water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Certain human activities, however, add to the levels of most of these naturally occurring gases. **Note :** Greenhouse gases act as blanket to the earth and keep it at about 33°C ; warmer than it would be without these gases in the atmosphere.
4. (a) Ozone is depleted by CF_2Cl_2 (dichlorodifluoromethane or freon.)
5. (d)
6. (c) The irritant red haze in the traffic and congested places is due to the presence of oxides of nitrogen.

Type B : Assertion Reason Questions

7. (b) It is correct that photochemical smog is produced by oxides of nitrogen and it is also a fact that vehicular pollution is a major source of nitrogen oxides but it is not the correct explanation of assertion.
8. (b) SPM (Suspended Particulate Matter) is defined as particles floating in the air with a diameter below $10 \mu\text{m}$. Studies have shown that high SPM concentrations in the air can have a detrimental impact on respiratory organs. SPM is generated from natural sources (e.g., volcanoes or dust storms) and human activities (vehicles, incinerators and industrial plants).

SPM	Other aerosols
Less than $10 \mu\text{m}$	Less than $100 \mu\text{m}$
Tend to float longer in Air due to small size	Tend to settle fairly quickly due to comparative heaviness

Catalytic converters is a device designed to reduce the amount of emissions from automobiles. The current (so-called three-way) systems use a heated metal catalyst to reduce the emissions of carbon monoxide (CO), hydrocarbons, and nitric oxide (NO), all of which contribute to the formation of photochemical smog. In an automobile’s exhaust system, a catalytic converter provides an environment for a chemical reaction where unburned hydrocarbons completely combust.

Chapter

15**The Solid State****TYPE A : MULTIPLE CHOICE QUESTIONS**

1. Schottky defect defines imperfection in the lattice structure of [2002]

(a) solid	(b) gas
(c) liquid	(d) plasma
2. An AB_2 type structure is found in [2002]

(a) NaCl	(b) CaF_2
(c) Al_2O_3	(d) N_2O
3. An element (atomic mass 100 g/mol) having *bcc* structure has unit cell edge 400 pm. The density of element is (No. of atoms in *bcc*, $Z=2$). [2002]

(a) 2.144 g/cm ³	(b) 7.289 g/cm ³
(c) 5.188 g/cm ³	(d) 10.376 g/cm ³
4. What is the coordination number of sodium in Na_2O ? [2003]

(a) 6	(b) 4
(c) 8	(d) 2
5. The crystal system of a compound with unit cell dimensions " $a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ " is: [2004]

(a) cubic	(b) hexagonal
(c) orthorhombic	(d) rhombohedral
6. If z is the number of atoms in the unit cell that represents the closest packing sequence ABC ABC , the number of tetrahedral voids in the unit cell is equal to: [2005]

(a) z	(b) $2z$
(c) $z/2$	(d) $z/4$
7. The compound, found in nature in gas phase but ionic in solid state is: [2006]

(a) PCl_5	(b) CCl_4
(c) PCl_3	(d) POCl_3
8. The Ca^{2+} and F^- are located in CaF_2 crystal, respectively at face centred cubic lattice points and in [2006]

(a) Tetrahedral voids	(b) Half of tetrahedral voids
(c) Octahedral voids	(d) Half of octahedral voids
9. The coordination number in *hcp* is [2007]

(a) 6	(b) 12
(c) 18	(d) 24
10. The space lattice of graphite is [2009]

(a) Cubic	(b) Tetragonal
(c) Rhombic	(d) Hexagonal
11. Coordination numbers of Zn^{2+} and S^{2-} in the crystal structure of wurtzite are [2010]

(a) 4,4	(b) 6,6
(c) 8,4	(d) 8,8
12. Gold has a face centred cubic lattice with an edge length of the unit cube of 407 pm. Assuming the closest packing, the diameter of the gold atom is [2011]

(a) 576.6 pm	(b) 287.8 pm
(c) 352.5 pm	(d) 704.9 pm
13. Which is *not* correct about the Schottky defects? [2011]

(a) Both cations and anions are missing from their lattice sites without affecting the stoichiometry of the compound	(b) Because of presence of holes the lattice energy decreases.
(c) The presence of holes causes the density of the crystal to decrease.	(d) The defect increases the electrical conductivity of the solid due to migration of the ions into the holes.
14. The existence of a substance in more than one solid modifications is known as [2012]

(a) isomorphism	(b) Polymorphism
(c) Amorphism	(d) Allotropy
15. An element (atomic mass = 100 g / mol) having *bcc* structure has unit cell edge 400 pm. Then, density of the element is [2013]

(a) 10.376 g/cm ³	(b) 5.188 g/cm ³
(c) 7.289 g/cm ³	(d) 2.144 g/cm ³

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs.21-26) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.

(c) If Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

21. **Assertion :** Graphite is an example of tetragonal crystal system.

Reason : For a tetragonal system, $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. [2006]

22. **Assertion :** No compound has both Schottky and Frenkel defects.

Reason : Both defects change the density of the solid. [2008]

23. **Assertion :** Stability of a crystal is reflected in the magnitude of its melting.

Reason : The stability of a crystal depends upon the strength of the interparticle attractive force. [2009]

24. **Assertion :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.

Reason : In Frenkel defect, no cation or anion leaves the crystal. [2011]

25. **Assertion :** On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.

Reason : The electrons change their spin on heating. [2014]

26. **Assertion :** In close packing of spheres, a tetrahedral void is surrounded by four spheres whereas an octahedral void is surrounded by six spheres.

Reason : A tetrahedral void has a tetrahedral shape whereas an octahedral void has an octahedral shape. [2015]

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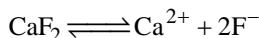
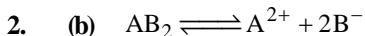
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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (a) Schottky defects are found in solids.



3. (c) Mass of two atoms = $\frac{100}{6.02 \times 10^{23}} \times 2 \text{ g}$
 $= \frac{2}{6.02} \times \frac{10^{-21}}{10^3} \text{ kg}$

$$\text{Volume of cell} = (4 \times 10^{-10})^3 = 64 \times 10^{-30}$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{2 \times 10^{-24}}{64 \times 10^{-30} \times 6.02}$$

$$\text{Density} = \frac{2}{6.02 \times 64} \times 10^6 \text{ kg/m}^3$$

 $= \frac{2 \times 10^6 \times 10^3}{6.02 \times 64 \times 10^6} \text{ g/cc}$

$$= \frac{2}{6.02 \times 64} \times 10^3 \text{ g/cc} = 5.188 \text{ g/cc}$$

4. (b) In Na_2O there is antifluorite structure. Here negative ions form the CCP arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion is surrounded by 8 positive ions. So coordination no. of Na^+ is 4.

5. (b) $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

These are the characteristics of a hexagonal system.

6. (b) In cubic closed pack system (CCP system)ABCABC..... type of arrangement of layers is found. In this system, there are atoms at the corners as well as centre of the unit cell.

$$\therefore \text{No. of atoms per unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

Hence, the no. of tetrahedral voids in a unit cell = $2z$

7. (a) PCl_5 exists in gas phase, however it remains in solid state in ionic form in the form of $[\text{PCl}_4]^+ [\text{PCl}_6]^-$. The cation is tetrahedral and anion is octahedral.

8. (a) F^- are in tetrahedral voids. Four atoms of Ca^{2+} and eight atoms of F^- are in unit cell. Each F^- atom occupies 8 tetrahedral voids.

9. (b) In this structure, each atom is surrounded by twelve nearest touching neighbours. Hence coordination number is 12.

10. (d) In graphite, the carbon atoms are arranged in regular hexagons in flat parallel layers and this fact is responsible for its softness and lubricating action.

11. (a) Wurtzite has *face centred cubic* structure in which each Zn^{2+} ion is attached to four S^{2-} ions and each S^{2-} ion remains in contact with four Zn^{2+} ions. Hence coordination number of each ion is 4.

12. (b) For fcc lattice,

$$4r = \text{diagonal of the face} = a\sqrt{2}$$

or $2r = \text{diameter}$

$$= \frac{a\sqrt{2}}{2} = \frac{407 \times \sqrt{2}}{2} = 287.8 \text{ pm}$$

13. (b)

14. (b)

15. (b) $\rho = \frac{z \times M}{N_A \times a^3} = \frac{2 \times 100}{6.023 \times 10^{23} \times (400 \times 10^{-10})^3}$
 $= 5.188 \text{ g/cm}^3$

16. (b) For each central atom there are two tetrahedral voids in AgI crystal. The number of Ag^+ ion is equal to number of I^- ion. It means only 50% of the void will be occupied by Ag^+ ion.

17. (a) ZnS has cubic close packed (CCP) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, S^{2-} ion is surrounded by four Zn^{2+} ions.

18. (c) C_6H_6 is diamagnetic (i - 5)
 CrO_2 is ferromagnetic (ii - 3)
 MnO is antiferromagnetic (iii - 1)
 Fe_3O_4 is ferrimagnetic (iv - 2)

Fe^{3+} is paramagnetic with 5 unpaired electron ($v - 4$)

19. (c) The *hcp* arrangement of atoms occupies 74% of the available space and thus has 26% vacant space.

20. (c) In bcc the atoms touch along body diagonal

$$\therefore 2r + 2r = \sqrt{3}a$$

$$\therefore r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.857\text{\AA}$$

Type B : Assertion Reason Questions

21. (d) Like quartz and ice, graphite is an example of hexagonal system for which $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ and $a = b \neq c$. So, A is incorrect and R is also incorrect as for tetragonal system $a = b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$.
22. (d) Certain ionic solids (for example, AgBr) have both Schottky and Frenkel defects. Only Schottky defects change the density of solids because anions or cations are

missing, while Frenkel defects do not involve any change in density because number of cations and anions are same, there is only change of position of ions.

23. (a) The stability of a crystal depends upon the strength of the interparticle attractive force. The melting point of a solid depends on the strength of the attractive force acting between the constituent particles. Therefore, the stability of a crystal gets reflected in its melting point.
24. (a) In a Frenkel defect an ion leaves its position in the lattice and occupies normally vacant interstitial position.
25. (a) All magnetically ordered solids (ferromagnetic, ferrimagnetic and antiferromagnetic solids) transform to the paramagnetic state at high temperature due to the randomisation of spins.
26. (c) Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally.

Chapter

16

Solutions

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The vapour pressure of benzene at 30°C is 121.8 mm. By adding 15 g of non-volatile solute in 250 g of benzene, its vapour pressure is decreased to 120.2 mm. The molecular weight of solute is:
 (a) 156.6 g (b) 267.4 g [1997]
 (c) 356.3 g (d) 467.4 g
2. Pure benzene freezes at 5.45°C. A 0.374 m solution of tetrachloroethane in benzene freezes at 3.55°C. The K_f for benzene is: [1998]
 (a) 0.508 (b) 5.08
 (c) 50.8 (d) 508
3. 0.450 g of urea (mol.wt.60) in 22.5 g of water show 0.170°C of elevation in boiling point. The molal elevation constant of water is: [1998]
 (a) 0.051°C (b) 0.51°C
 (c) 5.1°C (d) 0.83°C
4. Van't Hoff factor is: [2000]
 (a) More than one in case of association
 (b) Less than one in case of dissociation
 (c) $\frac{\text{normal molecular mass}}{\text{observed molecular mass}}$
 (d) $\frac{\text{observed molecular mass}}{\text{normal molecular mass}}$
5. On mixing 3 g of non - volatile solute in 200 mL of water, its boiling point (100°C) becomes 100.52°C. If K_b for water is 0.6 K/m then molecular wt. of solute is: [2000]
 (a) 10.5 g mol⁻¹ (b) 12.6 g mol⁻¹
 (c) 15.7 g mol⁻¹ (d) 17.3 g mol⁻¹
6. The colligative property is not represented by:
 (a) elevation in boiling point [2001]
 (b) osmotic pressure
 (c) optical activity
 (d) relative lowering of vapour pressure
7. 20 g of a substance were dissolved in 500 mL of water and the osmotic pressure of the solution was found to be 600 mm of mercury at 15°C. The molecular weight of substance is: [2001]
 (a) 998 (b) 1028
 (c) 1098 (d) 1198
8. Which one of the statements given below concerning properties of solutions, describes a colligative effect? [2003]
 (a) Boiling point of pure water decreases by the addition of ethanol
 (b) Vapour pressure of pure water decreases by the addition of nitric acid
 (c) Vapour pressure of pure benzene decreases by the addition of naphthalene
 (d) Boiling point of pure benzene increases by the addition of toluene
9. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream? [2004]
 (a) 0.16 mol/L (b) 0.31 mol/L
 (c) 0.60 mol/L (d) 0.45 mol/L
10. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is
 (a) 271 K (b) 273.15K [2006]
 (c) 269.07 K (d) 277.23 K
11. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g/mol). The vapour pressure of the solution then is 0.845 bar. What is the molecular mass of the solid substance?
 (a) 58 (b) 180 [2007]
 (c) 170 (d) 145.

12. 1 mol each of the following compounds is dissolved in 1L of solution. Which will have the largest ΔT_b value? [2007]
 (a) HF (b) HCl
 (c) HBr (d) HI.

13. 0.01 M solution of KCl and BaCl₂ are prepared in water. The freezing point of KCl is found to be -2°C. What is the freezing point of BaCl₂ to be completely ionised ? [2008]
 (a) -3°C (b) +3°C
 (c) -2°C (d) -4°C

14. An aqueous solution of hydrochloric acid
 (a) Obeys Raoult's law [2009]
 (b) Shows negative deviation from Raoult's law
 (c) Shows positive deviation from Raoult's law
 (d) Obeys Henry's law at all compositions

15. At 300K, the vapour pressure of an ideal solution containing 3 mole of A and 2 mole of B is 600 torr. At the same temperature, if 1.5 mole of A and 0.5 mole of C (non-volatile) are added to this solution the vapour pressure of solution increases by 30 torr. What is the value of p_B^0 ?
 (a) 940 (b) 405 [2009]
 (c) 90 (d) None of these

16. Exactly 1 g of urea dissolved in 75 g of water gives a solution that boils at 100.114°C at 760 torr. The molecular weight of urea is 60.1. The boiling point elevation constant for water is
 (a) 1.02 (b) 0.51 [2010]
 (c) 3.06 (d) 1.51

17. An aqueous solution of NaCl shows the depression of freezing point of water equal to 0.372 K. The boiling point of BaCl₂ solution of same molality will be [$K_f(H_2O) = 1.86 \text{ K kg mol}^{-1}$; $K_b(H_2O) = 0.52 \text{ K kg mol}^{-1}$] [2011]
 (a) 100.52°C (b) 100.104°C
 (c) 101.56°C (d) 100.156°C

18. 12g of urea is dissolved in 1 litre of water and 68.4 g of sucrose is dissolved in 1 litre of water. The lowering of vapour pressure of first case is
 (a) equal to second [2012]
 (b) greater than second
 (c) less than second
 (d) double that of second

19. At a particular temperature, the vapour pressures of two liquids A and B are respectively 120 and 180 mm of mercury. If 2 moles of A and 3 moles of B are mixed to form an ideal solution, the vapour pressure of the solution at the same temperature will be (in mm of mercury) [2013]
 (a) 156 (b) 145
 (c) 150 (d) 108

20. The freezing point of equimolal aqueous solution will be highest for [2013]
 (a) C₆H₅NH₃⁺Cl⁻ (b) Ca(NO₃)₂
 (c) La(NO₃)₂ (d) C₆H₁₂O₆

21. Which of the following 0.10 m aqueous solutions will have the lowest freezing point ? [2014]
 (a) Al₂(SO₄)₃ (b) C₆H₁₂O₆
 (c) KCl (d) C₁₂H₂₂O₁₁

22. A solution containing 10g per dm³ of urea (molecular mass = 60 gmol⁻¹) is isotonic with a 5% solution of a non volatile solute. The molecular mass of this non volatile solute is [2014]
 (a) 300 g mol⁻¹ (b) 350 g mol⁻¹
 (c) 200 g mol⁻¹ (b) 250 g mol⁻¹

23. The vapour pressure of a solvent decreases by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent if the decrease in the vapour pressure is to be 20 mm of Hg ? [2015]
 (a) 0.8 (b) 0.6
 (c) 0.4 (d) 0.2

24. A solution of urea (mol. mass 56 g mol⁻¹) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol⁻¹ respectively, the above solution will freeze at
 (a) 0.654°C (b) -0.654°C [2015]
 (c) 6.54°C (d) -6.54°C

25. A solution containing 1.8 g of a compound (empirical formula CH₂O) in 40 g of water is observed to freeze at -0.465°C. The molecular formula of the compound is (K_f of water = 1.86 kg K mol⁻¹) [2016]
 (a) C₂H₄O₂ (b) C₃H₆O₃
 (c) C₄H₈O₄ (d) C₆H₁₂O₆

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- 26.** Which observation(s) reflect(s) colligative properties? [2017]
- A 0.5 m NaBr solution has a higher vapour pressure than a 0.5 m BaCl₂ solution at the same temperature
 - Pure water freezes at the higher temperature than pure methanol
 - a 0.1 m NaOH solution freezes at a lower temperature than pure water
- Choose the correct answer from the codes given below
- (i), (ii) and (iii)
 - (i) and (ii)
 - (ii) and (iii)
 - (i) and (iii)
- 29. Assertion :** If red blood cells were removed from the body and placed in pure water, pressure inside the cells increases.
Reason : The concentration of salt content in the cells increases. [2006]
- 30. Assertion :** The water pouch of instant cold pack for treating athletic injuries breaks when squeezed and NH₄NO₃ dissolves lowering the temperature.
Reason : Addition of non-volatile solute into solvent results into depression of freezing point of the solvent. [2006]

Directions for (Qs.31-33) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 27-30) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- If the Assertion is correct but Reason is incorrect.
- If both the Assertion and Reason are incorrect.
- If the Assertion is incorrect but the Reason is correct.

- 27. Assertion :** Molecular mass of benzoic acid when determined by colligative properties is found high

Reason : Dimerisation of benzoic acid. [1998]

- 28. Assertion :** The molecular weight of acetic acid determined by depression in freezing point method in benzene and water was found to be different.

Reason : Water is polar and benzene is non-polar. [2005]

- If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- If Assertion is correct but Reason is incorrect.
- If both the Assertion and Reason are incorrect.

- 31. Assertion :** Lowering of vapour pressure is directly proportional to osmotic pressure of the solution. [2012]

Reason : Osmotic pressure is a colligative property.

- 32. Assertion :** If a liquid solute more volatile than the solvent is added to the solvent, the vapour pressure of the solution may increase i.e., $p_s > p^0$.
Reason : In the presence of a more volatile liquid solute, only the solute will form the vapours and solvent will not.

[2016]

- 33. Assertion :** If one component of a solution obeys Raoult's law over a certain range of composition, the other component will not obey Henry's law in that range. [2011, 2013, 2017]

Reason : Raoult's law is a special case of Henry's law.

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Type A : Multiple Choice Questions

1. (c) According to Raoult's law,

$$\frac{p^0 - p_s}{p_s} = \frac{w \times M}{m \times W}$$

$$\frac{121.8 - 120.2}{121.8} = \frac{15}{m} \times \frac{78}{250}$$

$$\therefore m = \frac{15 \times 78 \times 121.8}{250 \times 1.6} = 356.265 \text{ g}$$

2. (b) $\Delta T_f = K_f \times m$

$$(5.45 - 3.55) = K_f \times 0.374$$

$$K_f = \frac{1.9}{0.374} = 5.08$$

3. (b) $\Delta T = K_b \frac{w}{m} \cdot \frac{1000}{W}$

$$0.170 = K_b \frac{0.450}{60} \times \frac{1000}{22.5}$$

$$K_b = \frac{0.170 \times 60 \times 22.5}{1000 \times 0.450} = 0.51^\circ\text{C.}$$

4. (c) Van't Hoff factor

$$= \frac{\text{Normal Molecular Mass}}{\text{Observed Molecular Mass}}$$

5. (d) $\Delta T = K_b \frac{w}{m} \times \frac{1000}{W}$

$$0.52 = 0.6 \times \frac{3}{m} \times \frac{1000}{200}$$

$$m = \frac{1.8 \times 5}{0.52} = 17.3 \text{ g mol}^{-1}$$

6. (c) Optical activity is not dependent upon number of molecules of the compound, so it is not a colligative property.

7. (d) $\pi V = nRT$

$$\frac{500}{1000} \pi = \frac{20}{m} \times 0.082 \times (273 + 15)$$

$$\frac{500}{1000} \times \frac{600}{760} = \frac{20}{m} \times 0.082 \times 288$$

$$m = \frac{20 \times 0.082 \times 288 \times 1000 \times 760}{500 \times 600} = 1198$$

8. (c) The decrease in vapour pressure of benzene by addition of naphthalene is an example of colligative property.

Change in vapour pressure of solvent or change in boiling point of solvent may also be due to formation of hydrogen bond or interaction between solvent molecule and solute molecule.

9. (b) $\pi = cRT$

$$7.8 = c \times 0.082 \times 310$$

$$c = \frac{7.8}{0.082 \times 310} = 0.31 \text{ mol/L}$$

10. (c) From the relation

$$\Delta T_f = K_f \times \frac{w}{m} \times \frac{1000}{W}$$

It is obvious that

$$\Delta T_f \propto \frac{1}{m}$$

$$\therefore \frac{\Delta T_{f_1}}{\Delta T_{f_2}} = \frac{m_2}{m_1}$$

Cane sugar solution Glucose solution

$$\Delta T_{f_1} = 273.15 - 271 \quad \Delta T_{f_2} = ?$$

$$m_1 = 342 \quad m_2 = 180$$

$$\text{Hence } \frac{2.15}{\Delta T_{f_2}} = \frac{180}{342}$$

$$\Delta T_{f_2} = \frac{342 \times 2.15}{180} = 4.085 \text{ K}$$

So, freezing point of glucose solution

$$= 273.15 - 4.085$$

$$= 269.07 \text{ K}$$

11. (c) $p_{\text{benzene}}^{\circ} = 0.850 \text{ bar}; W_{\text{benzene}} = 39.0 \text{ g.}$

M.W. = 78 g/mol.

$$p_{\text{solution}}^{\circ} = 0.845 \text{ bar}; w = 0.5 \text{ g.}$$

Let n be the no. of moles of non volatile solid; w and m be the weight of solid and molecular mass respectively.

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Using, $\frac{P_{\text{benzene}}^{\circ} - P_{\text{solution}}^{\circ}}{P_{\text{benzene}}^{\circ}} = \frac{n_{\text{solid}}}{n_{\text{benzene}}}$

$$\frac{0.850 - 0.845}{0.850} = \frac{0.5}{\frac{m}{\frac{39}{78}}}$$

$$\frac{0.005}{0.850} = \frac{0.5}{m} \cdot \frac{78}{39}$$

$$m = \frac{100 \cdot 0.850}{0.005} = 170$$

- 12. (d)** The value of ΔT_b depends upon two factors 'i' and 'm'. It is given that 1 mol of each compound is dissolved in 1 L of solution. Hence molarity is same for all the compounds. Now the van't Hoff factor depends on number of particle i.e. on degree of ionisation which further depends on the bond dissociation energy which is in the order



i.e., bond dissociation energy of HI is least. Lower the bond dissociation energy, higher is the degree of ionisation and hence higher the number of particles, thus i will be maximum for HI and hence ΔT_b value will be larger for HI.

- 13. (a)** $\Delta T_f \propto i$

$$\therefore \frac{\Delta T_f \text{ for KCl}}{\Delta T_f \text{ for BaCl}_2} = \frac{i \text{ for KCl}}{i \text{ for BaCl}_2}$$

$$\therefore \frac{\Delta T_f \text{ for KCl}}{\Delta T_f \text{ for BaCl}_2} = \frac{2}{3} (\because \Delta T_f \text{ for KCl} = 2)$$

$$\therefore \Delta T_f \text{ for BaCl}_2 = \frac{3 \times 2}{2} = 3$$

$$\therefore \text{Freezing point of BaCl}_2 = -3^\circ\text{C}$$

- 14. (b)** Shows negative deviation from Raoult's law.
If the attraction between different molecules, for example between HCl and H₂O molecules, is stronger, the escaping tendency from the solution to the vapour

phase will be smaller, then the partial vapour pressure will be smaller than predicted by Raoult's law and the system exhibits a negative deviation.

- 15. (c)** $P = p_A^0 x_A + p_B^0 x_B$

$$600 = p_A^0 \left(\frac{3}{3+2} \right) + p_B^0 \left(\frac{2}{2+3} \right);$$

$$3p_A^0 + 2p_B^0 = 3000$$

$$630 = p_A^0 \left(\frac{4.5}{4.5+2+0.5} \right) + p_B^0 \left(\frac{2}{4.5+2+0.5} \right)$$

$$4.5 p_A^0 + 2 p_B^0 = 4410$$

$$1.5 p_A^0 = 1410; p_A^0 = 940 \text{ and } p_B^0 = 90$$

- 16. (b)** Weight of solute (w) = 1 g

Weight of solvent (W) = 75 g

Boiling point of solution = 100.114°C

Boiling point of solvent = 100°C

$$\Delta T = 100.114 - 100 = 0.114^\circ\text{C}$$

Molecular weight of solute (m) = 60.1

Boiling point elevation constant (K) = ?

$$m = \frac{1000 \times K \times w}{\Delta T \times W}$$

$$K = \frac{m \times \Delta T \times W}{1000 \times w}$$

$$= \frac{60.1 \times 0.114 \times 75}{1000 \times 1}$$

$$= \frac{513.8}{1000} = 0.513$$

- 17. (d)** $\frac{\Delta T_f}{\Delta T_b} = \frac{i_1 K_f m}{i_2 K_b m} = \frac{2 \times 1.86}{3 \times 0.52};$

$$\Delta T_f = 0.372. \text{ Hence, } \Delta T_b = 0.156^\circ\text{C}$$

$$\text{i.e., } T_b = 100.156^\circ\text{C}$$

- 18. (a)** Moles of urea = $\frac{12}{60} = 0.2$

$$\text{Moles of sucrose} = \frac{68.4}{342} = 0.2$$

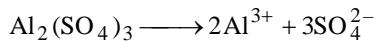
Both are non electrolyte hence lowering of V.P. will be same.

19. (a) Vapour pressure of solution = $P_A + P_B$
 $= p_A^o x_A + p_B^o x_B = \frac{120 \times 2}{5} + \frac{180 \times 3}{5} = 156 \text{ mm Hg}$

20. (d) Glucose is non electrolyte hence depression in freezing point will be minimum, hence freezing point will be highest.

21. (a) Depression in freezing point \propto No. of particles.
 (when concentration of different solutions is equal)

$\text{Al}_2(\text{SO}_4)_3$ provides five ions on ionisation



while KCl provides two ions



$\text{C}_6\text{H}_{12}\text{O}_6$ and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ are not ionised so they have single particle in solution.

Hence, $\text{Al}_2(\text{SO}_4)_3$ have maximum value of depression in freezing point or lowest freezing point.

22. (a) Molar concentration of urea = $\frac{10}{60}$ per dm^3

Molar concentration of volatile solute solution

$$= \frac{5}{M} \text{ per } 100 \text{ ml. or, } \frac{50}{M} \text{ per } \text{dm}^3$$

For solution of same concentration or, isotonic solution at same temperature

$$\frac{10}{60} = \frac{50}{M} \text{ or, } M = 300 \text{ g mol}^{-1}$$

23. (b) According to Raoult's law

$$\frac{\Delta p}{p^\circ} = \frac{n}{n+N} \text{ (mole fraction of solute)}$$

$$\frac{10}{p^\circ} = 0.2 \therefore p^\circ = 50 \text{ mm of Hg}$$

For other solution of same solvent

$$\frac{20}{p^\circ} = \frac{n}{n+N} \text{ (Mole fraction of solute)}$$

$$\Rightarrow \frac{20}{50} = \text{Mole fraction of solute}$$

\Rightarrow Mole fraction of solute = 0.4

As mole fraction of solute + mole fraction of solvent = 1

Hence, mole fraction of solvent = $1 - 0.4 = 0.6$

24. (b) As $\Delta T_f = K_f m$
 $\Delta T_b = K_b m$

$$\text{Hence, we have } m = \frac{\Delta T_f}{K_f} = \frac{\Delta T_b}{K_b}$$

$$\text{or } \Delta T_f = \Delta T_b \frac{K_f}{K_b}$$

$$\Rightarrow [\Delta T_b = 100.18 - 100 = 0.18^\circ\text{C}]$$

$$= 0.18 \times \frac{1.86}{0.512} = 0.654^\circ\text{C}$$

As the Freezing Point of pure water is 0°C ,

$$\Delta T_f = 0 - T_f$$

$$0.654 = 0 - T_f$$

$$\therefore T_f = -0.654$$

Thus the freezing point of solution will be -0.654°C .

25. (d) $\Delta T_f = K_f \times m$

$$M = \frac{1000 \times K_f \times w_2 (\text{solute})}{\Delta T_f \times w_1 (\text{solvent})}$$

$$= \frac{1000 \times 1.86 \times 1.8}{0.465 \times 40} \Rightarrow M = 180$$

Molecular formula = (empirical formula)_n

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$$

Molecular formula = $(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$.

26. (d) Colligative properties depends upon the no. of particles. Since methanol is non electrolyte hence cannot be considered.

Type B : Assertion Reason Questions

27. (a) A molecular mass of benzoic acid is found high because of dimerisation of benzoic acid.

28. (a) In polar solvent, acetic acid will dissociate leading to greater depression in freezing point.

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- 29.** (c) A is true. Pressure inside the cell increases due to osmosis. Water enters the cell because concentration is higher inside the cell. This results in lowering of concentration of medium inside the cell. So, A is true but R is false.

- 30.** (a) A is true and B is also true and B is correct explanation of A.

- 31.** (b) Both assertion and reason are correct but reason is not the correct explanation of assertion.

The relationship between lowering of vapour pressure and osmotic pressure can be derived as follows:

Van't Hoff equation for dilute solutions is

$$\pi = \frac{n}{V} RT \quad \dots\text{(i)}$$

In case of a dilute solution, the volume of solution can be taken as equal to that of solvent. If N is the number of moles of solvent of molecular weight M and density ρ , the volume V is given by

$$V = \frac{NM}{\rho} \quad \dots\text{(ii)}$$

$$\text{or } \frac{n}{N} = \frac{\pi M}{\rho R T} \quad \dots\text{(iii)}$$

From Raoult's law,

$$\frac{P^\circ - P}{P^\circ} = \frac{n}{N} \quad \dots\text{(iv)}$$

$$\therefore \frac{P^\circ - P}{P^\circ} = \frac{\pi M}{\rho R T} \quad [\text{From (iii) and (iv)}]$$

$$\text{or } (P^\circ - P) = \frac{\pi M}{\rho R T} \times P^\circ$$

The factor $\frac{MP^\circ}{\rho RT}$ is constant at constant temperature.

$$\therefore (P^\circ - P) \propto \pi$$

or lowering of V.P. \propto osmotic pressure
Thus assertion is correct.

Osmotic pressure is a colligative property is correct.

- 32.** (c) Both the solute and solvent will form the vapours but vapour phase will become richer in the more volatile component.

- 33.** (b)

Chapter

17

Electrochemistry

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Effect of dilution on conductivity of solution:
 (a) Increases (b) Decreases [1998]
 (c) Unchanged (d) None of the above
2. Through a solution of CuSO_4 a current of 3 amperes was passed for 2 hours. At cathode 3 g of Cu^{2+} ions were discharged. The current efficiency is [At. wt. of Cu = 63.5] [1998]
 (a) 33.3% (b) 42.2%
 (c) 48.7% (d) 54.4%
3. Which shows electrical conductance? [1999]
 (a) Sodium (b) Diamond
 (c) Potassium (d) Graphite
4. Which cannot displace hydrogen from its compound? [1999]
 (a) Al (b) Fe
 (c) Hg (d) Pb
5. For reducing one mole of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} the charge required is : [2000]
 (a) 3×96500 coulomb (b) 6×96500 coulomb
 (c) 0.3 Faradays (d) 0.6 Faradays
6. Which of the following reactions is used to make a fuel cell? [2003]
 (a) $\text{Cd(s)} + 2\text{Ni(OH)}_3(\text{s}) \longrightarrow \text{CdO(s)} + 2\text{Ni(OH)}_2(\text{s}) + \text{H}_2\text{O(l)}$
 (b) $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \longrightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$
 (c) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O(l)}$
 (d) $2\text{Fe(s)} + \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$
7. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is
 (a) 30 s (b) 10 s [2003]
 (c) 30,000 s (d) 10,000 s
8. Which of the following statements is true for the electrochemical Daniel cell? [2004]
 (a) Electrons flow from copper electrode to zinc electrode
 (b) Current flows from zinc electrode to copper electrode
 (c) Cations move toward copper electrode
 (d) Cations move toward zinc electrode
9. The chemical reaction,

$$2\text{AgCl}_{(\text{s})} + \text{H}_{2(\text{g})} \rightarrow 2\text{HCl}_{(\text{aq})} + 2\text{Ag}_{(\text{s})}$$
 taking place in a galvanic cell is represented by the notation : [2005]
 (a) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1 \text{ M KCl}_{(\text{aq})} | \text{AgCl}_{(\text{s})} | \text{Ag}_{(\text{s})}$
 (b) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1 \text{ M HCl}_{(\text{aq})} | 1 \text{ M Ag}^+_{(\text{aq})} | \text{Ag}_{(\text{s})}$
 (c) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1 \text{ M HCl}_{(\text{aq})} | \text{AgCl}_{(\text{s})} | \text{Ag}_{(\text{s})}$
 (d) $\text{Pt}_{(\text{s})} | \text{H}_{2(\text{g})}, 1 \text{ bar} | 1 \text{ M HCl}_{(\text{aq})} | \text{Ag}_{(\text{s})} | \text{AgCl}_{(\text{s})}$
10. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is : [2006]
 (a) 1F (b) 3F
 (c) 5F (d) 6F
11. The products formed when an aqueous solution of NaBr is electrolysed in a cell having inert electrodes are: [2006]
 (a) Na and Br_2
 (b) Na and O_2
 (c) H_2, Br_2 and NaOH
 (d) H_2 and O_2
12. The emf of Daniell cell at 298 K is E_1 [2008]
 $\text{Zn} | \text{ZnSO}_4(0.01 \text{ M}) || \text{CuSO}_4(1.0 \text{ M}) | \text{Cu}$
 When the concentration of ZnSO_4 is 1.0 M and that of CuSO_4 is 0.01 M, the emf changed to E_2 . What is the relation between E_1 and E_2 ?
 (a) $E_1 = E_2$ (b) $E_2 = 0 \neq E_2$
 (c) $E_1 > E_2$ (d) $E_1 < E_2$

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- 13.** Equivalent conductance of an electrolyte containing NaF at infinite dilution is 90.1 Ohm⁻¹cm². If NaF is replaced by KF what is the value of equivalent conductance? [2009]
 (a) 90.1 Ohm⁻¹cm² (b) 111.2 Ohm⁻¹cm²
 (c) 0 (d) 222.4 Ohm⁻¹cm²

- 14.** For a cell reaction involving two electron change, the standard EMF of the cell is 0.295 V at 20°C. The equilibrium constant of the reaction at 25°C will be [2010]
 (a) 29.5×10^{-2} (b) 10
 (c) 1×10^{10} (d) 2.95×10^{-10}

- 15.** A 0.5 M NaOH solution offers a resistance of 31.6 ohm in a conductivity cell at room temperature. What shall be the approximate molar conductance of this NaOH solution if cell constant of the cell is 0.367 cm⁻¹. [2010]
 (a) 234 S cm² mole⁻¹ (b) 23.2 S cm² mole⁻¹
 (c) 4645 S cm² mole⁻¹ (d) 5464 S cm² mole⁻¹

- 16.** Molar conductances of BaCl₂, H₂SO₄ and HCl at infinite dilutions are x_1 , x_2 and x_3 respectively. Equivalent conductance of BaSO₄ at infinite dilution will be: [2011]
 (a) $(x_1 + x_2 - x_3)/2$ (b) $x_1 + x_2 - 2x_3$
 (c) $(x_1 - x_2 - x_3)/2$ (d) $(x_1 + x_2 - 2x_3)/2$

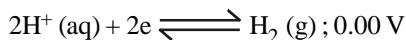
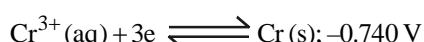
- 17.** Given that $E_{\text{K}^+/\text{K}}^\circ = -2.93\text{V}$;
 $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44\text{V}$; $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76\text{V}$;
 $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34\text{V}$

Based on this data, which of the following is the strongest reducing agent ? [2011]

- (a) Cu_(s) (b) K⁺_(aq)
 (c) Zn²⁺_(aq) (d) Fe_(s)

- 18.** The cell constant of a given cell is 0.47 cm⁻¹. The resistance of a solution placed in this cell is measured to be 31.6 ohm. The conductivity of the solution (in S cm⁻¹ where S has usual meaning) is [2012]
 (a) 0.15 (b) 1.5
 (c) 0.015 (d) 150

- 19.** The standard reduction potentials at 298K for the following half reactions are given against each



Which is the strongest reducing agent? [2013]

- (a) Zn (s) (b) Cr (s)
 (c) H₂(g) (d) Fe³⁺ (aq)

- 20.** A 1.0 M with respect to each of the metal halides AX₃, BX₂, CX₃ and DX₂ is electrolysed using platinum electrodes. If
 $E_{\text{A}^{3+}/\text{A}}^\circ = 1.50\text{V}$, $E_{\text{B}^{2+}/\text{B}}^\circ = 0.3\text{V}$,
 $E_{\text{C}^{3+}/\text{C}}^\circ = -0.74\text{V}$, $E_{\text{D}^{2+}/\text{D}}^\circ = -2.37\text{V}$.

The correct sequence in which the various metals are deposited at the cathode is [2014]

- (a) A, B, C, D (d) A, B, C
 (c) D, C, B, A (b) C, B, A

- 21.** A hydrogen electrode is immersed in a solution with pH=0 (HCl). By how much will the potential (reduction) change if an equivalent amount of NaOH is added to the solution.

(Take p_{H₂} = 1 atm), T = 298 K. [2015]

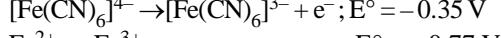
- (a) increase by 0.41 V (b) increase by 59 mV
 (c) decrease by 0.41 V (d) decrease by 59 mV

- 22.** Given that the standard reduction potentials for M^{+/M} and N^{+/N} electrodes at 298 K are 0.52 V and 0.25 V respectively. Which of the following is correct in respect of the following electrochemical cell ?



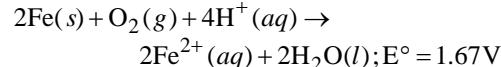
- (a) The overall cell reaction is a spontaneous reaction.
 (b) The standard EMF of the cell is -0.27 V.
 (c) The standard EMF of the cell is 0.77 V.
 (d) The standard EMF of the cell is -0.77 V.

- 23.** On the basis of the following E° values, the strongest oxidizing agent is : [2017]



- (a) [Fe(CN)₆]⁴⁻ (b) Fe²⁺
 (c) Fe³⁺ (d) [Fe(CN)₆]³⁻

- 24.** Consider the following cell reaction: [2017]



At [Fe²⁺] = 10⁻³ M, p(O₂) = 0.1 atm and pH = 3, the cell potential at 25°C is

- (a) 1.47V (b) 1.77V
 (c) 1.87V (d) 1.57V

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 25-32) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - If the Assertion is correct but Reason is incorrect.
 - If both the Assertion and Reason are incorrect.
 - If the Assertion is incorrect but the Reason is correct.
- 25. Assertion :** Electrical conductivity of copper increases with increase in temperature
Reason : The electrical conductivity of metals is due to motion of electrons. [1998]
- 26. Assertion :** A small amount of acid or alkali is added before electrolysis of water.
Reason : Pure water is weak electrolyte. [1999]
- 27. Assertion :** Copper reacts with HCl and liberates hydrogen.
Reason : Hydrogen is present above Cu in the reactivity series. [2000]
- 28. Assertion :** Copper metal gets readily corroded in an acidic aqueous solution.
Reason : Free energy change for this process is positive. [2004]
- 29. Assertion :** Galvanised iron does not rust.
Reason : Zinc has a more negative electrode potential than iron. [2005]
- 30. Assertion :** E° for Mn^{3+}/Mn^{2+} is more positive than Cr^{3+}/Cr^{2+}
Reason : The third ionization energy of Mn is larger than that of Cr. [2006]
- 31. Assertion :** For the Daniel cell, $Zn|Zn^{2+}||Cu^{2+}Cu$ with, $E_{cell} = 1.1$ V, the application of opposite potential greater than 1.1 V results into flow of electron from cathode to anode.
Reason : Zn is deposited at anode, and Cu is deposited at cathode. [2006]

- 32. Assertion :** The cell potential of mercury cell is 1.35V, which remains constant.

Reason : In mercury cell, the electrolyte is a paste of KOH and ZnO. [2008]

Directions for (Qs.33-37) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- If Assertion is correct but Reason is incorrect.
- If both the Assertion and Reason are incorrect.

33. Assertion : If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation :

$$\Lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

Reason : This is according to Kohlrausch law of independent migration of ions. [2011]

- 34. Assertion :** On increasing dilution, the specific conductance keep on increasing.
Reason : On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases. [2014]

35. Assertion : During electrolysis of $CuSO_4(aq)$ using copper electrodes, copper is dissolved at anode and deposited at cathode.

Reason : Oxidation takes place at anode and reduction at cathode. [2014]

- 36. Assertion :** On increasing dilution, the specific conductance keep on increasing.
Reason : On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases. [2015, 2016]

37. Assertion : Zinc can be used while copper cannot be used in the recovery of Ag from the complex $[Ag(CN)_2]^-$. [2017]

Reason : Zinc is a powerful reducing agent than copper.

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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (a) The conductivity of a weak electrolyte increases with increase in dilution due to increase in ionisation. Remember that conductivity of a strong electrolyte remains constant at all dilution because strong electrolytes are completely ionised under all dilutions.

2. (b) According to law of electrolysis,
Mass deposited (m) = $Z i t$

$$\text{or } i = \frac{m \times 96500}{t \times Z}$$

Here, $m = 3\text{g}$, $t = 2 \times 60 \times 60 = 7200 \text{ sec}$

$$z = \frac{\text{Eq.wt}}{96500}; \quad \text{Eq.wt.} = \frac{\text{At.wt}}{\text{Oxidation number}}$$

$$\therefore i = \frac{3 \times 96500 \times 2}{63.5 \times 7200} \\ = 1.266 \text{ A}$$

Efficiency of current

$$= \frac{\text{Current used}}{\text{Total current passed}} \times 100 \\ = \frac{1.266}{3} \times 100 = 42.22\%$$

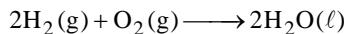
3. (d) Though sodium and potassium are metals and show electrical conductance but graphite has more conductance due to presence of π -electrons in its crystal lattice. Sodium and potassium have only one electron in its outermost shell. So, inspite of being metal, their conductivity is not so good.

4. (c) Hg is lower than hydrogen on the electrochemical series. So, mercury is incapable of displacing hydrogen from dilute acids.

5. (b) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

For reducing one mole of $\text{Cr}_2\text{O}_7^{2-}$, charge required = 6×96500 coulomb.

6. (c) Reaction used in fuel cell is



At anode : $[\text{H}_2 \longrightarrow 2\text{H}^+ + 2e] \times 2$

At cathode : $\text{O}_2 + 2\text{H}_2\text{O} + 4e \longrightarrow 4\text{OH}^-$

7. (a) $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

1 mole requires = 3×96500 coulomb

1 millimole (10^{-3} mole) requires

$$= 3 \times 96500 \times 10^{-3} \text{ C}$$

we know that, $Q = i t$

$$\text{or } t = \frac{Q}{i}$$

$$= \frac{3 \times 96500 \times 10^{-3}}{9.65}$$

$$= \frac{3 \times 9.65 \times 10}{9.65} = 30 \text{ sec.}$$

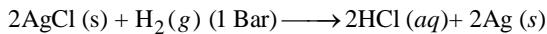
8. (c) Daniel cell is an electrochemical cell in which Cu acts as cathode and Zn acts as an anode. In Daniel cell,

(i) Electrons flow from Zn (anode) to Cu (cathode).

(ii) Current flows from Cu (cathode) to Zn (anode).

(iii) Cu^{2+} ions (cations) move towards Cu (cathode) and accumulated as Cu metal.

9. (b) In the given reaction



Silver is undergoing reduction ($\text{Ag}^+ \rightarrow \text{Ag}$),

hence it will act as cathode in the following cell.



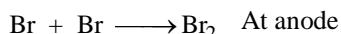
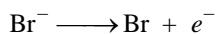
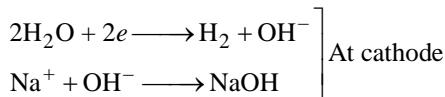
(i) Thus, since option (a) has KCl which is not present in the cell, it is incorrect.

(ii) Since option (c) has $\text{AgCl}(\text{s})$ which does not ionise, it is incorrect.

(iii) Since in option (d), at cathode, Ag is being oxidised to Ag^+ which is not possible, so it is also incorrect.

10. (b) $\text{MnO}_4^- + 4\text{H}^+ + 3e^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$
 So, 3 F of charge will be required to reduce 1 mole of MnO_4^- .

11. (c) $\text{NaBr} \rightleftharpoons \text{Na}^+ + \text{Br}^-$



So the products are H_2 and NaOH (at cathode) and Br_2 (at anode)

12. (c) Using the relation

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{anode}]}{[\text{cathode}]} \\ &= E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \end{aligned}$$

Substituting the given values in two cases.

$$\begin{aligned} E_1 &= E^0 - \frac{0.0591}{2} \log \frac{0.01}{1.0} \\ &= E^0 - \frac{0.0591}{2} \log 10^{-2} \\ &= E^0 + \frac{0.0591}{2} \times 2 \text{ or } (E^0 + 0.0591)\text{V} \end{aligned}$$

$$\begin{aligned} E_2 &= E^0 - \frac{0.0591}{2} \log \frac{1}{0.01} \\ &= E^0 - \frac{0.0591}{2} \log 10^2 \\ &= E^0 - \frac{2 \times 0.0591}{2} \text{ or } (E^0 - 0.0591)\text{V} \end{aligned}$$

Thus, $E_1 > E_2$

13. (a) Because at infinite dilution the equivalent conductance of strong electrolytes furnishing same number of ions is same.

14. (c) Using the relation,

$$\begin{aligned} E_{\text{cell}}^0 &= \frac{2.303 \text{RT}}{\text{nF}} \log K_c = \frac{0.0591}{\text{n}} \log K_c \\ \therefore 0.295 \text{V} &= \frac{0.0591}{2} \log K_c \end{aligned}$$

$$\text{or } \log K_c = \frac{2 \times 0.295}{0.0591} = 10$$

15. (b) or $K_c = 1 \times 10^{10}$
 Here, $R = 31.6 \text{ ohm}$

$$\therefore C = \frac{1}{R} = \frac{1}{31.6} \text{ ohm}^{-1} = 0.0316 \text{ ohm}^{-1}$$

$$\begin{aligned} \text{Specific conductance} \\ &= \text{conductance} \times \text{cell constant} \\ &= 0.0316 \text{ ohm}^{-1} \times 0.367 \text{ cm}^{-1} \\ &= 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Now, molar concentration} &= 0.5 \text{ M} \quad (\text{given}) \\ &= 0.5 \times 10^{-3} \text{ mole cm}^{-3} \end{aligned}$$

$$\therefore \text{Molar conductance} = \frac{k}{\text{molar conc.}}$$

$$\begin{aligned} &= \frac{0.0116}{0.5 \times 10^{-3}} \\ &= 23.2 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} 16. (d) \quad \lambda_m^\infty(\text{BaSO}_4) &= \lambda_{\text{Ba}^{2+}}^\infty + \lambda_{\text{SO}_4^{2-}}^\infty \\ &= \lambda_m^\infty(\text{BaCl}_2) + \lambda_m^\infty(\text{H}_2\text{SO}_4)^- - 2\lambda_{(\text{HCl})}^\infty \\ &= x_1 + x_2 - 2x_3; \quad \lambda_e^\circ = \frac{1}{2} \lambda_m^\circ(\text{BaSO}_4) \end{aligned}$$

17. (d) $\text{K}_{(\text{aq})}^+$ and $\text{Zn}_{(\text{aq})}^{2+}$ can not lose electron(s). Fe has greater tendency to lose electrons than Cu.

$$[E_{\text{Fe}/\text{Fe}^{2+}}^\circ = 0.44 \text{ V} > E_{\text{Cu}/\text{Cu}^{2+}}^\circ = -0.34 \text{ V}]$$

$$18. (c) \quad k = \frac{1}{R} \times \text{Cell constant} = \frac{0.47}{31.6} = 0.01487$$

19. (a) Since oxidation potential of Zn is highest hence strongest reducing agent.

20. (b) The more the reduction potential, the more is the deposition of metals at cathode. Cation having E° value less than -0.83 V (reduction potential of H_2O) will not deposit from aqueous solution.

21. (c) pH changes from 0 to 7.

$$\therefore [\text{H}^+] \text{ changes from 1 to } 10^{-7} \text{ M.}$$

$$\begin{aligned} \text{Accordingly } E_{\text{red.}} &= \frac{-0.059}{\text{n}} \log \frac{1}{[\text{H}^+]} \\ &= 0.059 \log 10^{-7} \end{aligned}$$

$$\text{i.e., } 0.059 \times (-7) = -0.41 \text{ volt.}$$

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22. (b) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$

$$E_{\text{cell}}^{\circ} = 0.25 - 0.52 = -0.27 \text{ V}$$

23. (c) From the given data we find Fe^{3+} is strongest oxidising agent. More the positive value of E° , more is the tendency to get oxidized. Thus correct option is (c).

24. (d) Here $n = 4$, and $[\text{H}^+] = 10^{-3}$ (as $\text{pH} = 3$)

Applying Nernst equation

$$\begin{aligned} E &= E^{\circ} - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]^2}{[\text{H}^+]^4 (\text{p}_{\text{O}_2})} \\ &= 1.67 - \frac{0.059}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1} \\ &= 1.67 - \frac{0.059}{4} \log 10^7 \\ &= 1.67 - 0.103 = 1.567 \end{aligned}$$

Type B : Assertion Reason Questions

25. (e) Electrical conductivity of every metal decreases with increase in temperature due to increase in molecular motion which increases resistance.

26. (a) Water is a covalent compound, hence pure water is a weak electrolyte and feebly ionised and thus bad conductor of electricity. However, addition of a small amount of acid or alkali increases ionisation of water making it a good conductor of electricity.

27. (e) Copper does not liberate hydrogen from HCl because copper is above hydrogen in reactivity series.

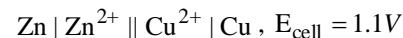
28. (d) Copper lies below hydrogen in electrochemical series so it cannot displace H_2 from dilute acids. Hence it is not easily corroded in acidic solutions. Further, corrosion is a spontaneous process for which free energy change must be negative.

29. (a) Galvanised iron does not rust easily because zinc (which is present in the form of coating) has more negative electrode

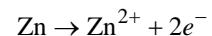
potential (-0.76 V) than iron (-0.41 V) i.e., Zn is less reactive than Fe.

30. (a) Reduction potential of Mn^{3+} is more than Cr^{3+} . So, Mn^{3+} is easily reduced in comparison with Cr^{3+} or Cr^{2+} is easily oxidised than Mn^{2+} . Hence Mn^{2+} will lose electrons with difficulty or ionisation potential of Mn^{2+} is more than Cr^{2+} . Both A and R are true.

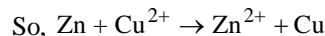
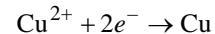
31. (a) In a Daniell cell,



The oxidation half cell is



The reduction half cell is



Thus here Zn is oxidised and deposited at anode, and Cu is reduced and deposited at cathode. If the opposite potential is greater than 1.1 V, then electrons flow from cathode to anode. So both A and R are correct.

32. (b) $\text{Zn}(l) + \text{HgO}(s) \rightarrow \text{Zn}(s) + \text{Hg}(l)$

The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration changes during its life time.

33. (a) According to Kohlrausch law, "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

34. (d) The specific conductivity decreases while equivalent and molar conductivities increase with dilution.

35. (a) At cathode : $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$
(Reduction)

- At anode : $\text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2e^-$
(Oxidation)

36. (d) The specific conductivity decreases while equivalent and molar conductivities increase with dilution.

37. (a)

Chapter

18

Chemical Kinetics

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The rate constant of first order reaction is 3×10^{-6} per second. The initial concentration is 0.10 M. The initial rate is: [1998]

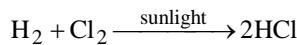
- (a) 3×10^{-7} mol/litre/sec
- (b) 3×10^{-8} mol/litre/sec
- (c) 3×10^{-5} mol/litre/sec
- (d) 3×10^{-8} mol/litre/sec

2. Which of the following statement is true for the reaction, $H_2 + Br_2 \rightarrow 2HBr$. The rate law is

$$\frac{dx}{dt} = k[H_2][Br_2]^{1/2}; \quad [2000]$$

- (a) order of reaction is 1.5
- (b) molecularity of the reaction is 2
- (c) by increasing the concentration of Br_2 four times the rate of reaction is doubled
- (d) all the above are correct.

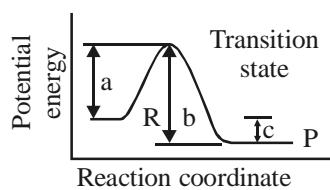
3. For the reaction :



the order of reaction is [2002]

- (a) 0
- (b) 2
- (c) 1
- (d) 3

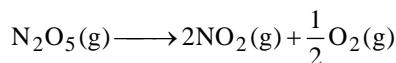
4. The potential energy diagram for a reaction $R \rightarrow P$ is given below



ΔH° of the reaction corresponds to the energy : [2003]

- (a) a
- (b) b
- (c) c
- (d) a + b

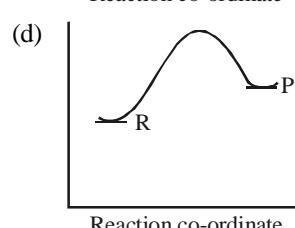
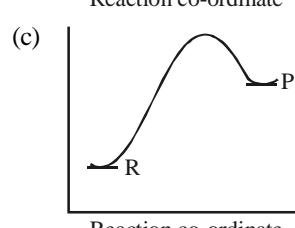
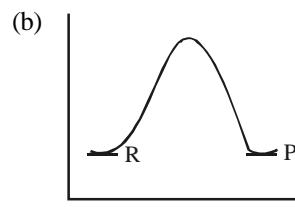
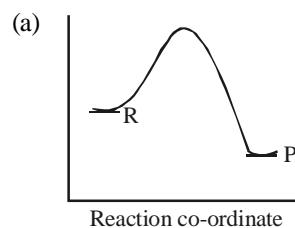
5. The rate constant k , for the reaction



is $1.3 \times 10^{-2}s^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time ? $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and at time t .

- (a) $[N_2O_5]_t = [N_2O_5]_0 + kt$ [2004]
- (b) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$
- (c) $\log [N_2O_5]_t = \log [N_2O_5]_0 + kt$
- (d) $\log \frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$

6. An endothermic reaction with high activation energy for the forward reaction is given by the diagram : [2005]



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7. For reaction $aA \rightarrow xP$, when $[A] = 2.2 \text{ mM}$, the rate was found to be 2.4 mMs^{-1} . On reducing concentration of A to half, the rate changes to 0.6 mMs^{-1} . The order of reaction with respect to A is: [2005]

(a) 1.5 (b) 2.0
(c) 2.5 (d) 3.0

8. Which of the following graphs represent relation between initial concentration of reactants and half-life for third order reaction?

(a)

(b)

(c)

(d)

9. For the reaction,

$$2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$$

the rate of reaction is : [2006]

(a) $\frac{1}{2} \frac{d}{dt} [\text{N}_2\text{O}_5]$ (b) $2 \frac{d}{dt} [\text{N}_2\text{O}_5]$
(c) $\frac{1}{4} \frac{d}{dt} [\text{NO}_2]$ (d) $4 \frac{d}{dt} [\text{NO}_2]$

10. For a first order reaction, to obtain a positive slope, we need to plot {where [A] is the concentration of reactant A} [2008]
(a) $-\log_{10}[\text{A}] \text{ vs } t$ (b) $-\log_e[\text{A}] \text{ vs } t$
(c) $\log_{10}[\text{A}] \text{ vs } \log t$ (d) $[\text{A}] \text{ vs } t$

11. T_{50} of first -order reaction is 10 min. Starting with 10 mol L^{-1} , rate after 20 min is [2008]
(a) $0.0693 \text{ mol L}^{-1} \text{ min}^{-1}$
(b) $0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$
(c) $0.0693 \times 5 \text{ mol L}^{-2} \text{ min}^{-1}$
(d) $0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$

12. The first order rate constant for a certain reaction increases from $1.667 \times 10^{-6} \text{ s}^{-1}$ at 727°C to $1.667 \times 10^{-4} \text{ s}^{-1}$ at 1571°C . The rate constant at 1150°C , assuming constancy of activation energy over the given temperature range is [Given : $\log 19.9 = 1.299$] [2009]
(a) $3.911 \times 10^{-5} \text{ s}^{-1}$ (b) $1.139 \times 10^{-5} \text{ s}^{-1}$
(c) $3.318 \times 10^{-5} \text{ s}^{-1}$ (d) $1.193 \times 10^{-5} \text{ s}^{-1}$

13. In most cases, for a rise of 10K temperature the rate constant is doubled to tripled. This is due to the reason that [2011]
(a) collision frequency increases by a factor of 2 to 3.
(b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3
(c) Activation energy is lowered by a factor of 2 to 3.
(d) none of these

14. The rate constant for the reaction,

$$2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$$
 is $3.0 \times 10^{-4} \text{ s}^{-1}$. If start made with 1.0 mol L^{-1} of N_2O_5 , calculate the rate of formation of NO_2 at the moment of the reaction when concentration of O_2 is 0.1 mol L^{-1} .
(a) $2.7 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ [2011]
(b) $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
(c) $4.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
(d) $9.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

- 15.** A reaction which is of first order w.r.t. reactant A, has a rate constant 6 min^{-1} . If we start with $[A] = 0.5 \text{ mol L}^{-1}$, when would $[A]$ reach the value of 0.05 mol L^{-1} [2013]
- (a) 0.384 min (b) 0.15 min
 (c) 3 min (d) 3.84 min
- 16.** Half-lives of a first order and a zero order reaction are same. Then the ratio of the initial rates of first order reaction to that of the zero order reaction is [2014]
- (a) $\frac{1}{0.693}$ (b) 2×0.693
 (c) 0.693 (d) $\frac{2}{0.693}$
- 17.** Select the rate law that corresponds to the data shown for the following reaction $A + B \longrightarrow C$ [2012, 2015]
- | Expt. No. | (A) | (B) | Initial Rate |
|-----------|-------|-------|--------------|
| 1 | 0.012 | 0.035 | 0.10 |
| 2 | 0.024 | 0.070 | 0.80 |
| 3 | 0.024 | 0.035 | 0.10 |
| 4 | 0.012 | 0.070 | 0.80 |
- (a) Rate = $k[B]^3$ (b) Rate = $k[B]^4$
 (c) Rate = $k[A][B]^3$ (d) Rate = $k[A]^2[B]^2$
- 18.** Collision theory is used to explain how chemical species undergo a reaction. Using this theory and the kinetic molecular model, which of the following does NOT influence the rate of a chemical reaction? [2016]
- (a) The temperature of the system
 (b) The geometry or orientation of the collision
 (c) The velocity of the reactants at the point of collision
 (d) All of the above influence the rate
- 19.** For the following reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$, the rate law is: Rate = $k[\text{NO}_2]^2$. If 0.1 mole of gaseous carbon monoxide is added at constant temperature to the reaction mixture which of the following statements is true? [2016]
- (a) Both k and the reaction rate remain the same
 (b) Both k and the reaction rate increase
 (c) Both k and the reaction rate decrease
 (d) Only k increases, the reaction rate remain the same
- 20.** Which of the following relation represents correct relation between standard electrode potential and equilibrium constant? [2017]
- I. $\log K = \frac{nFE^\circ}{2.303 RT}$
 II. $K = e^{\frac{nFE^\circ}{RT}}$
 III. $\log K = \frac{nFE^\circ}{2.303 RT}$
 IV. $\log K = 0.4342 \frac{nFE^\circ}{RT}$
- Choose the correct statement(s).
- (a) I, II and III are correct
 (b) II and III are correct
 (c) I, II and IV are correct
 (d) I and IV are correct

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 21-26) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.
- 21.** **Assertion :** According to transition state theory for the formation of an activated complex, one of the vibrational degree of freedom is converted into a translational degree of freedom.
Reason : Energy of the activated complex is higher than the energy of reactant molecules. [2006]
- 22.** **Assertion :** The order of a reaction can have fractional value.
Reason : The order of a reaction cannot be written from balanced equation of a reaction. [2008]

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23. **Assertion :** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.
Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate. [2009]
24. **Assertion :** The rate of the reaction is the rate of change of concentration of a reactant or a product.
Reason : Rate of reaction remains constant during the course of reaction. [2010]
25. **Assertion :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant. [2015]
Reason : Lower the activation energy, faster is the reaction.
26. **Assertion :** The kinetics of the reaction –
$$mA + nB + pC \longrightarrow m'X + n'Y + p'Z$$
obey the rate expression as $\frac{dX}{dt} = k[A]^m[B]^n$.
Reason : The rate of the reaction does not depend upon the concentration of C.[2011, 17]

HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (a) $\frac{dc}{dt} = k[c] = 3 \times 10^{-6} \times 0.1$
 $\frac{dc}{dt} = 3 \times 10^{-7} \text{ mol litre}^{-1} \text{ sec}^{-1}$

2. (d) All the statements are correct.

Order of reaction = $1 + \frac{1}{2} = 1.5$

Molecularity = $1 + 1 = 2$

$$\frac{dx}{dt} \propto [Br_2]^{1/2}$$

So, reaction rate will be doubled if concentration of Br_2 is increased by 4 times.

3. (a) The order of all photochemical reactions is zero as it does not depend upon the concentration of reactants.

4. (c) Activation energy of forward reaction = a
 Activation energy of backward reaction = b
 $\therefore \Delta H = b - a$

Since $b > a$, therefore reaction is exothermic

5. (d) As the unit of rate constant is sec^{-1} , so the reaction is first order reaction. Hence

$$k = \frac{1}{t} = \log \frac{a}{(a-x)} \text{ or } kt = \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

6. (c) Reactions which involve absorption of heat energy are called endothermic reactions. For such reactions.

$$\Sigma H_p > \Sigma H_r$$

In graphs (c) and (d), the heat of products is more than heat of reactants and thus they represent endothermic reactions. But in (d) only small amount of energy is absorbed (less difference between energy of reactants and products). Thus, (c) represents maximum activation energy.

Note : Activation energy is the excess energy that the reactant molecule must possess to cross energy barrier.

7. (b) When the concentration of reactant is reduced to half its initial value, the rate is reduced by $\frac{2.4}{0.6} = 4$ times

It means, rate $\propto [\text{reactant}]^2$

So, order of reaction = 2

8. (d) Graph (d) represents graph between $t_{1/2}$ and initial concentration for 3rd order reaction :
 (a) Zero order reaction
 (b) 1st order reaction
 (c) 2nd order reaction.

9. (c) Rate of reaction

$$= -\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt}$$

10. (b) For a first order reaction the positive slope is obtained when we plot $-\log_e [A]$ vs t .

11. (b) Initial concentration = 10 mol L^{-1}
 \therefore Conc. after 20 min (two half lives) = 2.5 mol L^{-1}

$$\text{Now, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ min}}$$

$$\text{or } 0.0693 \text{ min}^{-1}$$

$$\therefore \text{rate} = k \times [\text{reactant}] \\ = 0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1}$$

12. (c) $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

or $2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

$$2.303 \log \left[\frac{1.667 \times 10^{-4}}{1.667 \times 10^{-6}} \right] = -\frac{E_a}{R} \left[\frac{1}{1844} - \frac{1}{1000} \right]$$

$$2.303 \times 2 = \frac{E_a}{R} \times \frac{844}{1844 \times 1000} \quad \dots\dots(1)$$

$$\therefore \frac{E_a}{R} = \frac{4.606 \times 1844 \times 1000}{844}$$

$$2.303 \log \left[\frac{k_3}{1.667 \times 10^{-6}} \right] = \frac{E_a}{R} \times \frac{1423 - 1000}{1423 \times 1000}$$

$$= \frac{E_a}{R} \times \frac{423}{1423 \times 1000} \quad \dots\dots(2)$$

Dividing equation (2) by equation (1)

$$\log \left[\frac{k_3}{1.667 \times 10^{-6}} \right] \\ 2$$

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$$= \frac{423}{1423 \times 1000} \times \frac{1844 \times 1000}{844}$$

$$\therefore \log \left[\frac{k_3}{1.667 \times 10^{-6}} \right]$$

$$= 2 \times \frac{423 \times 1844}{1423 \times 844} = 1.299$$

On taking Antilog, $k_3 = 19.9$
 $\therefore k_3 = 19.9 \times 1.667 \times 10^{-6} = 3.318 \times 10^{-5} \text{ s}^{-1}$

13. (b) For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

14. (d) Mol L⁻¹ of N₂O₅ reacted = 2 × 0.1 = 0.2

$$[\text{N}_2\text{O}_5]_{\text{left}} = 1.0 - 0.2 = 0.8 \text{ mol L}^{-1}$$

$$\text{Rate of reaction} = k \times [\text{N}_2\text{O}_5]$$

$$= 3.0 \times 10^{-4} \times 0.8$$

$$= 2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of formation of NO₂
 $= 4 \times 2.4 \times 10^{-4} = 9.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

15. (a) $t = \frac{2.303}{k} \log \frac{a}{a-x}$
 $= \frac{2.303}{6} \log \frac{0.5}{0.05} = 0.384 \text{ min.}$

16. (b) For first order reaction,

$$\text{Rate} = kA_0 = \frac{0.693}{t_{1/2}} A_0$$

For zero order reaction, Rate = $kA_0^0 = \frac{A_0}{2t_{1/2}}$

Ratio in rates = 2×0.693

17. (a) Let the rate law be $r = k[A]^x[B]^y$

$$\text{Divide (3) by (1)} \frac{0.10}{0.10} = \frac{[0.024]^x [0.035]^y}{[0.012]^x [0.035]^y}$$

$$\therefore 1 = [2]^x, x = 0$$

$$\text{Divide (2) by (3)} \frac{0.80}{0.10} = \frac{[0.024]^x [0.070]^y}{[0.024]^x [0.035]^y}$$

$$\therefore 8 = (2)^y, y = 3$$

Hence rate equation, R = $k[A]^0[B]^3 = k[B]^3$

18. (d)

19. (a) k remains constant at constant temperature and CO does not effect the rate of reaction.

20. (c) $\Delta G = -2.303 RT \log K$
 $-nFE^\circ = -2.303 RT \log K$

$$\log K = \frac{nFE^\circ}{2.303 RT}$$

$$= 0.4342 \frac{nFE^\circ}{RT} \quad \dots\dots \text{(i)}$$

$$\ln K = \frac{nFE^\circ}{RT}$$

$$K = e^{\frac{nFE^\circ}{RT}} \quad \dots\dots \text{(ii)}$$

Type B : Assertion Reason Questions

21. (b) The formation of an activated complex takes place when vibrational degree of freedom convert into a translational degree of freedom. This statement is given by transition statement theory. Also the energy of activated complex is higher than the energy of reactant molecule is true but it is not the correct explanation of the assertion.

22. (b) The order of a reaction can have fractional value. Assertion is true.
The order of a reaction can not be written from balanced equation of a reaction because its value changes with pressure, temperature and concentration. It can only be determined experimentally. Thus the reason is also correct, but the reason is not the correct explanation of assertion.

23. (a) Rate law is always written according to the slowest step and thus the exponents for concentrations do not necessarily match the stoichiometric coefficients.

24. (c) Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.

25. (b) According to Arrhenius equation, $k = Ae^{-E_a / RT}$

When $E_a = 0$, $k = A$.

26. (a) Rate expression $\frac{dX}{dt} = k[A]^m[B]^n$ shows that the total order of reaction is $m + n + 0 = m + n$

As the rate of reaction is independent of concentration of C, i.e., the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

Chapter

19

Surface Chemistry

TYPE A : MULTIPLE CHOICE QUESTIONS

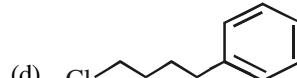
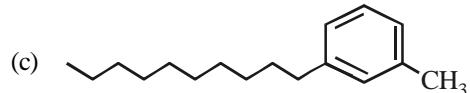
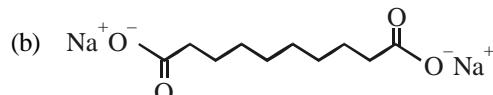
1. The physical adsorption of gases on the solid surface is due to: [1998]
 - (a) Covalent bond
 - (b) Hydrogen bond
 - (c) Ionic bond
 - (d) Van der waal's forces
2. The electrical charge on a colloidal particle is observed by: [1998]
 - (a) Ultramicroscope
 - (b) Scattering
 - (c) Brownian movement
 - (d) Electrophoresis
3. Lyophilic colloids are stable due to: [1998]
 - (a) Small size of the particle
 - (b) Large size of the particle
 - (c) Layer of dispersion medium on the particle
 - (d) Charge on the particle
4. Purple of cassius is colloidal solution of :

(a) Silver	(b) Lead
(c) Gold	(d) Mercury

[1999]
5. Milk is colloid in which : [2000]
 - (a) Liquid is dispersed in liquid
 - (b) Gas is dispersed in liquid
 - (c) Sugar is dispersed in water
 - (d) Solid is dispersed in liquid
6. The colloid is : [2001]

(a) urea	(b) blood
(c) cane sugar	(d) NaCl
7. The movement of colloidal particles, under applied electric current is known as : [2001]
 - (a) electrodialysis
 - (b) dialysis
 - (c) electrophoresis
 - (d) none of the above
8. The size of colloidal particle is [2002]
 - (a) 10^{-3} to 10^{-9} m
 - (b) 10^{-3} to 10^{-12} m
 - (c) 10^{-6} to 10^{-9} m
 - (d) 10^{-12} to 10^{-19} m
9. Which of the following molecules is most suitable to disperse benzene in water ? [2005]

(a)	(b)
-----	-----



10. A catalyst [2007]
 - (a) changes the equilibrium constant
 - (b) lowers the activation energy
 - (c) increases the forward and backward reactions at different speeds.
 - (d) follows same mechanism for the reaction.
11. Which of the following is a lyophobic colloidal solution ? [2008]
 - (a) Aqueous starch solution
 - (b) Aqueous protein solution
 - (c) Gold solution
 - (d) Polymer solvent in some organic solvents
12. The density of gold is 19 g/cm^3 . If $1.9 \times 10^{-4} \text{ g}$ of gold is dispersed in one litre of water to give a sol having spherical gold particles of radius 10 nm , then the number of gold particles per mm^3 of the sol will be [2010]

(a) 1.9×10^{12}	(b) 6.3×10^{14}
(c) 6.3×10^{10}	(d) 2.4×10^6
13. Which of the following electrolyte will have maximum flocculation value for Fe(OH)_3 sol? [2010]

(a) NaCl	(b) Na_2S
(c) $(\text{NH}_4)_3\text{PO}_4$	(d) K_2SO_4
14. Which of the following ions will have the minimum coagulating value for the sol obtained by adding FeCl_3 solution to slight excess of NaOH [2011]

(a) SO_4^{2-}	(b) $[\text{Fe}(\text{CN})_6]^{3-}$
(c) Ba^{2+}	(d) Al^{3+}

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15. Preparation of Lyophobic sols by chemical method involves [2012]
 (a) double decomposition
 (b) oxidation & reduction
 (c) hydrolysis
 (d) all of these
16. A colloidal solution is subjected to an electrical field. The particles move towards anode. The coagulation of same sol is studied using NaCl, BaCl₂ and AlCl₃ solutions. Their coagulating power should be [2013]
 (a) NaCl > BaCl₂ > AlCl₃
 (b) BaCl₂ > AlCl₃ > NaCl
 (c) AlCl₃ > BaCl₂ > NaCl
 (d) BaCl₂ > NaCl > AlCl₃
17. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl, Na₂SO₄ and Na₃PO₄ solutions. Their coagulating values will be in the order [2014]
 (a) NaCl > Na₂SO₄ > Na₃PO₄
 (b) Na₂SO₄ > Na₃PO₄ > NaCl
 (c) Na₃PO₄ > Na₂SO₄ > NaCl
 (d) Na₂SO₄ > NaCl > Na₃PO₄
18. Gold numbers of protective colloids A, B, C and D are 0.50, 0.01, 0.10 and 0.005, respectively. The correct order of their protective powers is [2015]
 (a) D < A < C < B (b) C < B < D < A
 (c) A < C < B < D (d) B < D < A < C
19. The disease kala azar is caused by [2016]
 (a) colloidal antimony
 (b) milk of magnesia
 (c) argyrols
 (d) colloidal gold
20. Which one of the following impurities present in colloidal solution cannot be removed by electrodialysis? [2017]
 (a) Sodium chloride
 (b) Potassium sulphate
 (c) Urea
 (d) Calcium chloride
- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.
21. **Assertion:** A catalyst is more effective in finely divided form.
Reason: Finely divided form has more surface area. [1998]
22. **Assertion :** Sky appears blue.
Reason : Colloidal particles of dust scatter blue light. [2000]
23. **Assertion :** Physical absorption of molecules takes place on surface only.
Reason : In this process, the bonds of the absorbed molecules are broken. [2002]
24. **Assertion :** The micelle formed by sodium stearate in water has —COO⁻ groups at the surface.
Reason : Surface tension of water is reduced by the addition of stearate. [2003]
25. **Assertion :** Aqueous gold colloidal solution is red in colour.
Reason : The colour arises due to scattering of light by colloidal gold particles. [2004]
26. **Assertion :** Alcohols are dehydrated to hydrocarbons in the presence of acidic zeolites.
Reason : Zeolites are porous catalysts. [2004]
27. **Assertion :** Colloidal solutions are stable but colloidal particles do not settle down.
Reason : Brownian movement counters the force of gravity actively on colloidal particles. [2008]

Directions for (Qs.28-31) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 (c) If Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 21-27) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

28. **Assertion :** In chemisorption, adsorption first increases with temperature and then decreases.
Reason : Heat keeps on providing more and more activation energy. [2009]
29. **Assertion :** A catalyst does not alter the equilibrium constant of a reaction.
Reason : The catalyst forms a complex with the reactants and provides an alternate path with lower energy of activation for the reaction; the forward and the backward reactions are affected to the same extent. [2010]
30. **Assertion :** The relation $\frac{x}{m} = k.p^{1/n}$ is known as Freundlich adsorption isotherm, where x is the mass of gas adsorbed by m grams of adsorbate, p is the equilibrium pressure, k and n are constants for given system and temperature.
Reason : When several substances have same value of $\frac{1}{n}$, the lines by which their adsorption isotherms can be represented will meet at a point. [2013]
31. **Assertion :** The enthalpy of physisorption is greater than chemisorption. [2016, 17]
Reason : Molecules of adsorbate and adsorbent are held by van der Waal's forces in physisorption and by chemical bonds in chemisorption.

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Type A : Multiple Choice Questions

1. (d) Vander Waal's forces are responsible for formation of bonds in case of physical adsorption.
2. (d) The electrical change on a colloidal particle is observed by electrophoresis. Under electric field, charged particles move in a particular direction.
3. (c) Lyophilic colloids are stable due to layer of dispersion medium on the particle.
4. (c) Purple of cassius is colloidal solution of gold.
5. (a) Milk is colloid in which liquid (liquid fat) is dispersed in liquid (water).
6. (b) Blood is a colloidal solution with plasma as dispersion medium and biomolecules as colloidal particles.
7. (c) The movement of colloidal particles under applied electric potential is known as electrophoresis.
8. (c) Size of colloidal particle = 10^{-9} to 10^{-6} m.
9. (c) Benzene is non-polar and hence dissolves non-polar compounds (like dissolves like). Among the given compounds, only (c) is non-polar hence it dissolves in benzene.
10. (b) A catalyst lowers down the activation energy. Greater is decrease in activation energy, higher will be the reaction rate.
11. (c) Of the given solution the gold sol is lyophobic colloidal solution. Gold particles have very less affinity towards dispersion medium, hence its sol can be easily coagulated.
12. (d) Volume of gold present in solution

$$= \frac{\text{Mass of gold}}{\text{Density of gold}} = \frac{1.9 \times 10^{-4} \text{ g}}{19 \text{ g/cm}^3} \\ = 0.1 \times 10^{-4} \text{ cm}^3.$$

For spherical particles of gold with radius equal to 10 nm

The volume of each particle

$$= \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10 \times 10^{-7} \text{ cm})^3 \\ = \frac{88}{21} \times 10^{-18} \text{ cm}^3$$

Number of gold particles present

$$= \frac{\text{Volume of gold in solution}}{\text{Volume of each particle}}$$

$$= \frac{0.1 \times 10^{-4} \text{ cm}^3}{\frac{88}{21} \times 10^{-18} \text{ cm}^3}$$

$$= \frac{21}{88} \times 10^{13} \text{ particles}$$

$= 2.4 \times 10^{12}$ particles

2.4×10^{12} particles of gold are present in 1000 cm^3 (1 litre).

\therefore Number of particles present per mm^3

$$= \frac{2.4 \times 10^{12}}{10^6} \quad [1 \text{ L} = 10^6 \text{ mm}^3]$$

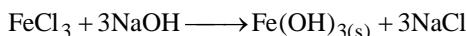
$$= 2.4 \times 10^6$$

13. (a) Flocculating value $\propto \frac{1}{(z)}$, where z = valency

of coagulating ion.

Since, Fe(OH)_3 is a positively charged sol so it will be coagulated by negative ions considering the valencies of various negative ions used i.e., Cl^- , S^{2-} , PO_4^{3-} and SO_4^{2-} , we find that the valency of Cl^- is least so it will have maximum flocculation value i.e., NaCl .

14. (d)



The sol is negatively charged and would be coagulated most effectively by Al^{3+} .

15. (d)

16. (c) The movement towards anode shows that sol is negative. For coagulation of negative sol. Cation with higher charge is more effective.

17. (a) Since the sol particles migrate towards cathode, they are positively charged. Hence, anions would be effective in coagulation.

- Greater is the valence of effective ion, smaller will be its coagulating value.
- 18. (c)** For a protective colloid lesser the value of gold number more will be the protective power. Thus the correct order of protective power of A, B, C and D is
 $\Rightarrow \quad (A) < (C) < (B) < (D)$
 Gold number 0.50 0.10 0.01 0.005
 Hence (c) is the correct answer
- 19. (a)** Colloidal antimony is used in curing kala-azar.
- 20. (c)** Electrodialysis involves movement of ions towards oppositely charged electrodes. Urea being a covalent compound does not dissociate to give ions and hence it cannot be removed by electrodialysis. However all the other given compounds are ionic which can undergo dissociation to give oppositely charged ions and thus can be separated.
- Type B : Assertion Reason Questions**
- 21. (a)** A catalyst is more effective in finely divided form because of more surface area.
- 22. (a)** Sky appears blue colour due to scattering of light by the colloidal particles (dust) of air. Most scattered ray is blue.
- 23. (d)** The assertion that physical absorption of molecules takes place on surface only is false. Actually absorption takes place on the whole body. Further it is a simple physical phenomenon which involves no breaking of bond. Hence, both are false.
- 24. (b)** The assertion that the micelle formed by sodium stearate in water has $-COO^-$ groups at the surface is true as it is hydrophilic end. The given reason is also true but is not the correct explanation. Micelle is formed if molecules with polar and nonpolar ends assemble in the bulk.
- 25. (a)** The colour of the gold sol is due to scattering of light by colloidal particles.
- 26. (b)** In petroleum industry zeolites are used to convert alcohol directly to hydrocarbon by dehydrating it. Zeolites are porous catalysts but this is not the reason for its use to convert alcohol into petrol.
- 27. (a)** The Brownian movement of particles is due to bombardment on the particles by the molecules of the dispersion medium. Thus Brownian movement does not permit the particles to settle down and induces stability of colloidal solution.
- 28. (c)** In chemisorption, adsorption first increases with temperature and then decreases. The heat initially supplied acts as activation energy for the chemical reaction occurring between adsorbate and adsorbent.
- 29. (a)** Catalyst has an equal effect over forward and backward reactions and hence, it does not affect the equilibrium state.
- 30. (c)** Assertion is true, reason is false.
 When several lines have the same value of $\frac{1}{n}$, then the lines by which their adsorption isotherms can be represented will be parallel and will not meet at a point.
- 31. (d)** Assertion is false but Reason is true. The enthalpy of chemisorption is of the order of $40 - 400 \text{ kJ mol}^{-1}$ while for physical adsorption it is of the order of $20 - 40 \text{ kJ mol}^{-1}$.

Chapter

20

General Principles and Processes of Isolation of Elements

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The process does not involve a catalyst is : [1997]
 - (a) Haber process
 - (b) Contact process
 - (c) Thermite process
 - (d) Ostwald process
2. Chief ore of Al is : [1997]
 - (a) cryolite
 - (b) bauxite
 - (c) feldspar
 - (d) kaolin
3. Froth floatation is a process of: [1998]
 - (a) Oxidation
 - (b) Reduction
 - (c) Refining
 - (d) Concentration
4. Flux is used to remove: [1999]
 - (a) basic impurities
 - (b) acidic impurities
 - (c) all types of impurities
 - (d) acidic and basic both impurities
5. Mac Arthur process is used for the extraction of: [2000]
 - (a) Au
 - (b) Pt
 - (c) Cu
 - (d) Zn
6. In the extraction of copper from its sulphide ore, the metal is formed by reduction of Cu_2O with :
 - (a) FeS
 - (b) CO [2003]
 - (c) Cu_2S
 - (d) SO_2
7. Which of the following is a carbonate ore?
 - (a) Pyrolusite
 - (b) Malachite [2005]
 - (c) Diaspore
 - (d) Cassiterite
8. Carbon and CO gas are used to reduce which of the following pairs of metal oxides for extraction of metals? [2007]
 - (a) FeO, SnO
 - (b) SnO, ZnO
 - (c) $\text{BaO}, \text{Na}_2\text{O}_2$
 - (d) FeO, ZnO
9. In metallurgical process of aluminium, cryolite is mixed with alumina in its molten state, because it [2011]
 - (a) decreases the amount of alumina
 - (b) oxidises the alumina
 - (c) increases the melting point of alumina
 - (d) decreases the melting point of alumina

10. Match list I with list II and select the correct answer using the codes given below the lists:

List I	List II
I. Cyanide process	A. Ultrapure Ge
II. Floatation process	B. Pine oil
III. Electrolytic reduction	C. Extraction of Al
IV. Zone refining	D. Extraction of Au

Codes: [2013]

- (a) I-C, II-A, III-D, IV-B
- (b) I-D, II-B, III-C, IV-A
- (c) I-C, II-B, III-D, IV-A
- (d) I-D, II-A, III-C, IV-B

11. Sulfide ores are common for the metals [2015]

- (a) Ag, Cu and Pb
- (c) Ag, Cu and Sn
- (b) Ag, Mg and Pb
- (d) Al, Cu and Pb

12. Match List I with List II and select the correct answer using the codes given below the list [2015]

List I	List II
1. Ti	A. Bauxite
2. Si	B. Cerussite
3. Al	C. Van-Arkel method
4. Pb	D. Zone refining

- (a) 1-B, 2-A, 3-C, 4-D
- (b) 1-B, 2-C, 3-A, 4-B
- (c) 1-C, 2-A, 3-B, 4-D
- (d) 1-C, 2-D, 3-A, 4-B

13. The main reactions occurring in blast furnace during extraction of iron from haematite are _____.

- (i) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
- (ii) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
- (iii) $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
- (iv) $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$ [2016]

- (a) (i) and (iii)
- (b) (ii) and (iv)

- (c) (i) and (iv)
- (d) (i), (ii) and (iii)

14. $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$

Which process of metallurgy of copper is represented by above equation? [2017]

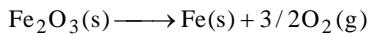
- (a) Concentration
- (b) Roasting
- (c) Reduction
- (d) Purification

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Q. 15) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
 - (e) If the Assertion is incorrect but the Reason is correct.
15. **Assertion :** Extraction of iron metal from iron oxide ore is carried out by heating with coke.

Reason : The reaction,



is a spontaneous process.

[2005]

Directions for (Qs.16-18) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

16. **Assertion :** Copper obtained after bassemerization is known as **blister copper**.

Reason : Blisters are produced on the surface of the metal due to escaping of dissolved SO_2 .

[2013]

17. **Assertion :** Coke and flux are used in smelting.

[2017]

Reason : The phenomenon in which ore is mixed with suitable flux and coke is heated to fusion is known as smelting.

18. **Assertion :** Galvanised iron does not rust.

[2017]

Reason : Zinc has a more negative electrode potential than iron.

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Type A : Multiple Choice Questions

1. (c) In thermite process, no catalyst is required.
 $\text{Fe}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} + \text{Heat}$
 This reaction evolves a lot of heat which provides energy to the reaction.
2. (b)
3. (d) Froth floatation is a process of concentration of sulphide ore.
4. (d) Flux is the material which is used in the metallurgy of metals to remove acidic and basic impurities.
 Acidic flux like silica is used to remove basic impurities present in ore like CaO.
 $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$
 Basic flux like limestone is used to remove silica like acidic impurities.
 $\text{SiO}_2 + \text{CaCO}_3 \longrightarrow \text{CaSiO}_3 + \text{CO}_2$.
5. (a) Mac Arthur process involves extraction of gold from sulphide ore with the help of KCN.
6. (c) $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \longrightarrow 6\text{ Cu} + \text{SO}_2$
7. (b) Malachite is carbonate ore.
 $\text{Cu}(\text{OH})_2\text{CuCO}_3$
8. (d) $\text{ZnO} + \text{C } \xrightarrow[3/4]{3/4} \text{ Zn} + \text{CO}$
 $\text{FeO} + \text{C } \xrightarrow[3/4]{3/4} \text{ Fe} + \text{CO}$
 In the process of smelting the oxide ore is reduced by carbon and the metal may be obtained in the molten state or as vapours which are condensed. Metals like Zn, Fe, Pb or Sn are obtained by this process.
9. (d)
10. (b) Cyanide process is for gold (I-D); floatation process - pine oil (II-B); Electrolytic reduction - Al (III-C); Zone refining-Ge (IV-A).

11. (a) Silver, copper and lead are commonly found in earth's crust as Ag_2S (silver glance), CuFeS_2 (copper pyrites) and PbS (galena).

12. (d) Ti – van-Arkel method
 Si – Zone refining method
 Al – Bauxite (Al_2O_3)
 Pb – Cerussite (PbCO_3)

13. (c) 14. (b)

Type B : Assertion Reason Questions

15. (c) Iron is obtained from Fe_2O_3 by heating it with a mixture of coke and CaCO_3 in a blast furnace in which CO formed reduces Fe_2O_3 to Fe.
 $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
 However, the reason is false because the reaction $\text{Fe}_2\text{O}_3(s) \rightarrow \text{Fe}(s) + \frac{3}{2}\text{O}_2(g)$ is not spontaneous as for this reaction both ΔH and ΔS are negative, so ΔG will be positive.
16. (a) Both assertion and reason are correct and reason is the correct explanation of assertion.
17. (b) Both assertion and reason are true but reason is not the correct explanation of assertion. Non fusible mass present in ore in mixing with suitable flux are fused which are then reduced by coke to give free metal.
18. (a) Zinc metal which has a more negative electrode potential than iron will provide electrons in preference of the iron, and therefore corrodes first. Only when all the zinc has been oxidised, the iron starts to rust.

Chapter

21

The p-Block Elements (Group 15, 16, 17 and 18)

TYPE A : MULTIPLE CHOICE QUESTIONS

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17. The mixture of concentrated HCl and HNO_3 made in 3 : 1 ratio contains : [2003]

 - ClO_2
 - NOCl
 - NCl_3
 - N_2O_4

18. The element which forms oxides in all oxidation states varying from +1 to +5 is [2004]

 - N
 - P
 - As
 - Sb

19. The statement true for N_3^- is : [2004]

 - it has non-linear structure
 - it is called pseudohalogen
 - the formal oxidation state of nitrogen in this anion is -1
 - it is isoelectronic with NO_2

20. For electron affinity of halogens which of the following is correct? [2004]

 - $\text{Br} > \text{F}$
 - $\text{F} > \text{Cl}$
 - $\text{Br} > \text{Cl}$
 - $\text{F} > \text{I}$

21. The number of P–O–P bridges in the structure of phosphorus pentoxide and phosphorus trioxide are respectively : [2005]

 - 6, 6
 - 5, 5
 - 5, 6
 - 6, 5

22. The incorrect statement among the following is: [2006]

 - C_{60} is an allotropic form of carbon
 - O_3 is an allotropic form of oxygen
 - S_8 is the only allotropic form of sulphur.
 - Red phosphorus is more stable in air than white phosphorus

23. Tincture of iodine is : [2006]

 - Aqueous solution of I_2
 - Solution of I_2 in aqueous KI
 - Alcoholic solution of I_2
 - Aqueous solution of KI

24. Which two of the following salts are used for preparing iodized salt? [2006]

 - KIO_3
 - KI
 - I_2
 - HII
 - (i) and (ii)
 - (i) and (iii)
 - (ii) and (iv)
 - (iii) and (iv)

25. XeF_6 on hydrolysis produces [2007]

 - XeOF_4
 - XeO_2F_2
 - XeO_3
 - XeO_2

26. Inert gases are mixed in iodine vapours. Then there are _____ between them. [2007]

 - H-bonding
 - vander Waal's forces
 - Electrostatic forces
 - Metallic bonds.

27. The element which is the most abundant in the earth crust is [2007]

 - O
 - S
 - Al
 - H.

28. Cyanogen gas is obtained in the reaction [2007]

 - $\text{CuSO}_4(\text{aq}) + \text{KCN} \longrightarrow$
 - $\text{K}_4[\text{Fe}(\text{CN})_6] \xrightarrow{\text{heat}}$
 - $\text{CH}_3\text{CN} + \text{H}_2\text{O} \xrightarrow{\Delta}$
 - $\text{CH}_3\text{CONH}_2 + \text{P}_2\text{O}_5 \xrightarrow{\Delta}$

29. Perdisulphuric acid has the following bond [2008]

 - $\text{O} \leftarrow \text{O} = \text{O}$
 - $\leftarrow \text{O} = \text{O} \rightarrow$
 - $> \text{O} \rightarrow \text{O} <$
 - ---O---O---

30. S^{2-} and SO_3^{2-} can be distinguished by using [2008]

 - $(\text{CH}_3\text{COO})_2\text{Pb}$
 - $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
 - both (a) and (b)
 - None of these

31. Choose the correct statement – [2009]

 - White or yellow phosphorus is stored under water
 - Ignition temperature of red phosphorus is low
 - Black phosphorus is non crystalline in nature
 - Phosphorus does not form hydrides.

32. An element (X) forms compounds of the formula XCl_3 , X_2O_5 and Ca_3X_2 , but does not form XCl_5 . Which of the following is the element [2009]

 - B
 - Al
 - N
 - P

33. H_2S gas is not evolved when SO_3^{2-} ion reacts with following reagents. [2009]

 - Zn + dil. H_2SO_4
 - Al + Conc. NaOH
 - Al + dil. HCl
 - None of these

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50. What is X and Y in the given reactions ? [2016]
 $2X_2(g) + 2H_2O(l) \rightarrow 4H^+(aq) + 4X^-(aq) + O_2(g)$
 $Y_2(g) + H_2O(l) \rightarrow HY(aq) + HOY(aq)$
 (a) X=Cl, Y=F (b) X=Cl, Y=Br
 (c) X=F, Y=Cl (d) X=I, Y=F
51. Which of the following fluorides does not exist? [2017]
 (a) NF₅ (b) PF₅
 (c) AsF₅ (d) SbF₅
52. Which of the following are peroxyacids of sulphur? [2017]
 (a) H₂SO₅ and H₂S₂O₈
 (b) H₂SO₅ and H₂S₂O₇
 (c) H₂S₂O₇ and H₂S₂O₈
 (d) H₂S₂O₆ and H₂S₂O₇

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 53-64) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

53. **Assertion:** A mixture of He and O₂ is used for respiration for deep sea divers.

Reason: He is soluble in blood. [1998]

54. **Assertion:** Iodine is more soluble in water than in carbon tetrachloride.

Reason: Iodine is a polar compound. [1999]

55. **Assertion:** Inert gases are monoatomic.

Reason: Inert gases have stable configuration. [1999]

56. **Assertion :** Anhydrous BaO₂ is used for preparing H₂O₂.

Reason : Hydrated BaO₂ is not available.

[2001]

57. **Assertion :** Fluorine exists only in -1 oxidation state.

Reason : Fluorine has $2s^22p^5$ configuration. [2001]

58. **Assertion :** The fluorine has lower reactivity.
Reason : F – F bond has low bond dissociation energy. [2002]

59. **Assertion :** Dinegative anion of oxygen (O²⁻) is quite common but dinegative anion of sulphur (S²⁻) is less common.

Reason : Covalency of oxygen is two. [2002]

60. **Assertion :** The halogens absorb visible light.
Reason : All halogens are coloured. [2002]

61. **Assertion :** HClO₄ is a strong acid than HClO₃.
Reason : Oxidation state of Cl in HClO₄ is +7 and in HClO₃, it is +5. [2004]

62. **Assertion :** Reaction of SO₂ and H₂S in the presence of Fe₂O₃ catalyst gives elemental sulphur.
Reason : SO₂ is a reducing agent [2005]

63. **Assertion :** Ozone is an allotrope of oxygen.
Reason : Oxygen is bluish coloured liquid and in singlet state it is para-magnetic. [2007]

64. **Assertion :** F is more electronegative than Cl.
Reason : F has high electron affinity than Cl. [2007]

Directions for (Qs.65-73) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

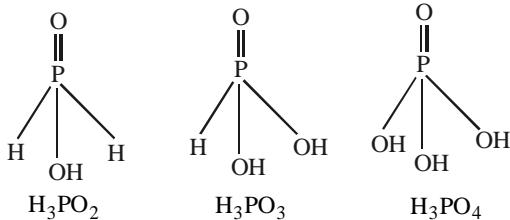
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

65. **Assertion :** The S–S–S bond angle in S₈ molecule is 105°.
Reason : S₈ has a V-shape. [2008, 2009]

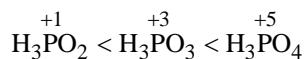
66. **Assertion :** Sulphuric acid is more viscous than water.
Reason : Concentrated sulphuric acid has a great affinity for water. [2009]

67. **Assertion :** Although PF_5 , PCl_5 and PBr_5 are known, the pentahalides of nitrogen have not been observed.
Reason : Phosphorus has lower electronegativity than nitrogen. [2010]
68. **Assertion :** White phosphorus is more reactive than red phosphorus.
Reason : Red phosphorus consists of P_4 tetrahedral units linked to one another to form linear chains. [2012]
69. **Assertion :** When a metal is treated with conc. HNO_3 it generally yields a nitrate, NO_2 and H_2O .
Reason : Conc. HNO_3 reacts with metal and first produces a metal nitrate and nascent hydrogen. The nascent hydrogen then further reduces HNO_3 to NO_2 . [2013]
70. **Assertion :** Silicones are hydrophobic in nature. [2015]
Reason : Si – O – Si linkages are moisture sensitive.
71. **Assertion :** SF_6 cannot be hydrolysed but SF_4 can be.
Reason : Six F atoms in SF_6 prevent the attack of H_2O on sulphur atom of SF_6 . [2016]
72. **Assertion :** Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2 . [2017]
Reason : Oxygen forms $\text{p}\pi - \text{p}\pi$ multiple bond due to small size and small bond length but $\text{p}\pi - \text{p}\pi$ bonding is not possible in sulphur.
73. **Assertion :** HClO_4 is a stronger acid than HClO_3 . [2017]
Reason : Oxidation state of Cl in HClO_4 is +VII and in HClO_3 +V.

16. (d) (i) The geometry of phosphorus is tetrahedral in all the three.



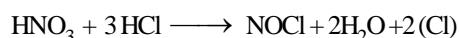
(ii) The acidity increases with increase in oxidation number of central atom



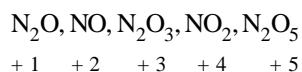
(iii) H_3PO_4 is not reducing.

(iv) H_3PO_3 is diabasic, while H_3PO_2 is monobasic.

17. (b) The mixture of 1 part of conc. HNO_3 and 3 parts of conc. HCl is known as aqua regia. It contains NOCl .



18. (a) Nitrogen has oxidation states from + 1 to + 5 in its oxides

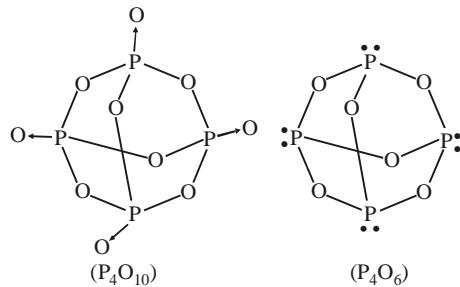


19. (d) Azide ion, N_3^- has a linear structure. It has 22 ($21 + 1$) electrons, thus it is iso-electronic with N_2O ($14 + 8 = 22$).

20. (d) Electron affinity decreases in a group from top to bottom due to increase in size, so the expected order of electron affinity for halogens is $\text{F} > \text{Cl} > \text{Br} > \text{I}$

However, it is not so. The electron affinity of elements of III period is higher than that of II period because elements of II period have small size and greater electron density so the incoming electrons suffer a repulsive force. Thus the order of electron affinity is $\text{Cl} > \text{F} > \text{Br} > \text{I}$.

21. (a) Both have six P—O—P bonds as shown in the figure.



Hence, number of P—O—P bridges is 6 in both.

22. (c) S_8 is not the only allotropic form of sulphur.

23. (c) Tincture of iodine is 2% solution of iodine in alcohol.

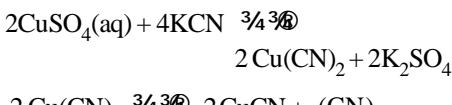
24. (a) KIO_3 and KI are used for preparing iodised salt.

25. (c) Complete hydrolysis of XeF_6 yields XeO_3 , $\text{XeF}_6 + 3\text{H}_2\text{O} \xrightarrow{3/4 \text{ } 3\text{ } \text{R}} \text{XeO}_3 + 6\text{HF}$

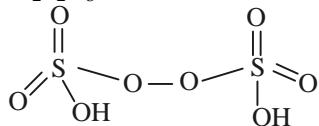
26. (b) All molecules have short range London dispersive forces which is type of vander Waals forces. When inert gases are mixed in iodine vapours there exists short range London dispersive forces.

27. (a) A little more than 47% of earth crust consists of oxygen. The more common rock constituents of earth's crust are nearly all oxides.

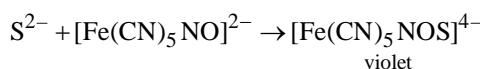
28. (a) Among the given options, only CuSO_4 (aq.) and KCN react to form an unstable copper (II) cyanide which rapidly decomposes to give copper (I) cyanide and cyanogen.



29. (d) The structure of peroxydisulphuric acid ($\text{H}_2\text{S}_2\text{O}_8$) is



30. (c) $\text{S}^{2-} + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow$



Thus S^{2-} and SO_3^{2-} can be distinguished by using both the given reagents.

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- 31. (a)** Due to low ignition temperature of white phosphorus, it undergoes oxidation in presence of air which slowly raises its temperature and after a few moments it catches fire spontaneously. Due to this reason, it is stored under water. Ignition temperature of red phosphorus is high. Black phosphorus is crystalline in nature. Phosphorus forms a number of hydrides.
- 32. (c)** N forms NCl_3 , N_2O_5 and Ca_3N_2 . Nitrogen, due to absence of empty d-orbitals, cannot extend its covalency by more than three and hence do not form NCl_5 . Due to its small size and high electronegativity it can accept 3 electrons to form N^{3-} ion (Ca_3N_2)
- 33. (b)** $\text{SO}_3^{2-} + 2\text{Al} + 2\text{OH}^- + 3\text{H}_2\text{O} \longrightarrow \text{S}^{2-} + 2[\text{Al}(\text{OH})_4]^-$
 H_2S does not evolve as liberated H_2S is neutralized by NaOH and Na_2S is formed.
- 34. (b)** The hydrides have a pyramidal or tetrahedral shape with a lone pair of electrons in one of the orbitals. The H–M–H bond angle is less than the original $109^\circ 28'$ tetrahedral bond angle (H–N–H in NH_3 is $106^\circ 45'$) because of greater repulsion between lone pair and a bond pair than between two bond pairs of electrons. Because electro-negativity of M decreases from N to Bi, the bond pair lie farther away from the central atom, and the lone pair causes greater distortion of bond angle. Thus H–P–H bond in PH_3 is 94° , while in AsH_3 and SbH_3 it is about 91.8° and 91.3° respectively (closer to 90°). This suggests that orbitals used for bonding are closer to pure p-orbitals.
- 35. (d)** The oxide with the highest positive oxidation state on the element other than O should be most acidic. Oxidation state of V in V_2O_5 and N in N_2O_5 are +5. But the electronegativity of N is higher, making N_2O_5 the most acidic oxide.
- 36. (b)** Iodised salt is table salt mixed with a minute amount of one of the four iodine containing salts of hydroiodic acid or iodic acid : potassium iodate or potassium iodide and sodium iodate or sodium iodide.
- 37. (b)** Br_2 , formed by adding chlorine water to a solution of KBr , further reacts with Cl_2 to form reddish yellow or orange red BrCl .
- 38. (c)** $\text{Br}_2 + \text{Cl}_2 \longrightarrow 2\text{BrCl}$
Stability of carbon tetrahalides decreases with increase in the size of halogen atom. So, CF_4 is the most stable halide among the given options.
- 39. (d)** Activated charcoal is a very good absorbent of gas, whereas anhydrous CaCl_2 , Fe(OH)_3 and conc. H_2SO_4 are dehydrating agents.
- 40. (d)** Among the hydrides of group 16 elements, boiling point of H_2O is higher than H_2S (difference in boiling points of H_2O and H_2S is around 200°C) because of strong intermolecular hydrogen bonding. After the decrease in boiling point from H_2O to H_2S , from H_2S to H_2Te , it increases due to increase in size of the atoms from S to Te which increases the magnitude of van der Waal's forces among the molecules. So, the correct order of boiling points is

$$\text{H}_2\text{O} > \text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S}$$
- 41. (b)**
- 42. (b)** $2\text{XeF}_6 + \text{SiO}_2 \xrightarrow{\text{(glass)}} 2\text{XeOF}_4 + \text{SiF}_4$
 $2\text{XeOF}_4 + \text{SiO}_2 \longrightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$
 $2\text{XeO}_2\text{F}_2 + \text{SiO}_2 \longrightarrow 2\text{XeO}_3 + \text{SiF}_4$
(explosive)
- 43. (c)** $2\text{XeF}_6 + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{XeOF}_4$
- 44. (c)** $\text{P}_4\text{O}_{10} + 2\text{H}_2\text{O} \xrightarrow{\text{Acidic}} 4\text{HPO}_3$
meta phosphoric acid
 $\xrightarrow{\text{NH}_3} \text{NH}_4\text{PO}_3$
basic meta ammonium phosphate
- 45. (b)** H - S bond is weaker than H—O bond due to large size of S. Moreover due to high electronegativity of oxygen it forms hydrogen bond in H_2O .

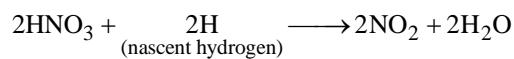
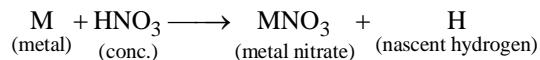
46. (a) $2\text{NaOH} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{NaOCl} + \text{H}_2\text{O}$
hence Cl^- and OCl^-
47. (c) Br_2 reacts with NaI only to get I_2 .
 $2\text{NaI} + \text{Br}_2 \rightarrow 2\text{NaBr} + \text{I}_2$
48. (c) Helium is twice as heavy as hydrogen it is inflammable but not lighter than hydrogen. Helium has the lowest melting and boiling point of any element which makes liquid helium an ideal coolant for many extremely low temperature application such as super conducting magnet and cryogenic research where temperature close to absolute zero are needed. He is used in gas cooled atomic reactors as a heat transfer agent.
49. (d)
50. (c) $2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}^+(\text{aq}) + 4\text{F}^-(\text{aq}) + \text{O}_2(\text{g})$
 $\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{aq}) + \text{HOCl}$
51. (a) NF_5 does not exist because N does not form pentahalides due to the absence of d-orbital in its valence shell. While P, As and Sb form pentahalides of the general formula MX_5 (where, M = P, As and Sb) due to the presence of vacant d-orbitals in their respective valence shell.
52. (a) Both have peroxy linkage
- Type B : Assertion Reason Questions
53. (c) A mixture of He and O_2 is used for respiration by deep sea divers but He is not soluble in blood.
54. (d) Iodine is less soluble in water than in carbon tetrachloride. Iodine is a non polar compound.
Iodine, being a non-polar compound is more soluble in CCl_4 (non-polar compound) than in water because "like dissolves like". so both the assertion and reason are false.
55. (a) Inert gases are monoatomic because they have stable configuration as their octet is complete.
56. (d) H_2O_2 is prepared by the action of H_2SO_4 on hydrated BaO_2 and not on dehydrated BaO_2 . When dehydrated BaO_2 is used, then a layer of BaSO_4 is formed around it which prevents reaction to proceed.
- Ba $\text{O}_2 \cdot 8\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2 + 8\text{H}_2\text{O}$
57. (a) Fluorine exists in only -1 oxidation state as it does not have vacant d-orbital to receive more than one electron.
58. (e) Fluorine is a highly reactive non-metal due to low bond dissociation energy.
59. (c) Dinegative anion of oxygen is quite common due to higher electron gain enthalpy of oxygen.
60. (a) All halogens are coloured as they absorb light in the visible region.
61. (a) HClO_4 is a stronger acid than HClO_3 because in the former Cl is in higher oxidation state (+7) than that in HClO_3 (+5).
62. (c) $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S} \downarrow$
Here H_2S is oxidised to sulphur, while SO_2 is reduced to water. Thus SO_2 is oxidising agent and H_2S is reducing agent.
63. (c) Here the assertion given is true and reason is false. Ozone (O_3) is a triatomic molecule consisting of three oxygen atoms. It is an allotrope of oxygen that is much less stable than the diatomic O_2 . Liquid O_2 is a clear substance with a light sky blue colouration. In triplet form it is paramagnetic due to spin magnetic moments of the unpaired electrons in the molecule and the negative exchange energy between neighbouring O_2 molecules.
In singlet oxygen all the electron spins are paired and hence it is not paramagnetic in nature.
64. (c) Here assertion is true but reason is false. F is more electronegative than chlorine, in fact it is most electronegative element of the periodic table but its electron affinity, the tendency to accommodate electrons, is less than the Cl due to non availability of d-electrons.
65. (c) S_8 has puckered ring type structure and S-S-S bond angle ranges from $102\text{--}108^\circ$. Thus, assertion is correct but reason is incorrect.
66. (b) Both assertion and reason are true but reason is not the correct explanation of assertion. Molecules of H_2SO_4 are

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- associated due to large number of intermolecular H-bonds.
67. (b) Nitrogen cannot form pentahalides because it cannot expand its octet due to non-availability of *d*-orbitals. So, Reason is not the correct explanation of Assertion .
68. (b) White phosphorus exists as P_4 tetrahedral molecule having P-P-P bond angle 60° . Hence the molecule is under strain and more reactive. On the other hand red phosphorus exists as P_4 tetrahedra which are joined together through covalent bonds giving polymeric structure.
69. (a) Both assertion and reason are true and reason is the correct explanation of assertion.



70. (b) 71.(a) 72. (a)
73. (b) Both Assertion and Reason are true but reason is not the correct explanation of assertion. Greater the number of negative atoms present in the oxy-acid make the acid stronger. In general, the strengths of acids that have general formula $(HO)_m ZO_n$ can be related to the value of *n*. As the value of *n* increases, acidic character also increases. The negative atoms draw electrons away from the Z-atom and make it more positive. The Z-atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that bonded to hydrogen. In turn, the electrons of H – O bond are drawn more strongly away from the H-atom. The net effect makes it easier from the proton release and increases the acid a strength.

Chapter

22

The *d*- and *f*-Block Elements

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Malachite is an ore of: [1998]
 - (a) Silver
 - (b) Mercury
 - (c) Magnesium
 - (d) Copper
2. The chief ore of Hg is: [1999]
 - (a) Pyrolusite
 - (b) Bauxite
 - (c) Galena
 - (d) Cinnabar
3. The transition element which shows the highest oxidation state is: [1999]
 - (a) Iron
 - (b) Vanadium
 - (c) Manganese
 - (d) Chromium
4. Gun metal is: [1999]
 - (a) Cu + Zn
 - (b) Cu + Sn + Zn
 - (c) Cu + Sn
 - (d) Zn + Sn
5. Transition elements form coloured ions due to: [1999]
 - (a) *d-d* transition
 - (b) fully filled *d*-orbitals
 - (c) smaller atomic radii
 - (d) availability of *s*-electrons
6. CuSO₄ and KCN react to produce: [1999]
 - (a) CuCN₂
 - (b) CuCN
 - (c) K₃[Cu(CN)₄]
 - (d) K₄[Cu(CN)₆]
7. Which of the following is greatest paramagnetic?
 - (a) Cu⁺
 - (b) Fe²⁺
 - (c) Fe³⁺
 - (d) Cu²⁺
8. The Mohr's salt is shown by: [2000]
 - (a) FeSO₄(NH₄)₂SO₄.6H₂O
 - (b) FeSO₄(NH₃)₂SO₄.6H₂O
 - (c) K₂SO₄Al₂(SO₄)₃.24H₂O
 - (d) FeSO₃(NH₂)₄SO₄.6H₂O
9. German silver is an alloy of: [2000]
 - (a) Fe, Cr, Ni
 - (b) Ag, Cu, Au
 - (c) Cu, Zn, Ni
 - (d) Cu, Zn, Sn
10. The composition of duralumin is: [2001]
 - (a) Al 94%, Mg 6%
 - (b) Cu 56%, Zn 24%, Ni 20%
 - (c) Cu 95%, Al 5%
 - (d) Al 95%, Cu 4%, Mn 0.5%, Mg 0.5%
11. The number of water molecules in Mohr's salt is: [2001]
 - (a) 2
 - (b) 4
 - (c) 6
 - (d) 8
12. Philosopher's wool on heating with BaO at 1100°C produces: [2001]
 - (a) Ba + ZnCl₂
 - (b) BaCdO₂
 - (c) BaZnO₂
 - (d) BaO₂ + Zn
13. Which of the following is not an ore of iron?
 - (a) limonite
 - (b) casiterite [2002]
 - (c) magnetite
 - (d) none of these
14. The colourless species is: [2003]
 - (a) VCl₃
 - (b) VOSO₄
 - (c) Na₃VO₄
 - (d) [V(H₂O)₆]SO₄.H₂O
15. Lanthanide for which +II and +III oxidation states are common is: [2003]
 - (a) La
 - (b) Pr
 - (c) Ce
 - (d) Eu
16. Among the following pairs of ions, the lower oxidation state in aqueous solution is more stable than the other, in: [2005]
 - (a) Ti⁺, Ti³⁺
 - (b) Cu⁺, Cu²⁺
 - (c) Cr²⁺, Cr³⁺
 - (d) V²⁺, VO²⁺
17. F₂ is formed by reacting K₂MnF₆ with: [2005]
 - (a) SbF₅
 - (b) MnF₃
 - (c) KSbF₆
 - (d) MnF₄
18. The colour imparted by Co(II) compounds to glass is: [2006]
 - (a) Green
 - (b) Deep blue
 - (c) Yellow
 - (d) Red

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- Which of the above is/are true ?
- (a) (I) and (III) (b) (II) and (III)
 (c) (II) only (d) (I) and (II)
- 33.** For d-block elements the first ionization potential is of the order [2017]
 (a) $Zn > Fe > Cu > Cr$ (b) $Sc = Ti < V = Cr$
 (c) $Zn < Cu < Ni < Co$ (d) $V > Cr > Mn > Fe$
- TYPE B : ASSERTION REASON QUESTIONS**
- Directions for (Qs. 34-42) :** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.
- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.
- 34.** **Assertion :** Pure iron is not used for making tools and machines.
Reason : Pure iron is hard. [1998]
- 35.** **Assertion :** Iron is found in free state in nature.
Reason : Iron is highly reactive element. [2001]
- 36.** **Assertion :** A solution of $FeCl_3$ in water produces brown precipitate on standing.
Reason : Hydrolysis of $FeCl_3$ takes place in water. [2001]
- 37.** **Assertion :** Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{2+}) does not.
Reason : Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{2+}) is blue in the aqueous solution. [2002]
- 38.** **Assertion :** Solution of Na_2CrO_4 in water is intensely coloured.
Reason : Oxidation state of Cr in Na_2CrO_4 is +VI [2003]
- 39.** **Assertion :** The free gaseous Cr atom has six unpaired electrons
Reason : Half-filled s orbital has greater stability. [2004]
- 40.** **Assertion :** SnI_4 is an orange solid.
Reason : The colour arises due to charge transfer. [2007]
- 41.** **Assertion :** Magnetic moment of Dy is highest among lanthanoids.
Reason : Orbital motion contributes magnetic moment. [2007]
- 42.** **Assertion :** C – O bond in metal carbonyls is long.
Reason : There is delocalisation of electrons from filled d orbitals into the empty orbitals on the CO ligands. [2007]
- Directions for (Qs.43-47) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 (c) If Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
- 43.** **Assertion :** Europium (II) is more stable than cerium (II).
Reason : Cerium salts are used as catalyst in petroleum cracking. [2010]
- 44.** **Assertion :** Lead, tin and bismuth are purified by liquation method.
Reason : Lead, tin and bismuth have low m.p. as compared to impurities [2010]
- 45.** **Assertion :** Transition metals are good catalysts. [2015]
Reason : V_2O_5 or Pt is used in the preparation of H_2SO_4 by contact process.
- 46.** **Assertion :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Reason : Actinide elements are strongly paramagnetic. [2013, 2016]
- 47.** **Assertion :** Transition metals show variable valency.
Reason : Transition metals have a large energy difference between the ns^2 and $(n-1)d$ electrons. [2017]

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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (d) Malachite is an ore of copper
 $\text{Cu(OH)}_2 \cdot \text{CuCO}_3$
2. (d) The chief ore of mercury is HgS (cinnabar).
3. (c) Out of all the elements given, manganese has the highest oxidation state of + 7 in KMnO_4 . Chromium has highest oxidation state of +6 in $\text{K}_2\text{Cr}_2\text{O}_7$, Vanadium has +5 in V_2O_5 and iron has maximum of +3 in Fe_2O_3 .
4. (b) Gun metal is an alloy of Cu, Zn and Sn.
5. (a) Transition elements form coloured ions due to $d-d$ transitions. In the presence of ligands, there is splitting of energy levels of d -orbitals. They no longer remain degenerated. So, electronic transition may occur between two d -orbitals.
6. (c) CuSO_4 and KCN reacts to form complex.

$$\text{CuSO}_4 + 2\text{KCN} \longrightarrow \text{Cu}(\text{CN})_2 + \text{KSO}_4$$

$$\text{Cu}(\text{CN})_2 \longrightarrow 2\text{Cu CN} + (\text{CN})_2$$

$$2\text{Cu CN} + 6\text{KCN} \longrightarrow 2\text{K}_3[\text{Cu}(\text{CN})_4]$$
7. (c) The paramagnetic character is exhibited by species having unpaired electrons. Further paramagnetic character is directly proportional to number of unpaired electrons.

Configuration	Unpaired electron
Cu^+ [Ne] $3s^2 p^6 d^{10}$	0
Cu^{2+} [Ne] $3s^2 p^6 d^9$	1
Fe^{2+} [Ne] $3s^2 p^6 d^6$	4
Fe^{3+} [Ne] $3s^2 p^6 d^5$	5
8. (a) Mohr's salt is $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
9. (c) German silver is alloy of Cu, Zn and Ni. Cu is 60%, Zn is 20%, and Ni is 20%.
10. (d) Composition of duralumin is 95% Al, 4% Cu, 0.5% Mn, 0.5% Mg.
It is light tough and anti-corrosive alloy which is used in making aeroplanes etc.
11. (c) Mohr's salt is $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$.
12. (c) $\text{BaO} + \text{ZnO} \rightarrow \text{BaZnO}_2$
Philosopher's wool
13. (b) Casiterite is an ore of tin (Sn).

14. (c) Species having incompletely filled d -orbitals also have unpaired electron in d -orbital and hence will be coloured. Species having completely filled or vacant d -orbitals does not have any unpaired electron in d orbital, hence it will be colourless.
 V^{3+} in VCl_3 : [Ne] $3s^2 p^6 d^2$
 V^{2+} in VSO_4 : [Ne] $3s^2 p^6 d^3$
 V^{5+} in Na_3VO_4 : [Ne] $3s^2 p^6 d^0$
 V^{2+} in $[\text{V}(\text{H}_2\text{O})_6]\text{SO}_4$: [Ne] $3s^2 p^6 d^3$
15. (d)
16. (a) As we move down in groups 13, 14 and 15, inertness of s^2 electrons of valence shell increases (inert pair effect). Thus in metals present at the bottom of the groups 13, 14, and 15 lower oxidation state becomes more important, viz. Pb (+2 state rather +4), Bi (+3 state rather +5) and Ti (+1 rather than +3).
17. (a) SbF_5 , being the stronger Lewis acid, displaces the weaker one (MnF_4) from its salt. MnF_4 , being unstable, decomposes to give MnF_3 and fluorine.

$$\text{K}_2\text{MnF}_6 + 2\text{SbF}_5 \rightarrow 2\text{SbF}_6 + \text{MnF}_4$$

Unstable

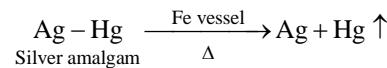
$$\text{MnF}_4 \rightarrow \text{MnF}_3 + \frac{1}{2}\text{F}_2$$
18. (b) Deep Blue.
19. (d) Co-60 is used as anticancerous among the given radioactive isotopes. It emits β -particles and energetic gamma rays, for which reason it is used in radiation therapy.
20. (d) The colour is due to presence of unpaired d -electrons.
 $\text{Ti}^{3+} = [\text{Ar}] 3d^1$ (one unpaired electron)
 $\text{Fe}^{3+} = [\text{Ar}] 3d^5$ (five unpaired electrons)
 $\text{Co}^{2+} = [\text{Ar}] 3d^7$ (three unpaired electrons)
So all of them are coloured.
21. (a) The permanganate ion has an intense purple colour. Mn (+ VII) has a d^0 configuration. So the colour arises from charge transfer and not from $d-d$ spectra.

In MnO_4^- an electron is momentarily changing O^- to O^- and reducing the oxidation state of the metal from Mn(VII) to Mn (VI). Charge transfer requires that the energy levels on the two different atoms are fairly close.



Hence the charge transfer occurs from $\text{L} \rightarrow \text{M}$.

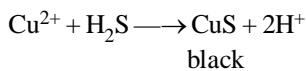
22. (b) Fe and Pt do not form amalgam



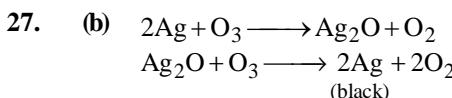
Vessel made of other metal will form amalgam with liberated mercury.

23. (c) Chromium is in VI oxidation state in CrO_4^{2-} ion and therefore, it has no unpaired electron in its d -orbital. However, due to charge transfer $\text{Cr} \longrightarrow \text{O}$, this ion shows intense yellow colour.
24. (b) Fe^{3+} does not form complex compound with NH_3 whereas Cu^{2+} and Zn^{2+} form complex with NH_3 .

25. (b) Copper sulphide is black in colour. Cu^{2+} is placed in II group of inorganic qualitative analysis. It is precipitated in the form of sulphide by passing H_2S in presence of dil. HCl.



26. (b) The ionic radii of trivalent lanthanides decreases progressively with increase in atomic number. This decrease is known as lanthanide contraction.



28. (b) Mn^{2+} ($3d^5$) is more stable than Mn^{3+} ($3d^4$).

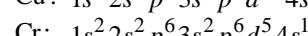
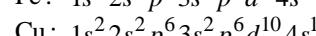
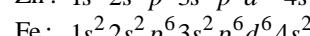
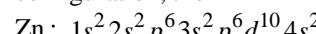
29. (d) In $\text{Cu}^+ [\text{Ar}]3\text{d}^{10}$ there is no unpaired electron, $\text{Cu}^{2+} [\text{Ar}]3\text{d}^9$ contains one unpaired electron hence coloured.

30. (d) Magnetic moment $\mu = \sqrt{n(n+2)}$ where
 $n = \text{number of unpaired electrons}$
 $\sqrt{15} = \sqrt{n(n+2)} \therefore n = 3$

31. (b) As a result of lanthanoid contraction change in ionic radii on going from elements of $4d$ to $5d$ transition series is very small. Thus chemical properties of $4d$ and $5d$ series of transition elements are similar.

32. (b) As a result of lanthanide contraction Zr^{4+} and Hf^{4+} possess almost the same ionic radii. Ce^{4+} is an oxidising agent. Ce^{4+} gains electron to acquire more stable Ce^{3+} state. $\text{La}(\text{OH})_3$ is the most basic among lanthanide hydroxides.

33. (a) The ionisation energies increase with increase in atomic number. However, the trend is irregular among some d -block elements. On the basis of electronic configuration, the



IE₁ follows the order : $\text{Zn} > \text{Fe} > \text{Cu} > \text{Cr}$

Type B : Assertion Reason Questions

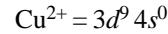
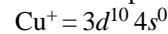
34. (c) Pure iron is not used for making tools and machines as it is soft. However, an alloy of iron with carbon is hard and less reactive than pure iron.

35. (e) Iron is not found in free state in nature because it is highly reactive.

36. (a) Solution of FeCl_3 produces brown precipitate on standing due to hydrolysis in water



37. (e) Cu^+ (cuprous ion) does not have any unpaired electron while cupric (Cu^{2+}) ion has one unpaired electron in $3d$ shell.



Cuprous ion is colourless because it does not have any unpaired electron but Cu^{2+} ion is blue in aqueous solution due to formation of complex with water molecules. So assertion is wrong but reason is true.

38. (b) The colour of CrO_4^{2-} is due to charge transfer spectra. There is no electron in the d -orbital of Cr (VI). So, no electronic excitation is possible with their d -orbital.

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39. (c) The free gaseous Cr atom has six unpaired electrons, because one electron jumps from $4s^2$ orbital to $3d$ orbital making latter exactly half-filled, a comparatively stable entity. $\text{Cr}_{24} [\text{Ar}] 3d^5 4s^1$.
40. (a) The orange colour of SnI_4 is due to charge transfer spectra. Blue light is absorbed by the compound which causes the transfer of an e^- from I to Sn. (Here charge is transferred from one atom to another atom.) The reflected light thus contains a higher proportion of red and orange.
41. (a) In lanthanide ions the $4f e^-$ are well shielded from external field by the overlying $5s$ and $5p$ electrons. Thus the magnetic effect of the motion of the electron in its orbital is not quenched out. Thus the magnetic moment must be calculated taking into account both the magnetic moment from unpaired e^- spins and that from orbital motion.
- $$\mu = g\sqrt{J(J+1)}$$
- Where $g = 1 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$
- $J = L - S$ when the shell is less than half fill
 $= L + S$ when the shell is more than half fill.
 In Dy^{3+} ($[\text{Xe}] 4f^9$) f -level is more than half fill hence spin and orbital motion work together, highest in lanthanoids.
 Hence, both assertion and reason are true and reason is correct explanation of assertion.
42. (a) In metal carbonyls a pair of π -bond arises from overlap of filled d -orbitals on the metal with a pair of π -antibonding orbitals projecting from the carbon of the CO. The π -bonding has the effect of weakening the C–O bond as compared with free CO. Hence C–O bond in metal carbonyls is long. Hence assertion and reason both are true and reason is a correct explanation of assertion.
43. (b) The electronic configurations of Europium (II) and cerium (II) are $\text{Eu}^{2+} : [\text{Xe}] 4f^7, 5d^{10}$
 $\text{Ce}^{2+} : [\text{Xe}] 4f^1, 5d^1$
 In Eu^{2+} , f -subshell is half filled and d -subshell is completely filled and thus more stable.
44. (a)
45. (b) Due to larger surface area and variable valencies to form intermediate absorbed complex easily, transition metals are used as catalysts.
46. (b) The magnetic moment values are lesser than the theoretically predicted values due to the fact that $5f$ electrons of actinides are less effectively shielded which results in quenching of orbital contribution.
47. (c) The assertion is correct but the reason is false. Actually transition metal show variable valency due to very small difference between the ns^2 and $(n-1)d$ electrons.

Chapter

23

Coordination Compounds

TYPE A : MULTIPLE CHOICE QUESTIONS

1. The compound which is not coloured is [1997]
 - (a) $K_4[Fe(CN)_6]$
 - (b) $K_3[Fe(CN)_6]$
 - (c) $Na_2[CdCl_4]$
 - (d) $Na_2[CuCl_4]$
2. The number of unpaired electrons in $Ni(CO)_4$ is
 - (a) 0
 - (b) 1 [1997]
 - (c) 3
 - (d) 5
3. The organometallic compound is : [1997]
 - (a) $Ti(OCOCH_3)_4$
 - (b) $Ti(C_2H_5)_4$
 - (c) $Ti(OC_6H_5)_4$
 - (d) $Ti(OC_2H_5)_4$
4. Mercuric chloride is soluble in KI solution due to :
 - (a) the formation of complex ion [1997]
 - (b) common iodide ion
 - (c) none of the above
 - (d) both (a) and (b)
5. The EAN of Zn in $Zn(OH)_4^{2-}$ complex is:
 - (a) 16
 - (b) 26 [2000]
 - (c) 36
 - (d) 46
6. The reagent commonly used to determine hardness of water titrimetrically is : [2003]
 - (a) oxalic acid
 - (b) disodium salt of EDTA
 - (c) sodium citrate
 - (d) sodium thiosulphate
7. The ion which is not tetrahedral in shape is
 - (a) BF_4^-
 - (b) NH_4^+ [2003]
 - (c) $[Cu(NH_3)_4]^{2+}$
 - (d) $NiCl_4^{2-}$
8. The complex used as an anticancer agent is
 - (a) *meso*- $[Co(NH_3)_3Cl_3]$ [2003]
 - (b) *cis*- $[PtCl_2(NH_3)_2]$
 - (c) *cis*- $K_2[PtCl_2Br_2]$
 - (d) Na_2CoCl_4
9. The ligand called π acid is : [2003]
 - (a) CO
 - (b) NH_3
 - (c) $C_2O_4^{2-}$
 - (d) Ethylenediamine
10. Which one of the following forms, with an excess of CN^- (cyanide), a complex having co-ordination number two? [2004]
 - (a) Cu^+
 - (b) Ag^+
 - (c) Ni^{2+}
 - (d) $Al(OH)_3$
11. Which of the following is not considered as an organometallic compound? [2004]
 - (a) *cis*-platin
 - (b) Ferrocene
 - (c) Zeise's salt
 - (d) Grignard reagent
12. Which of the following does not have optical isomer? [2004]
 - (a) $[Co(NH_3)_3Cl_3]$
 - (b) $[Co(en)_3]Cl_3$
 - (c) $[Co(en)_2Cl_2]Cl$
 - (d) $[Co(en)(NH_3)_2Cl_2]Cl$
13. In which of the following pairs both the complexes show optical isomerism? [2005]
 - (a) *cis*- $[Cr(C_2O_4)_2Cl_2]^{3-}$, *cis*- $[Co(NH_3)_4Cl_2]$
 - (b) $[Co(en)_3]Cl_3$, *cis*- $[Co(en)_2Cl_2]Cl$
 - (c) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$
 - (d) $[Co(NO_3)_3(NH_3)_3]$, *cis*- $[Pt(en)_2Cl_2]$
14. An aqueous solution of $CoCl_2$ on addition of excess of concentrated HCl turns blue due to formation of : [2005]
 - (a) $[Co(H_2O)_4Cl_2]$
 - (b) $[Co(H_2O)_2Cl_4]^{2-}$
 - (c) $[CoCl_4]^{2-}$
 - (d) $[Co(H_2O)_2Cl_2]$
15. The diamagnetic species is : [2005]
 - (a) $[Ni(CN)_4]^{2-}$
 - (b) $[NiCl_4]^{2-}$
 - (c) $[CoCl_4]^{2-}$
 - (d) $[CoF_6]^{2-}$
16. The correct order for the wavelength of absorption in the visible region is : [2005]
 - (a) $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+}$
 $< [Ni(H_2O)_6]^{2+}$
 - (b) $[Ni(NO_2)_6]^{4-} < [Ni(H_2O)_6]^{2+}$
 $< [Ni(NH_3)_6]^{2+}$
 - (c) $[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+}$
 $< [Ni(NO_2)_6]^{4-}$
 - (d) $[Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$
 $< [Ni(NO_2)_6]^{4-}$

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17. The pair in which both species have same magnetic moment (spin only value) is : [2006]
- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{CoCl}_4]^{2-}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}, [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{CoCl}_4]^{2-}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
18. The number of possible isomers of an octahedral complex $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{NH}_3)_2]$ is : [2006]
- 1
 - 2
 - 3
 - 4
19. The ligands in anti-cancer drug *cis*-platin are:
- NH_3, Cl
 - $\text{NH}_3, \text{H}_2\text{O}$
 - $\text{Cl}, \text{H}_2\text{O}$
 - NO, Cl
20. Which statement is true for ferrocene? [2007]
- All Fe-C are of equal length
 - It has sandwich type structure
 - It was the first discovered organometallic compound
 - All of these.
21. During estimation of nickel, we prepare nickel dimethylglyoxime, a scarlet red solid. This compound is _____. [2007]
- ionic
 - covalent
 - metallic
 - non-ionic complex.
22. Which of the following metal ions will form complexes with the same magnetic moment and geometry irrespective of the nature of ligands?
- Ni^{2+}
 - Fe^{2+}
 - Cu^{2+}
 - Co^{2+}
23. Wavelength of red light is absorbed by the complex [2007]
- $[\text{Cu}(\text{CN})_4]^{2-}$
 - $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 - CuSO_4
 - $\text{Cu}(\text{CN})_2$
24. in the change $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \xrightarrow{\text{HCl}} [\text{CuCl}(\text{H}_2\text{O})_5]^+$, the colour changes from [2007]
- blue to green
 - blue to pink
 - pink to green
 - pink to blue.
25. $[\text{Fe}(\text{NO}_2)_3\text{Cl}_3]$ and $[\text{Fe}(\text{ONO})_3\text{Cl}_3]$ shows [2008]
- linkage isomerism
 - geometrical isomerism
26. Among the following the compound that is both paramagnetic and coloured is [2009]
- $\text{K}_2\text{Cr}_2\text{O}_7$
 - $(\text{NH}_4)_2[\text{TiCl}_6]$
 - VOSO_4
 - $\text{K}_3\text{Cu}(\text{CN})_4$
27. Which of the following complex has zero magnetic moment (spin only)? [2009]
- $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$
 - $\text{Na}_3[\text{FeF}_6]$
 - $[\text{Cr}(\text{H}_2\text{O})_6]\text{SO}_4$
 - $\text{K}_4[\text{Fe}(\text{CN})_6]$
28. A chemist wants to determine the molecular geometry of the $[\text{CoCl}_4]^{2-}$ ion. Which of the following gives the best suggestion for a measurement and for the interpretation of that measurement? [2009]
- Using absorption spectroscopy, measure λ_{max} then calculate Δ_o for octahedral geometry
 - Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be square planar; otherwise, it is likely to be tetrahedral
 - Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be square planar
 - Measure the molecule's magnetic moment and use the result to estimate the number of unpaired spins in the molecule. If this number is low, the geometry is likely to be tetrahedral; otherwise, it is likely to be octahedral
29. How many pairs of enantiomers are possible for following complex compound, $[\text{M}(\text{AB})(\text{CD})\text{ef}]^{\pm}$ (where AB, CD– Unsymmetrical bidentate ligand, e, f–monodentate ligands) [2009]
- 20
 - 5
 - 10
 - 8

30. A complex $[CoL_6]^{n+}$ where L is neutral ligand has a magnetic moment $\mu = 4.5$ B. M. Hence,
 (a) Co must be in +2 oxidation state [2010]
 (b) L must be a strong ligand
 (c) The complex must be highly dist
 (d) Co must be in +3 oxidation state
31. Silver chloride dissolves in: [2010]
 (a) Water (b) Conc. HCl
 (c) NH_4OH (d) CCl_4
32. The IUPAC name of the complex $Hg[Co(CNS)_4]$ is [2010]
 (a) mercury tetrathiocyanatocobaltate (II)
 (b) mercury cobalttetrasulphocyano (II)
 (c) mercury tetrasulphocyanidecobalt (II)
 (d) tetrasulphocyanotocobalt mercurate (II)
33. What is incorrect about homoleptic metal carbonyls? [2010]
 (a) M – C, σ -bond is formed by donation of lone pair of electrons from CO
 (b) M – C, π -bond is formed by back donation of electron from filled d -orbital of metal to vacant p -orbital of carbon
 (c) M – CO bonding produce synergic effect
 (d) Metal carbonyl contain only σ -bonds
34. In $Fe_2(CO)_9$, the two iron atoms are [2011]
 (a) linked only directly
 (b) linked directly along with 3 CO molecules as bridging ligands
 (c) linked only through 3 CO molecules as bridging ligands
 (d) joined through one CO group as bridging ligands.
35. Which method can be used to distinguish $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_6][Co(NO_2)_6]$ [2011]
 (a) by measurement of their conductivity
 (b) by titration method
 (c) by precipitation method with $AgNO_3$
 (d) by electrolysis of their aqueous solutions
36. The $[Fe(CN)_6]^{3-}$ complex ion [2011]
 (a) exhibits planar geometry
 (b) is diamagnetic
 (c) should be very stable
 (d) has 2 unpaired electrons
37. When $AgNO_3$ is added to a solution of $Co(NH_3)_5Cl_3$, the precipitate of $AgCl$ shows two ionizable chloride ions. This means : [2012]
 (a) Two chlorine atoms satisfy primary valency and one secondary valency
 (b) One chlorine atom satisfies primary as well as secondary valency
 (c) Three chlorine atoms satisfy primary valency
 (d) Three chlorine atoms satisfy secondary valency
38. The hypothetical complex chloro-diaquatriaminecobalt (III) chloride can be represented as [2013]
 (a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
 (b) $[Co(NH_3)_3(H_2O)Cl_3]$
 (c) $[Co(NH_3)_3(H_2O)_2Cl]$
 (d) $[Co(NH_3)_3(H_2O)_3]Cl_3$
39. The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4)]NO_2$ (where (en) is ethylene diamine) are, respectively,
 (a) 6 and 2 (b) 4 and 2 [2014]
 (c) 4 and 3 (d) 6 and 3
40. In the isoelectronic series of metal carbonyl, the CO bond strength is expected to increase in the order: [2014]
 (a) $[Mn(CO)_6]^+ < [Cr(CO)_6] < [V(CO)_6]^-$
 (d) $[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$
 (c) $[V(CO)_6]^- < [Mn(CO)_6]^+ < [Cr(CO)_6]$
 (d) $[Cr(CO)_6] < [Mn(CO)_6]^+ < [V(CO)_6]^-$

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- 41.** Which of the following is paramagnetic? [2014]
- (a) $[\text{Fe}(\text{CN})_6]^{4-}$ (b) $[\text{Ni}(\text{CO})_4]$
 (c) $[\text{Ni}(\text{CO})_4]^{2-}$ (d) $[\text{CoF}_6]^{3-}$
- 42.** Coordination compounds have great importance in biological systems. In this context which of the following statements is **incorrect**? [2015]
- (a) Cyanocobalamin is B_{12} and contains cobalt
 (b) Haemoglobin is the red pigment of blood and contains iron
 (c) Chlorophylls are green pigments in plants and contain calcium
 (d) Carboxypeptidase - A is an exzyme and contains zinc.
- 43.** Consider the following complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$. The coordination number, oxidation number, number of *d*-electrons and number of unpaired *d*-electrons on the metal are respectively [2015]
- (a) 6, 3, 6, 0 (b) 7, 2, 7, 1
 (c) 7, 1, 6, 4 (d) 6, 2, 7, 3
- 44.** The deep blue colour produced on adding excess of ammonia to copper sulphate is due to presence of [2016]
- (a) Cu^{2+} (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (c) $[\text{Cu}(\text{NH}_3)_6]^{2+}$ (d) $[\text{Cu}(\text{NH}_3)_2]^{2+}$
- 45.** 0.02 mole of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$ and 0.02 mole of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ are present in 200 cc of a solution X. The number of moles of the precipitates Y and Z that are formed when the solution X is treated with excess silver nitrate and excess barium chloride are respectively [2016]
- (a) 0.02, 0.02 (b) 0.01, 0.02
 (c) 0.02, 0.04 (d) 0.04, 0.02
- 46.** Which of the following coordination compounds would exhibit optical isomerism? [2017]
- (a) pentamminenitrocobalt(III) iodide
 (b) diamminedichloroplatinum(II)
 (c) trans-dicyanobis (ethylenediamine) chromium (III) chloride
 (d) tris-(ethylenediamine) cobalt (III) bromide
- TYPE B : ASSERTION REASON QUESTIONS**
- Directions for (Qs. 47-52) :** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.
- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 (c) If the Assertion is correct but Reason is incorrect.
 (d) If both the Assertion and Reason are incorrect.
 (e) If the Assertion is incorrect but the Reason is correct.
- 47.** **Assertion:** AgCl dissolves in NH_4OH solution.
Reason: Due to formation of a complex [1998]
- 48.** **Assertion :** NF_3 is a weaker ligand than $\text{N}(\text{CH}_3)_3$
Reason : NF_3 ionizes to give F^- ions in aqueous solution. [2003]
- 49.** **Assertion :** The $[\text{Ni}(\text{en})_3]\text{Cl}_2$ ($\text{en} = \text{ethylene-diamine}$) has lower stability than $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$.
Reason : In $[\text{Ni}(\text{en})_3]\text{Cl}_2$, the geometry of Ni is trigonal bipyramidal. [2004]
- 50.** **Assertion :** Potassium ferrocyanide is diamagnetic, whereas potassium ferricyanide is paramagnetic.
Reason : Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion. [2005]

51. **Assertion :** $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$ does not show optical isomerism.
Reason : It has a plane of symmetry. [2006]
52. **Assertion :** Copper sulphate solution is not stored in zinc vessel.
Reason : Zinc forms complex with CuSO_4 . [2007]
- Directions for (Qs.53-58) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
53. **Assertion :** When NO reacts with FeSO_4 , a brown coloured complex is formed.
Reason : In the complex, the coordination number of Fe is 6. [2009]
54. **Assertion :** A chelating ligand must possess two or more lone pairs at such a distance that it may form suitable strain free rings at the metal ion.
Reason : $\text{H}_2\text{N}-\text{NH}_2$ is a chelating ligand. [2010]
55. **Assertion :** Low spin complexes have lesser number of unpaired electrons.
Reason : $[\text{FeF}_6]^{3-}$ is a low spin complex. [2011]
56. **Assertion :** $[\text{FeF}_6]^{3-}$ is a low spin complex.
Reason : Low spin complexes have lesser number of unpaired electrons. [2013]
57. **Assertion :** Ethylenediaminetetraacetate ion forms an octahedral complex with the metal ion.
Reason : It has six donor atoms which coordinate simultaneously to the metal ion. [2014]
58. **Assertion :** $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.
Reason : $[\text{Fe}(\text{CN})_6]^{3-}$ has +3 oxidation state while $[\text{Fe}(\text{CN})_6]^{4-}$ has +2 oxidation state. [2017]

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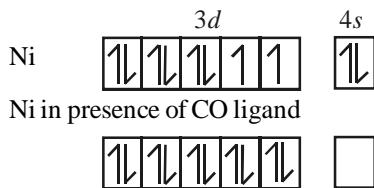
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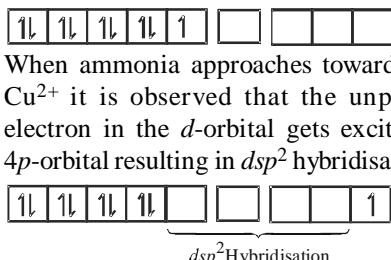
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TYPE A : MULTIPLE CHOICE QUESTIONS

1. (c) In $\text{Na}_2[\text{CdCl}_4]$, Cd has oxidation state +2, so, its electronic configuration is $4\text{d}^{10}4\text{s}^0$. or all the 4 d orbitals are fully filled. Hence, there will not be $d-d$ transition resulting in colour. So, it is colourless.
2. (a) No. of unpaired electrons in $\text{Ni}(\text{CO})_4$ is zero as CO is a strong ligand which pairs up the unpaired electrons of Ni.

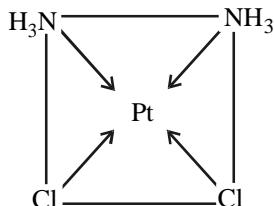


3. (b) Organo-metallic compound is (b) as it contains metal-carbon bonds. In others, direct link of carbon with metal is not present.
4. (a) $\text{HgCl}_2 + 4\text{KI} \longrightarrow \text{K}_2\text{HgI}_4 + 2\text{KCl}$
 HgCl_2 is soluble due to formation of complex ion HgI_4^{2-} ion.
5. (c) EAN for any complex ion
 $= [\text{At.No. of the central atom} - \text{Oxd. No. of the central atom}] + 2$ (coordination No. of central atom)
 $= 30 - 2 + 2(4) = 36$
6. (b) The reagent commonly used is EDTA (ethylene diamine tetraacetate) which acts as ligand for metal ions responsible for hardness of water. They form metal ligand complex which renders the metal ion inactive by making them non-ionisable.
7. (c) In $[\text{Cu}(\text{NH}_3)_4]^{2+}$ the hybridisation is dsp^2
 $\text{Cu}^{2+} = 3d^94s^0$

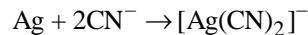


When ammonia approaches towards the Cu^{2+} it is observed that the unpaired electron in the d -orbital gets excited to $4p$ -orbital resulting in dsp^2 hybridisation.

8. (b) The shape of dsp^2 hybridisation is square planar.
The complex used as an anticancer agent is *cis*-platin, cis - $[\text{PtCl}_2(\text{NH}_3)_2]$.

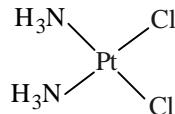


9. (a) Due to back bonding present between metal and carbonyl ligand in metal carbonyl, CO is termed as π -acid ligand.
10. (b) Among the given metal ions only Ag^+ forms complex with CN^- having co-ordination number 2.



Coordination number of metals is defined as the number of σ bonds by which ligands are attached to the metal atom.

11. (a) The structural formula of *cis*-platin is

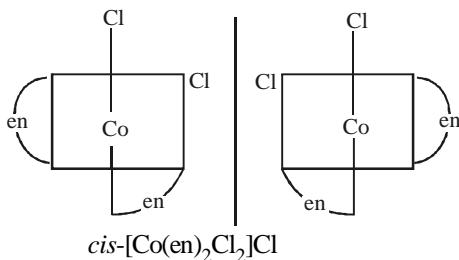


Since no carbon–metal bond is present, it is not an organometallic compound.

12. (c)
-

As clear from the figure, the mirror image is superimposable. So, they are not different compounds.

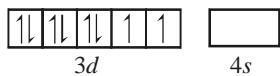
13. (b)
- $[\text{Co}(\text{en})_3]^{+3}$



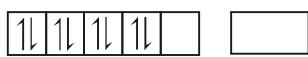
They form non-superimposable mirror image, so, they are optically active compounds.

- 14. (c)** CoCl_2 is a weak Lewis acid. It reacts with chloride ion to produce salt containing the tetrahedral $[\text{CoCl}_4]^{2-}$ ion which is blue in colour.

- 15. (a)** In $[\text{Ni}(\text{CN})_4]^{2-}$, nickel has oxidation no. of +2. So, electronic configuration of its outer most orbital is as follows :



However, CN^- is a strong ligand which forces the electron to pair up. Thus two unpaired electrons are forced to pair up by CN^- .



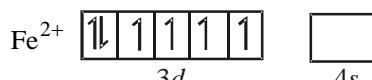
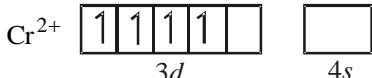
So, it becomes diamagnetic.

- 16. (a)** For any metal cation, the magnitude of Δ_0 depends upon the nature of ligand. Higher the value of Δ_0 , lower will be the wave length absorbed. Δ_0 is crystal field stabilisation energy.

The value of Δ_0 for ligands varies as follows
 $\text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^-$

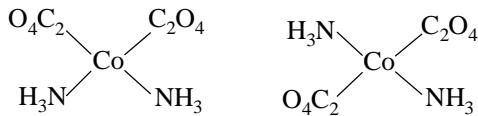
So, the wavelength absorbed will vary in reverse order or $\text{NO}_2^- < \text{NH}_3 < \text{H}_2\text{O}$

- 17. (b)** $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$. Here Cr is in Cr^{2+} form



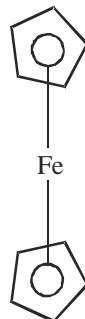
In $[\text{Fe}(\text{H}_2\text{O})]^{2+}$, Fe is in Fe^{2+} form. Both will have 4 unpaired electrons.

- 18. (c)** The complex has three isomers (*cis*- and *trans*); *cis*-isomer shows optical isomerism



- 19. (a)** The ligands in *cis*-platin $[\text{PtCl}_2(\text{NH}_3)_2]$ are Cl and NH_3 .

- 20. (d)**



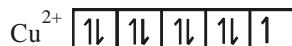
Ferrocene was the first organometallic compound discovered by G. Wilkinson in 1957. The bonding in these aromatic sandwich type structure is better considered as π -bonding involving the lateral overlap of d_{xz} and d_{yz} orbitals on Fe with the delocalized π -aromatic orbital from each cyclopentadienyl ring. All the five C-atoms are equidistant from Fe.

Hence all of these statements are true.

- 21. (d)** Nickel dimethylglyoxime is a non ionic complex.

- 22. (c)** Cu^{2+} forms complexes with the same magnetic moment and geometry irrespective of the nature of ligand. It can be explained by electronic configuration.

3d



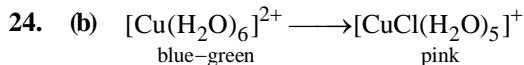
It has 9 electrons in 3d shell. Hence any incoming ligand whether it is strong or weak will result in the formation of same geometry (if number of ligands is same) because any ligand can do nothing with this unpaired e^- in 3d shell. Moreover, the complex formed will have same magnetic moment due to this unpaired e^- .

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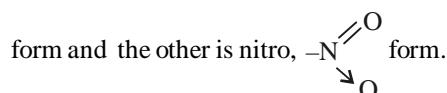
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23. (b) The compound which appears blue green, absorb red light as blue-green is complementary to red colour.
Here $[\text{Cu}(\text{NH}_3)_4]^{2+}$ appears blue-green, so it absorbs red colour.



25. (a) The given compound contains $-\text{NO}_2$ group which can donate electrons either from O or from $-\text{N}$. Thus, it shows linkage isomerism. Thus the two given compounds are linkage isomers, one is nitrite $-\text{O}-\text{N}=\text{O}$



26. (c) (d) In $\text{K}_3[\text{Cu}(\text{CN})_4]$ Cu is in +1 oxidation state hence has no unpaired electron hence colourless and diamagnetic.

- (b) In $(\text{NH}_4)_2[\text{TiCl}_6]$ Ti is in +4 oxidation state, hence has no unpaired electron hence colourless and diamagnetic.

- (c) In VOSO_4 , V is in +4 oxidation state hence has one unpaired electron, thus it is coloured and paramagnetic.

- (a) In $\text{K}_2\text{Cr}_2\text{O}_7$, Cr is in +6 oxidation state, hence has no unpaired electron and thus it is diamagnetic. Though $\text{K}_2\text{Cr}_2\text{O}_7$ has no unpaired electron but it is coloured. This is due to charge transfer.

27. (d) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ sp³d² hybridisation

2 unpaired electrons

- $\text{Na}_3[\text{FeF}_6]$ sp³d² hybridisation

3 unpaired electrons

- $[\text{Cr}(\text{H}_2\text{O})_6]\text{SO}_4$ d²sp³ hybridisation

3 unpaired electrons

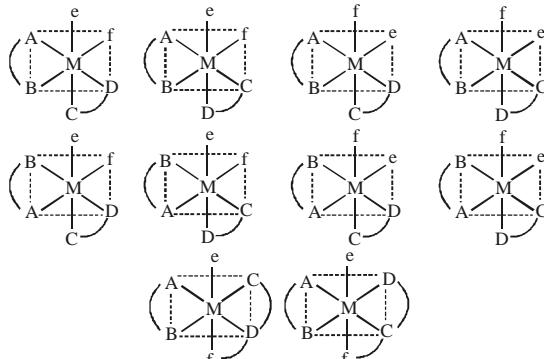
- $\text{K}_4[\text{Fe}(\text{CN})_6]$ d²sp³ hybridisation

No unpaired electron

Zero magnetic moment means all the electrons paired.

28. (b) In the complexes of C.N. 4, square planar geometry gives rise to low spin (spin paired) configurations whereas tetrahedral complexes display high spin configurations.

29. (c)

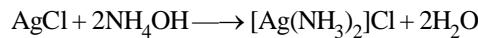


30. (d) Co must be in +3 oxidation state and the ligand L should be a weak ligand.



$n = 4$, $\mu = 4.5$ BM.

31. (c) AgCl is insoluble in water, conc. HCl and CCl_4 . It dissolves in NH_4OH solution due to the formation of complex salt.

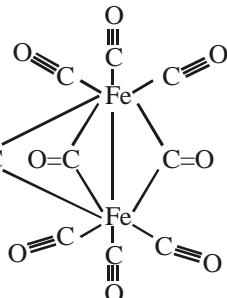


Diamminesilver (I) chloride

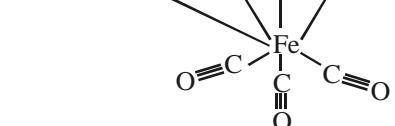
32. (a) The IUPAC name of the given complex is mercury tetrathiocyanatocobaltate (II).

33. (c) It is incorrect statement.

All other statements, i.e. (a), (b) and (d) are correct.



34. (b)

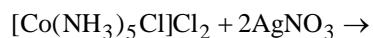


35. (d) In one case, on electrolysis of aqueous solution, the complex ion of cobalt i.e., $[\text{Co}(\text{NH}_3)_6]^{3+}$ of the complex $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode finally cobalt would be deposited. In another case, on electrolysis of aqueous solution, the complex ion of chromium i.e., $[\text{Cr}(\text{NH}_3)_6]^{3+}$ of the complex

$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ moves towards cathode (i.e., negative electrode) and on this electrode chromium would finally be deposited.

36. (c) Both the high charge density of Fe^{3+} in $[\text{Fe}(\text{CN})_6]^{3-}$ and strong basic (Lewis) character of the ligand CN^- attribute to the stability of the complex.

37. (a) Since the precipitate of AgCl shows two ionisable chloride ion the complex must have the structure.



Hence two chlorine atoms satisfy the primary valency and one, secondary valency.

38. (a) The complex chlorodiaquatriammine cobalt (III) chloride can have the structure $[\text{CoCl}(\text{NH}_3)_3(\text{H}_2\text{O})_2]\text{Cl}_2$

39. (d) In the given complex we have two bidentate ligands (i.e en and C_2O_4), so coordination number of E is 6

$$(2 \times 2 + 1 \times 2 = 6)$$

Let the oxidation state of E in complex be x, then

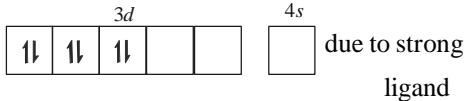
$$[x + (-2)] = 1 \text{ or } x - 2 = 1$$

or $x = +3$, so its oxidation state is + 3

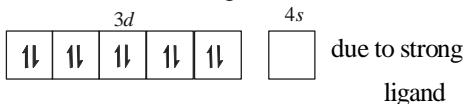
Thus option (d) is correct.

40. (b) CO bond strength is reciprocal to the extent of back donation involved in synergic bonding.

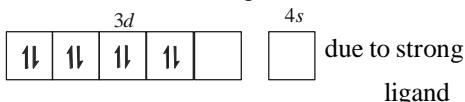
41. (d) Fe^{2+} has electronic configuration



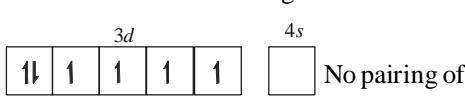
Ni has electronic configuration



Ni^{2+} has electronic configuration



Co^{3+} has electronic configuration



electrons due to weak ligand hence $[\text{CoF}_6]^{3-}$ is paramagnetic.

42. (c) The chlorophyll molecule plays an important role in photosynthesis, contain porphyrin ring and the metal Mg not Ca.

43. (a) $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$. Six monodentate ligands are attached to Co hence C. N. of Co = 6;

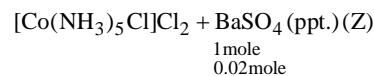
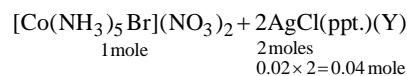
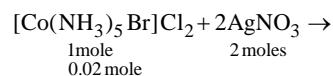
$$\text{O. N.} = x + 5 \times (0) + 1 \times (-2) + 1 \times (-1) = 0$$

$\therefore x = +3$; electronic configuration of $\text{Co}^{3+}[\text{Ar}] 3d^64s^0$ hence number of d electrons is 6. All d-electrons are paired due to strong ligand hence unpaired electron is zero.

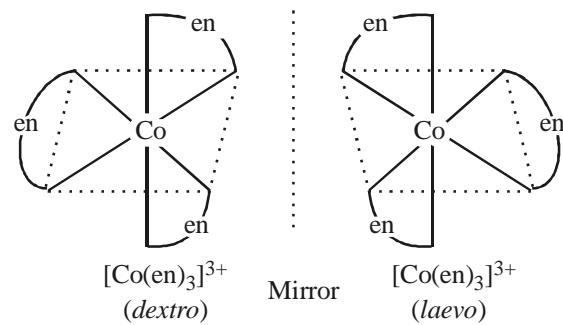
44. (b) $\text{CuSO}_4 + 4\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

Blue complex due to $[\text{Cu}(\text{NH}_3)_4]^{2+}$

45. (d) When excess of AgNO_3 and BaCl_2 are added to solution X.



46. (d) The optical isomers are pair of molecules which are non superimposable mirror images of each other.



The two optically active isomers are collectively called enantiomers.

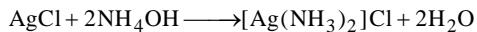
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Type B : Assertion Reason Questions

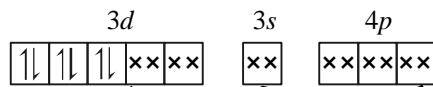
47. (a) AgCl dissolves in NH₄OH due to formation of complex.



48. (c) NF₃ is a weak ligand due to high electronegativity of fluorine which withdraws electrons from N, with the result lone pair of electrons on N atom can't be ligated. N(CH₃)₃ is a strong ligand because CH₃ groups are electron releasing and thus increase electron availability on N atom.

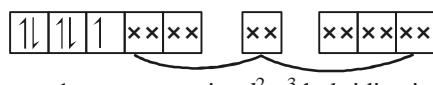
49. (d) [Ni(en)₃]Cl₂ is more stable than [Ni(NH₃)₆]Cl₂ because ethylenediamine is a bidentate ligand, hence it forms chelating ring with Ni²⁺ ion.

50. (c) In potassium ferrocyanide, Fe is in the form Fe²⁺ and in potassium ferricyanide, Fe is in the form Fe³⁺. CN⁻ is a strong legand. So, it will pair up all the 3d⁶ electrons of Fe³⁺ and make it diamagnetic. In Fe²⁺, all the 3d⁵ electrons are not paired up. One electron remains unpaired. So, it is paramagnetic. Fe²⁺ in presence of CN⁻ in K₄[Fe(CN)₆]



$n = 0$, diamagnetic, d^2sp^3 hybridization

Fe³⁺ in presence of CN⁻ in K₃[Fe(CN)₆]

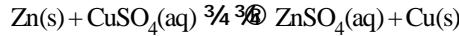


$m = 1$, paramagnetic, d^2sp^3 hybridization

However, the reason is false because crystal field splitting in ferrocyanide is less than in ferricyanide ion (higher the oxidation state of the metal, greater the crystal field splitting).

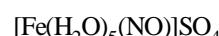
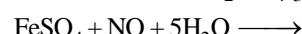
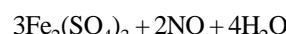
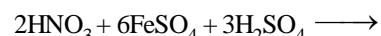
51. (a) Optical isomerism is found in octahedral complexes with 1, 2 or 3 symmetrical bidentate ligands only. Since given compound is not having any bidentate ligand, it will not show optical isomerism. It is because it has plane of symmetry, a plane which is perpendicular to equitorial plane. Thus both A and R are true and R is explantion of A.

52. (c) Copper sulphate solution is not stored in zinc vessel as Zn is more reactive than copper and has tendency to replace Cu from its aqueous solution.



Zn cannot form complex with CuSO₄ although [Zn(H₂O)₄]SO₄ exists in aqueous ZnSO₄ solution. Hence assertion is true but reason is false.

53. (b) In the qualitative analysis of nitrate, brown ring is formed due to the formation of [Fe(H₂O)₅(NO)]²⁺. The chemical reactions showing the formation of complex are as follows:



It is clearly seen from the formula, that the coordination number of Fe in the brown ring complex is six (five H₂O and one NO). Thus both assertion and reason correct but reason is not the correct explanation of assertion.

54. (c) H₂N-NH₂ does not act as chelating ligand. The coordination by hydrazine leads to a three membered highly unstable strained ring and thus, it does not act as chelating agent.

55. (c) [FeF₆]³⁻ is a high spin complex since F⁻ is a weak ligand.

56. (d) [FeF₆]³⁻ is a high spin complex since F⁻ is a weak ligand.

57. (a) Reason is the correct explanation of Assertion.

58. (b) Both Assertion and Reason are true but Reason is not the correct explanation of statement-1. [Fe(CN)₆]³⁻ is weakly paramagnetic as it has unpaired electrons while [Fe(CN)₆]²⁻ has no unpaired electron.
 \therefore It is diamagnetic.

Chapter

24

Haloalkanes and Haloarenes

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Chloroform and conc. HNO_3 react to produce [1997]
 - (a) CHCl_2NO_2
 - (b) $\text{CHCl}_2\text{HNO}_3$
 - (c) CCl_3NO_2
 - (d) CCl_3NO_3
2. Benzene diazonium chloride reacts with hypophosphorous acid to produce: [1998]
 - (a) phenol
 - (b) benzene
 - (c) *p*-hydroxyazobenzene
 - (d) benzonitrile
3. B.H.C. is used as an: [1998]
 - (a) Insecticide
 - (b) Disinfectant
 - (c) Mosquito repellent
 - (d) Antiseptic
4. Which one of the following produces acyl halide by treatment with PCl_5 ? [1998]
 - (a) Alcohols
 - (b) Esters
 - (c) Acids
 - (d) Carbonyl compounds
5. When two halogens are attached to same carbon atom, it is known as : [1997, 1999]
 - (a) *vic*-dihalide
 - (b) *gem*-dihalide
 - (c) α, ω -dihalide
 - (d) α, β -dihalide
6. Gammexane is: [1999]
 - (a) Chloral
 - (b) BHC
 - (c) DDT
 - (d) HCB
7. The product obtained by treating $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow ?$ [1999]
 - (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$
 - (b) $\text{CH}_3-\underset{\substack{| \\ \text{Br}}}{\text{CH}}-\text{CH}_3$
 - (c) $\text{CH}_2\text{BrCH}=\text{CH}_2$
 - (d) $\text{CH}_3-\text{CH}=\text{CHBr}$

8.  $\xrightarrow[\text{Heat}]{\text{conc. HNO}_3 + \text{conc. H}_2\text{SO}_4}$
X $\xrightarrow{\text{Cl}_2/\text{FeCl}_3}$ Y
The product Y is [2000]
 - (a) *p*-chloronitrobenzene
 - (b) *m*-chloronitrobenzene
 - (c) *o*-chloronitrobenzene
 - (d) *o,p*-dichloronitrobenzene
9. Among the following, insecticide is : [2001]
 - (a) BHC
 - (b) Phosphene
 - (c) Chloral
 - (d) Aspirin
10. Which of the following is a chiral compound? [2002]
 - (a) hexane
 - (b) *n*-butane
 - (c) methane
 - (d) 2,3,4-trimethylhexane
11. The reaction :

$$\text{C}_2\text{H}_5\text{OH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{C}_2\text{H}_5\text{Cl} + \text{SO}_2 + \text{HCl}$$

is known as [2002]
 - (a) Kharasch effect
 - (b) Williamson's synthesis
 - (c) Darzen's procedure
 - (d) Hunsdiecker reaction
12. Which of the following is most stable? [2002]
 - (a) 1-butene
 - (b) 1-pentene
 - (c) 2-butene
 - (d) 2-pentene
13. Among the following, the most reactive towards alcoholic KOH is : [2004]
 - (a) $\text{CH}_2=\text{CHBr}$
 - (b) $\text{CH}_3\text{COCH}_2\text{CH}_2\text{Br}$
 - (c) $\text{CH}_3\text{CH}_2\text{Br}$
 - (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
14. Among the following, the dissociation constant is highest for : [2004]
 - (a) $\text{C}_6\text{H}_5\text{OH}$
 - (b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 - (c) $\text{CH}_3\text{C}\equiv\text{CH}$
 - (d) $\text{CH}_3\text{NH}_3^+\text{Cl}^-$

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- 15.** Among the following which one can have a *meso* form? [2006]
- $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{Cl})\text{C}_2\text{H}_5$
 - $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$
 - $\text{C}_2\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$
 - $\text{HOCH}_2\text{CH}(\text{Cl})\text{CH}_3$
- 16.** The correct increasing order of the reactivity of halides for S_N1 reaction is : [2006]
- $\text{CH}_3 - \text{CH}_2 - \text{X} < (\text{CH}_3)_2\text{CH} - \text{X} < \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{X} < \text{PhCH}_2 - \text{X}$
 - $(\text{CH}_3)_2\text{CH} - \text{X} < \text{CH}_3 - \text{CH}_2 - \text{X} < \text{CH}_2 = \text{CH} - \text{CH}_2\text{X} < \text{PhCH}_2 - \text{X}$
 - $\text{PhCH}_2 - \text{X} < (\text{CH}_3)_2\text{CH} - \text{X} < \text{CH}_3 - \text{CH}_2 - \text{X} < \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{X}$
 - $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{X} < \text{PhCH}_2 - \text{X} < (\text{CH}_3)_2\text{CH} - \text{X} < \text{CH}_3 - \text{CH}_2 - \text{X}$
- 17.** Which of the following compounds has the highest boiling point? [2006]
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
 - $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
 - $(\text{CH}_3)_3\text{CCl}$
- 18.** The major product formed in the following reaction:
- $$\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2 - \text{CH}_2\text{OH} \xrightarrow{\text{Aq.KOH}} \text{is:}$$
- $\text{CH}_3\text{CH} = \text{CH} - \text{CH}_2\text{OH}$ [2006]
 - $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$
 - $\text{CH}_3 - \text{CH} - \underset{\substack{| \\ \text{O} - \text{CH}_2}}{\text{CH}_2}$
 - $\text{CH}_3 - \text{CH} - \underset{\substack{| \\ \text{OH}}}{\text{CH}_2} - \text{CH}_2\text{OH}$
- 19.** In the following sequence of the reactions, what is D? [2007]
- $$\begin{array}{ccccccc}
 \text{C}_6\text{H}_5\text{CH}_3 & \xrightarrow{[\text{O}]} & \text{A} & \xrightarrow{\text{SOCl}_2} & \text{B} \\
 & & & & & & \\
 & \xrightarrow{\text{NaN}_3} & \text{C} & \xrightarrow{\text{Heat}} & \text{D} & &
 \end{array}$$
- 20.** Which of the following is optically inactive? [2007]
- -
 -
 - none of these.
- 21.** C_8H_{16} that can form *cis-trans* geometrical isomers and also has a chiral centre, is [2008]
- -
 - Both of these
 - None of these
- 22.** $(\text{CH}_3)_2\text{C} = \text{CHCH}_3 + \text{NOBr} \longrightarrow \text{product.}$ The structure of the product is [2009]
- $(\text{CH}_3)_2\text{C}(\text{NO}) - \text{CH}(\text{Br})\text{CH}_3$
 - $(\text{CH}_3)_2\text{C}(\text{Br}) - \text{CH}(\text{NO})\text{CH}_3$
 - $(\text{CH}_3)_2\text{CH} - \text{C}(\text{NO})(\text{Br})\text{CH}_3$
 -
- 23.**
 $\xrightarrow{\text{Br}_2/\text{hv}}$ Major (X) $\xrightarrow{\text{Alcoholic KOH}/\Delta}$ Major (Y) $\xrightarrow{\text{H-Br, Peroxide}}$ Major (Z)
Major final product (Z) is [2009]
- -
 -
 -

- 24.** The pesticide DDT slowly changes to [2012]
- $\text{CCl}_3\text{-CHO}$ and chlorobenzene
 - p, p' -Dichlorodiphenylethene
 - p, p' -Dichlorodiphenyldichloroethane
 - p, p' -Dichlorodiphenyldichloroethene
- 25.** Rectified spirit is a mixture of [2012]
- 95% ethyl alcohol + 5% water
 - 94% ethyl alcohol + 4.53 water
 - 94.4% ethyl alcohol + 5.43% water
 - 95.87% ethyl alcohol + 4.13% water
- 26.** Which of the following is an example of S_{N}^2 reaction? [2013]
- $\text{CH}_3\text{Br} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{Br}^-$
 - $\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_3 + \text{OH}^- \longrightarrow \text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_2 = \text{CH}_2$
 - $(\text{CH}_3)_3\text{C}-\text{Br} + \text{OH}^- \longrightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$
- 27.** Identify Z in
- $$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \xrightarrow{\text{Aq. NaOH}} \text{X}$$
- $$\xrightarrow{\text{Al}_2\text{O}_3} \text{Y} \xrightarrow{\text{Cl}_2 / \text{H}_2\text{O}} \text{Z}$$
- [2014]
- Mixture of $\text{CH}_3\text{CHClCH}_2\text{Cl}$ and $\text{CH}_3\text{CHOHCH}_2\text{Cl}$
 - $\text{CH}_3\text{CHOHCH}_2\text{Cl}$
 - $\text{CH}_3\text{CHClCH}_2\text{OH}$
 - $\text{CH}_3\text{CHClCH}_2\text{Cl}$
- 28.** Which of the following pairs is/are correctly matched? [2015]
- | Reaction | Product |
|---------------------------------|--|
| I. $\text{RX} + \text{AgCN}$ | RNC |
| II. $\text{RX} + \text{KCN}$ | RCN |
| III. $\text{RX} + \text{KNO}_2$ | $\begin{array}{c} \text{R}-\text{N} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array}$ |
| IV. $\text{RX} + \text{AgNO}_2$ | $\text{R}-\text{O}-\text{N}=\text{O}$ |
| (a) Only I | (b) I and II |
| (c) III and IV | (d) I, II, III and IV |
- 29.** The solution of a chemical compound reacts with AgNO_3 solution to form a white precipitate of Y which dissolves in NH_4OH to give a complex Z. When Z is treated with dilute HNO_3 , Y reappears. The chemical compound X can be: [2015]
- NaCl
 - CH_3Cl
 - NaBr
 - NaI
- 30.** The synthesis of alkyl fluorides is best accomplished by : [2017]
- Finkelstein reaction
 - Swarts reaction
 - Free radical fluorination
 - Sandmeyer's reaction

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 31-33) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- If the Assertion is correct but Reason is incorrect.
- If both the Assertion and Reason are incorrect.
- If the Assertion is incorrect but the Reason is correct.

- 31.** **Assertion :** The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.

Reason : The intermediate carbanion is stabilized due to the presence of nitro group.

[2006]

- 32.** **Assertion :** Chloral reacts with phenyl chloride to form DDT.

Reason : It is an electrophilic substitution reaction.

[2007]

- 33.** **Assertion :** Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone.

Reason : NaCl/NaBr are soluble in acetone while NaI is not.

[2007]

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Directions for (Qs. 34-42) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

34. Assertion : Phenol on oxidation with KMnO_4 gives *meso*-tartaric acid.

Reason : Pure phenol is colourless but turns pink due to oxidation to phenoquinone. [2009]

35. Assertion : S_N2 reactions always proceed with inversion of configuration.

Reason : S_N2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

[2010]

36. Assertion : 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.

Reason : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

[2010]

37. Assertion : Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicylic acid as the major product.

Reason : The reaction occurs through intermediate formation of dichlorocarbene.

[2010]

38. Assertion : Cyanide (CN^-) is a strong nucleophile.

Reason : Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

[2011]

39. Assertion : Iodide ion combines with smaller group to avoid steric hindrance.

Reason : With HI, anisole gives iodobenzene and methyl alcohol.

[2011]

40. Assertion : CHCl_3 is stored in dark bottles.

Reason : CHCl_3 is oxidised in dark. [2015]

41. Assertion : Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.

Reason : Alkyl halides are less reactive than acyl halides.

[2011, 2012, 2013, 2016]

42. Assertion : S_N2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

Reason : S_N2 reactions always proceed with retention of configuration.

[2013, 2017]

HINTS & SOLUTIONS

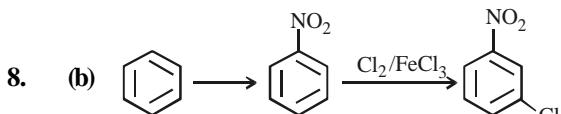
Type A : Multiple Choice Questions

- (c) Chloroform and HNO_3 react to produce CCl_3NO_2 which is also known as chloropicrin. It is used as insecticide.
 - (b) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \longrightarrow \text{C}_6\text{H}_6 + \text{N}_2 + \text{HCl} + \text{H}_3\text{PO}_3$
 - (a) B.H.C. is benzene hexachloride. It is used as an insecticide.
 - (c) Acid can give acyl halide with PCl_5

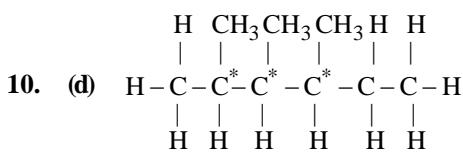
$$\text{CH}_3\text{COOH} + \text{PCl}_5 \longrightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}$$
 - (b)

$\begin{array}{c} \text{CHCl}_2 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2\text{Cl} \\ \\ \text{CH}_2\text{Cl} \end{array}$
<i>gem</i> -dihalide	<i>vic</i> -dihalide
 - (b) Gammexane is commercial name of benzene hexachloride (B.H.C). It is an effective insecticide. It is also known as (6, 6, 6). Chemically it is $\text{C}_6\text{H}_6\text{Cl}_6$.
 - (b) $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \longrightarrow$

Here Markownikoff's rule is followed which states that negative part of addendum goes to that carbon which has least hydrogen.



9. (a) BHC is also known as benzene hexachloride ($C_6H_6Cl_6$). It is an insecticide and sold under the brand name gammexane. It is also known as 6, 6, 6.



Carbon atoms marked star (*) are asymmetric. So it is a chiral compound.

11. (c) Alkyl halides can be prepared by treating alcohol with SOCl_2 .

$$\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{SO}_2 + \text{HCl}$$

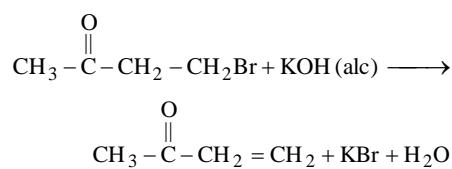
This reaction is known as Darzen's procedure.

Note : SOBr_2 and SOI_2 are not used in this reaction because SOBr_2 is less stable and SOI_2 does not exist.

12. (c) We can explain it on the basis of hyperconjugation.

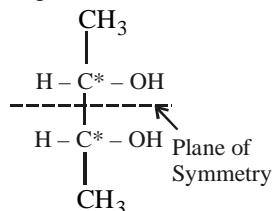
	no. of α -H atoms
(a) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$	2
(b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$	2
(c) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$	6
(d) $\text{CH}_3 \text{CH}_2 \text{CH} = \text{CHCH}_3$	5
(e) is most stable having largest no. of hyperconjugative structures as it has largest no. of α -H-atoms. (hyper-conjugative H)	

13. (b) In $\text{CH}_3-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\text{CH}_2\text{Br}$, the elimination reaction by alcoholic KOH will be facilitated due to presence of $\text{C}=\text{O}$ group which is electron with drawing group.



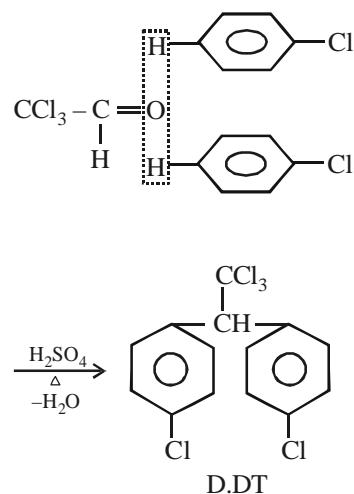
14. (d) Dissociation constant will be highest for $\text{CH}_3\text{NH}_3^+\text{Cl}^-$ because it is ionic in nature.

15. (b) A molecule having a plane of symmetry but having chiral carbons will have *meso* form



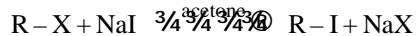
reason is correct explanation of the assertion.

32. (c) Chloral reacts with phenyl chloride to form D.D.T. in presence of conc. H_2SO_4 . A water molecule eliminates in this reaction.



Hence, assertion is true but reason is false.

33. (c) Alkyl halides on treatment with NaI in presence of acetone forms alkyl iodide. This is called Finkelstein reaction.



Here NaI is soluble in acetone but NaBr/NaCl are not soluble. Hence due to precipitation of salt, equilibrium is shifted to forward direction. Hence assertion is true but reason is false.

34. (b) Both assertion and reason are true and reason is not the correct explanation of assertion .

35. (c) Assertion is true, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon-halogen bond acquires partial double bond character, hence, it becomes shorter and stronger and thus, cannot be replaced by nucleophiles. However, Reason is false.

36. (b) As compared to chlorobenzene, the intermediate carbanion resulting from 4-nitrochlorobenzene is stabilized by $-R$ -effect of the NO_2 group.

37. (c) Dichlorocarbene ($:\text{CCl}_2$) attacks on the *ortho*-position of the phenolate ion to form an intermediate which on hydrolysis gives salicylic acid.

38. (c) Aryl halides (chlorobenzene) do not undergo nucleophilic substitution with KCN because of the low reactivity of the Cl atom, which is because of resonance in chlorobenzene. So assertion is true. Reason is false.

39. (c)

40. (c) CHCl_3 is stored in dark bottles to prevent oxidation of CHCl_3 in presence of sunlight.

41. (c) Alkyl halides give polyalkylation products.

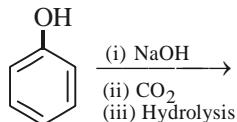
42. (d) Assertion is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. Also, Reason is false because S_N2 reactions proceeds with inversion of configuration.

Chapter

25**Alcohols, Phenols and Ethers****TYPE A : MULTIPLE CHOICE QUESTIONS**

1. The product obtained from the reaction is:

[1998]



2. Picric acid is: [2000]

- (a) Trinitrophenol (b) Trinitrotoluene
 (c) Trinitrobenzene (d) Tribromobenzene

3. Lucas reagent is: [2000]

- (a) anhy. AlCl₃ + conc. HCl
 (b) anhy. AlCl₃ + conc. HNO₃
 (c) anhy. ZnCl₂
 (d) anhy. ZnCl₂ + conc. HCl

4. Lucas test is used for the detection of [2002]

- (a) alcohols (b) alkyl halides
 (c) phenols (d) aldehydes

5. Intermolecular hydrogen bonding is strongest

in: [2003]

- (a) Methylamine (b) Phenol
 (c) Formaldehyde (d) Methanol

6. Propan-1-ol can be prepared from propene by:

[2003]

- (a) H₂O / H₂SO₄
 (b) Hg(OAc)₂ / H₂O followed by NaBH₄
 (c) B₂H₆ followed by H₂O₂
 (d) CH₃CO₂H / H₂SO₄

7. Among the following the one which reacts most readily with ethanol is [2004]

- (a) *p*-nitrobenzyl bromide
 (b) *p*-chlorobenzyl bromide
 (c) *p*-methoxybenzyl bromide
 (d) *p*-methylbenzyl bromide

8. The most suitable reagent for the conversion of RCH₂OH → RCHO is: [2004]

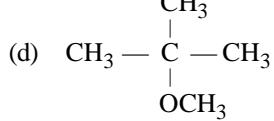
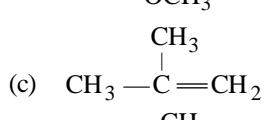
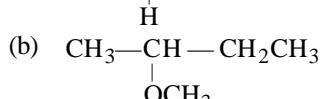
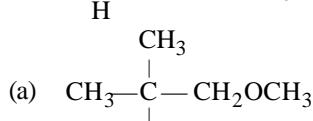
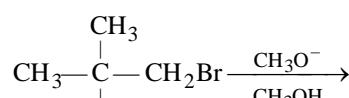
- (a) KMnO₄

- (b) K₂Cr₂O₇

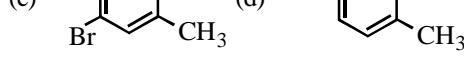
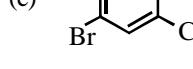
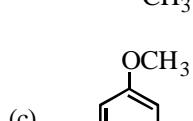
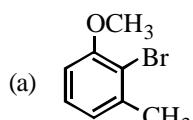
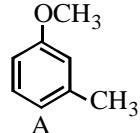
- (c) CrO₃

- (d) PCC (pyridine chlorochromate)

9. The major product formed in the following reaction is: [2005]



10. The major product obtained on the monobromination (with Br₂/FeBr₃) of the following compound A is: [2006]



- 11.** $\text{CH}_3\text{OC}_2\text{H}_5$ and $(\text{CH}_3)_3\text{C}-\text{OCH}_3$ are treated with hydroiodic acid. The fragments obtained after reactions are [2007]
- $\text{CH}_3\text{I} + \text{HOCH}_2\text{H}_5; (\text{CH}_3)_3\text{Cl} + \text{HOCH}_3$
 - $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{I}; (\text{CH}_3)_3\text{Cl} + \text{HOCH}_3$
 - $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{I}; (\text{CH}_3)_3\text{COH} + \text{CH}_3\text{I}$
 - $\text{CH}_3\text{I} + \text{HOCH}_2\text{H}_5; \text{CH}_3\text{I} + (\text{CH}_3)_3\text{COH}$.
- 12.** In which of the following reactions the product obtained is *t*-butyl methyl ether? [2008]
- $\text{CH}_3\text{OH} + \text{HO}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{conc. H}_2\text{SO}_4}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{Br}+\text{CH}_3\text{OH} \xrightarrow{\text{HO}^-\text{Na}^+} \\ | \\ \text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{Br}+\text{Na}^+\text{O}^--\text{C}-\text{CH}_3 \longrightarrow \\ | \\ \text{CH}_3 \end{array}$
 - $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{O}^-\text{Na}^++\text{CH}_3-\text{C}-\text{Br} \longrightarrow \\ | \\ \text{CH}_3 \end{array}$
- 13.** Which of the following is a primary halide? [2008]
- Iso-propyl iodide
 - Secondary butyl iodide
 - Tertiary butyl bromide
 - Neohexyl chloride
- 14.** An organic compound X on treatment with pyridinium chlorochromate in dichloromethane gives compound Y. Compound Y reacts with I_2 and alkali to form triiodomethane. The compound 'X' is [2008]
- $\text{C}_2\text{H}_5\text{OH}$
 - CH_3CHO
 - CH_3COCH_3
 - CH_3COOH
- 15.** The formation of diethyl ether from ethanol is based on : [2009]
- Dehydrogenation reaction
 - Hydrogenation reaction
 - Dehydration reaction
 - Heterolytic fission reaction
- 16.** Chloropicrin is obtained by the reaction of
- steam on carbon tetrachloride [2010]
 - nitric acid on chlorobenzene
 - chlorine on picric acid
 - nitric acid on chloroform
- 17.** Ethanol can be prepared more easily by which reaction? [2011]
- $\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$
 - $\text{CH}_3\text{CH}_2\text{Br} + \text{Ag}_2\text{O}$ (in boiling water) $\longrightarrow \text{CH}_3\text{CH}_2\text{OH}$
- by (i) reaction
 - by (ii) reaction
 - Both reactions proceed at same rate
 - by none
- 18.** An aromatic ether is not cleaved by HI even at 525 K. The compound is [2012]
- $\text{C}_6\text{H}_5\text{OCH}_3$
 - $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$
 - $\text{C}_6\text{H}_5\text{OC}_3\text{H}_7$
 - Tetrahydrofuran
- 19.** The product of the following reaction is [2013]
- $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 \end{array} \xrightarrow{\begin{array}{l} \text{(i) BH}_3/\text{THF} \\ \text{(ii) H}_2\text{O}_2, \text{OH}^- \end{array}}$$
- 1-Pentanol
 - 2-Pentanol
 - Pentane
 - 1,2-Pentanediol
- 20.** Ethanol when reacted with PCl_5 gives A, POCl_3 and HCl . A reacts with silver nitrite to form B (major product) and AgCl . A and B respectively are [2013]
- $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
 - C_2H_6 and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
 - $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_2\text{H}_5\text{NO}_2$
 - C_2H_6 and $\text{C}_2\text{H}_5\text{NO}_2$
- 21.** Polyvinylalcohol can be prepared by [2013]
- polymerization of vinyl alcohol
 - alkaline hydrolysis of polyvinyl acetate
 - polymerization of acetylene
 - reaction of acetylene with H_2SO_4 in presence of HgSO_4
- 22.** Compound 'A' of molecular formula $\text{C}_4\text{H}_{10}\text{O}$ on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively [2014]
- 2-methyl-2-propanol and 2-methyl-2-chloropropane
 - 2-methyl-1-propanol and 1-chloro-2-methylpropane
 - 2-methyl-1-propanol and 2-methyl-2-chloropropane
 - butan-2-ol and 2-chlorobutane

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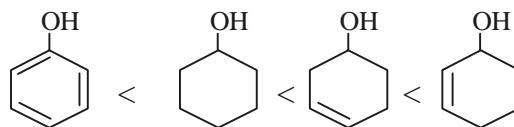
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23. Which of the following alcohols gives the best yield of dialkyl ether on being heated with a trace of sulphuric acid? [2014]
- 2-Pentanol
 - Cyclopentanol
 - 2-Methyl-2-butanol
 - 1-Pentanol
24. Which of the following reagents convert propene to 1-propanol? [2015]
- $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$
 - Aqueous KOH
 - $\text{MgSO}_4, \text{NaBH}_4/\text{H}_2\text{O}$
 - $\text{B}_2\text{H}_6, \text{H}_2\text{O}_2, \text{OH}^-$
25. Which of the following fact(s) explain(s) as to why *p*-nitrophenol is more acidic than phenol?
- I Effect of nitro group. [2015]
 - Greater resonance effect of *p*-nitrophenoxy group
 - Steric effect of bulky nitro group
- I and II
 - I and III
 - II and III
 - II alone
26. $\text{ClCH}_2\text{CH}_2\text{OH}$ is stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$ because of: [2016]
- I effect of Cl increases negative charge on O atom of alcohol
 - I effect of Cl disperses negative charge on O atom to produce more stable cation
 - I effect of Cl disperses negative charge on O atom to produce more stable anion
 - None of these
27. The ether that undergoes electrophilic substitution reactions is [2017]
- $\text{CH}_3\text{OC}_2\text{H}_5$
 - $\text{C}_6\text{H}_5\text{OCH}_3$
 - CH_3OCH_3
 - $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
28. A triglyceride can have how many different acyl groups? [2017]
- 3
 - 2
 - 1
 - 4
29. In the reaction
 $\text{Phenol} \xrightarrow{\text{NaOH}} (\text{A}) \xrightarrow[140^\circ]{\text{CO}_2 + \text{HCl}} (\text{B})$, here B is [2017]
- benzaldehyde
 - chlorobenzene
 - benzoic acid
 - salicylic acid
30. In the Victor-Meyer's test, the colour given by 1°, 2° and 3° alcohols are respectively. [2017]
- red, colourless, blue
 - red, blue, colourless
 - blue, red, violet
 - red, blue, violet

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 31-35) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - If the Assertion is correct but Reason is incorrect.
 - If both the Assertion and Reason are incorrect.
 - If the Assertion is incorrect but the Reason is correct.
31. **Assertion :** Resorcinol turns FeCl_3 solution purple.
Reason : Resorcinol have phenolic group. [2000]
32. **Assertion :** Phenol is a strong acid than ethanol.
Reason : Groups with +M effect decreases acidity at *p*-position. [2002]
33. **Assertion :** Benzyl bromide when kept in acetone water, it produces benzyl alcohol.
Reason : The reaction follows $\text{S}_{\text{N}}2$ mechanism. [2003]
34. **Assertion :** The major products formed by heating $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_3$ with HI are $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ and CH_3OH .
Reason : Benzyl cation is more stable than methyl cation. [2004]
35. **Assertion :** The ease of dehydration of the following alcohols is



Reason : Alcohols leading to conjugated alkenes are dehydrated to a greater extent. [2008]

Directions for (Qs.36-40) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

36. Assertion: Phenyl is used as a household germicide.

Reason : Phenyl is phenol derivative and phenol is an effective germicide. [2010]

37. Assertion : *ter*-Butyl methyl ether is not prepared by the reaction of *ter*-butyl bromide with sodium methoxide.

Reason : Sodium methoxide is a strong nucleophile. [2010]

38. Assertion : Ethers behave as bases in the presence of mineral acids.

Reason : Due to the presence of lone pairs of electrons on oxygen. [2013]

39. Assertion : Phenol undergo Kolbe reaction, ethanol does not. [2014, 2015]

Reason : Phenoxide ion is more basic than ethoxide ion.

40. Assertion : Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.

Reason : Cleavage of C–O bond takes place on ethyl-oxygen bond due to the more stable phenyl-oxygen bond. [2016]

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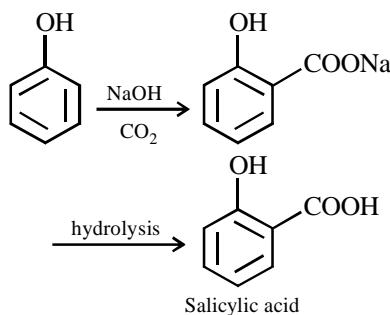
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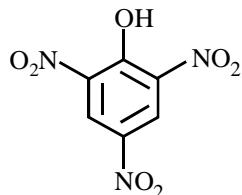
HINTS & SOLUTIONS

Type A : Multiple Choice Questions

2.



4.

(a) Picric acid is *sym*-trinitrophenol

5.

(d) Lucas reagent is anhydrous $\text{ZnCl}_2 + \text{HCl}$ which is used to distinguish between primary, secondary and tertiary alcohols.

6.

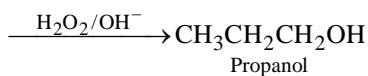
(a) Lucas test is used for the determination of primary, secondary and tertiary alcohols.

7.

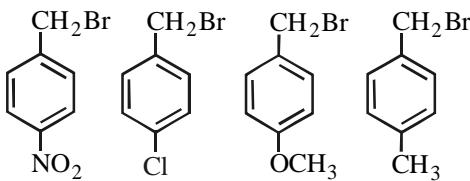
(d) Hydrogen bonding is formed in compounds in which H is attached to highly electronegative element like F, O and N.

- (i) In $\text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H}$, O is not having H atom so it shows very little H-bonding.
- (ii) N is less electronegative than O, so H—bond formed by amines will be weak than that by alcohols.
- (iii) $\text{C}_6\text{H}_5\text{OH}$ forms weak H-bonding due to steric hindrance due to bulky phenyl group.

8.

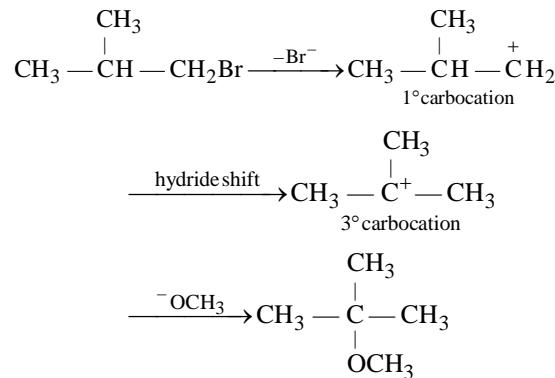
(c) $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{B}_2\text{H}_6} (\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B}$ 

9. (a) Among the given compounds,

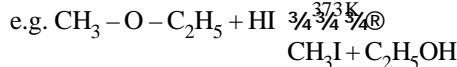


the first one can give carbonium ion most readily because the carbonium ion will be stabilised due to presence of NO_2 group on the ring.

10. (d) The most suitable reagent for converting alcohol to aldehyde is PCC. Other reagent will convert alcohol to acid.

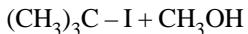
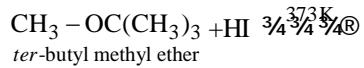
11. (d) The reaction is an example of $\text{S}_{\text{N}}1$ reaction12. (b) The reaction is an example of electrophilic aromatic substitution. Although both OCH_3 and CH_3 groups are *o,p*-directing, the OCH_3 group dominates. Product (b) is favoured because the new coming group (Br) experiences least hindrance.

13. (a) In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group.



The alkyl halide is formed from the smaller alkyl group.

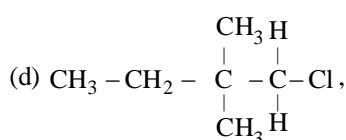
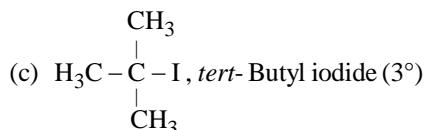
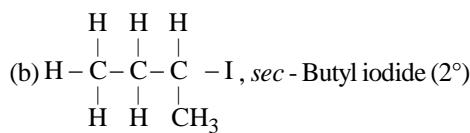
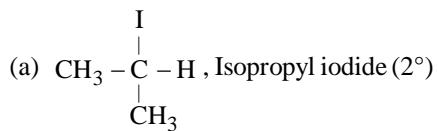
However, in case of tertiary alkyl ether following reaction occurs.



The alkyl halide is formed from the tertiary alkyl group and the cleavage of such ethers occurs by S_N1 mechanism as the product is controlled by the formation of more stable intermediate tertiary carbocation from protonated ether.

14. (c) It is *Williamson's synthesis*. It involves the nucleophilic attack of *alkoxide ion* on alkyl halide according to S_N2 mechanism. In order to prepare methyl tertiary butyl ether, we must use methyl halide (primary) and sodium tertiary butoxide, but not sodium ethoxide and *t*-alkyl halide because the latter undergoes elimination reaction rather than substitution.

- 15. (d)** Writing the structures, we get



Neohexyl chloride (1°)

Thus, (d) is a primary (1°) halide.

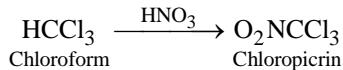
- 16. (a)** $\text{X} \xrightarrow{\text{PCC}} \text{Y} \xrightarrow{\text{I}_2/\text{alkali}} \text{CHI}_3$
 Compound Y must give iodoform test.
 Further since Y is obtained by the oxidation

of X which must be an alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) and thus Y is CH_3CHO .

17. (c) Ethanol on dehydration forms diethyl ether.

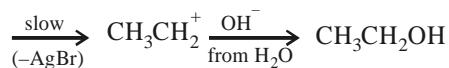
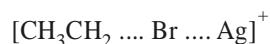


- 18. (d)** Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with HNO_3 .



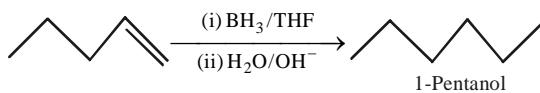
Chloropicrin is a liquid, poisonous and used as an insecticide and in war gas.

19. (b) Heavy metal ions, particularly Ag^+ , catalyse $\text{S}_{\text{N}}1$ reaction because of presence of empty orbital.



- 20. (b)** Due to greater electronegativity of sp^2 -hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like I^- .

- 21. (a)** Hydroboration-oxidation leads to *anti*-Markownikoff's hydration, thus



22. (c) $\text{C}_2\text{H}_5\text{NO}_2 \xleftarrow[\text{B}]{\text{AgNO}_2} \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{PCl}_5} \text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$
 $\quad \quad \quad [\text{A}]$

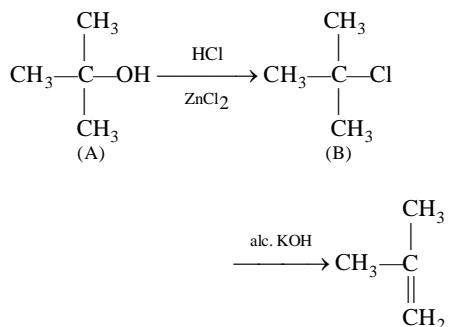
23. (b) Vinyl alcohol, $\text{CH}_2=\text{CHOH}$, monomer of polyvinyl alcohol exists mainly as CH_3CHO ; hence polyvinyl alcohol is best prepared by the alkaline hydrolysis of polyvinyl acetate which in turn is prepared by the polymerisation of vinyl acetate.

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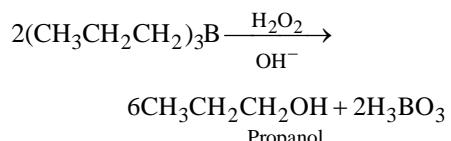
24. (a) Reaction involved is given as :



25. (d) 1-pentanol

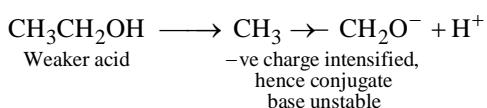
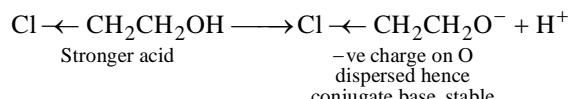
Primary alcohols readily form ether when heated with conc. H_2SO_4 .

26. (d) $6\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{ether, } 0^\circ\text{C}]{\text{B}_2\text{H}_6}$



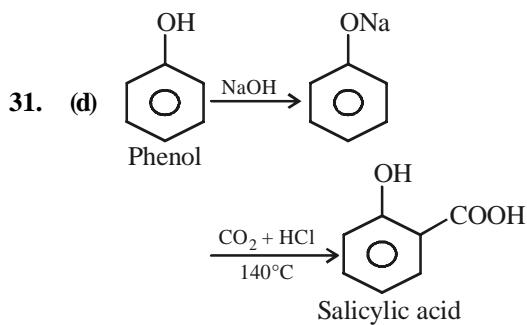
27. (a)

28. (c) $\text{ClCH}_2\text{CH}_2\text{OH}$ is stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$ due to – I effect of Cl.



29. (b)

30. (a) Since glycerol has three –OH groups, it can have three acyl (similar or different) groups



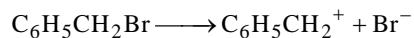
32. (b)

Type B : Assertion Reason Questions

33. (a) Phenols turn FeCl_3 solution purple Resorcinol has phenolic group.

34. (b) Phenol is strong acid than ethanol because phenoxide ion is resonance stabilised. When a group having +M effect is at *p*-position (like halide group) it decreases the acidity of phenols. So assertion and reason are correct but reason is not the explanation of assertion. So correct option is (b).

35. (c) The reaction follows $\text{S}_{\text{N}}1$ mechanism for two reasons :

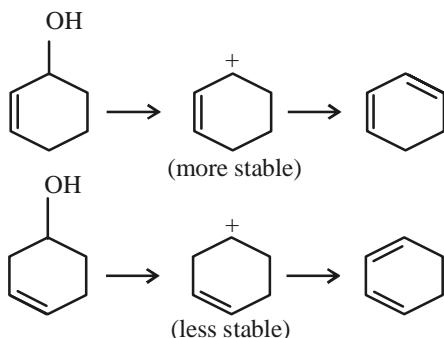


1. $\text{C}_6\text{H}_5\text{CH}_2^+$ is stabilised by resonance.
2. Steric hinderance of phenyl group.

36. (a) As benzyl cation ($\text{C}_6\text{H}_5\text{CH}_2^+$) is more stable than methyl cation (CH_3^+), so the product is $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ and CH_3OH

37. (a) The given order of dehydration is correct due to following reasons.

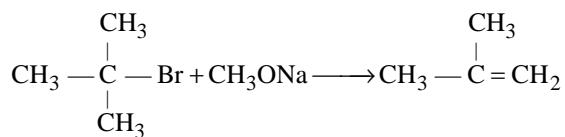
- (i) Alcohols leading to conjugated alkenes are dehydrated more readily.
(ii) 2-Cyclohexenol is dehydrated more easily than 3-cyclohexenol because the carbocation from the former is more stable than the latter.



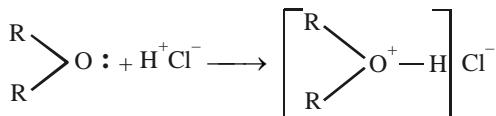
- (iii) Phenol is not dehydrated due to its highly stable character due to resonance.

38. (a) Phenol is an effective germicide. Phenyl is a derivative of phenol, that's why it also has germicidal property.

39. (b) On using *ter*-butyl bromide and sodium ethoxide as reactants, the major product would be 2-methylpropene and ethanol (elimination reaction).



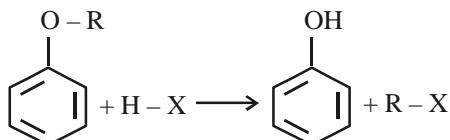
40. (a) Ethers have lone pair on oxygen, so they behave as Lewis base. It forms salt known as oxonium salt with acids.



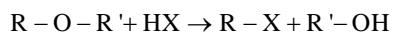
41. (c) It is correct that sodium phenoxide (sodium salt of phenol) and CO_2 on heating form

sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, Assertion is true. But the Reason that phenoxide ion is more basic than ethoxide ion is not correct.

42. (c) Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide



Ethers with two different alkyl groups are also cleaved in the same manner.



Chapter
26

Aldehydes, Ketones and Carboxylic Acids

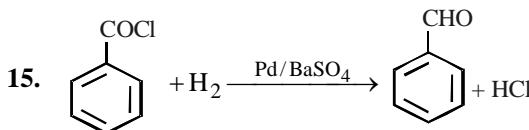
TYPE A : MULTIPLE CHOICE QUESTIONS

1. Reduction of benzoyl chloride with Pd and BaSO₄ gives : [1997]
 - (a) benzyl chloride
 - (b) benzaldehyde
 - (c) benzoic acid
 - (d) benzene sulphonyl chloride
2. Acetaldehyde does not respond to [1997]
 - (a) Tollen's test
 - (b) Benedict's test
 - (c) Lucas test
 - (d) Iodoform test
3. $2\text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{C}_2\text{H}_5\text{ONa}}$
 $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$ [1997]

The above reaction is known as :

 - (a) Claisen condensation
 - (b) Perkin reaction
 - (c) Schotten-Baumann reaction
 - (d) Curtius reaction

4. In a ring substitution of C₆H₅Z, the main product obtained is meta, the group Z is [1997]
 - (a) —COOH
 - (b) —Cl
 - (c) —NH₂
 - (d) —CH₃
5. Acetate ion contains: [1998]
 - (a) One C – O bond and one C = O bond
 - (b) Two C = O bonds
 - (c) Two C – O bonds
 - (d) Two C = O bonds and one C – O bond
6. Phenol $\xrightarrow{\text{NaOH}} \text{X} \xrightarrow{\text{CO}_2} \text{Y} \xrightarrow{\text{H}^+} \text{Z}$,
 Z is identified as: [1999]
 - (a) Benzoic acid
 - (b) Benzaldehyde
 - (c) Sodium benzoate
 - (d) Salicylic acid
7. Benzaldehyde can be prepared by the hydrolysis of: [1999]
 - (a) benzonitrile
 - (b) benzotrichloride
 - (c) benzyl chloride
 - (d) benzal chloride
8. Which produces ketone on treatment with Grignard reagent ? [1999]
 - (a) methyl cyanide
 - (b) acetaldehyde
 - (c) methyl alcohol
 - (d) acetic acid
9. Which of the following compound is formed when CH₂=CH(CH₂)₂COOH reacts with HBr? [2000]
 - (a) CH₃CH₂CH₂CH₂BrCOOH
 - (b) CH₃CHBrCH₂CH₂COOH
 - (c) CH₂BrCH₂(CH₂)₂COOH
 - (d) CH₃CH₂CH₂BrCH₂COOH
10. Ethyl alcohol reacts with chlorine to produce : [2000]
 - (a) CH₃CH₂Cl
 - (b) CH₂ClCH₂OH
 - (c) CHCl₂CH₂OH
 - (d) CCl₃CHO
11. Aldol condensation does not take place in: [2000]
 - (a) HCHO
 - (b) CH₃CHO
 - (c) CH₃CH₂CHO
 - (d) CH₃COCH₃
12. Acetic acid on heating with P₂O₅ produces : [2000]
 - (a) CH₃COCH₃
 - (b) CH₃CHO
 - (c) CH₃COCH₂CH₃
 - (d) (CH₃CO)₂O
13. Salol is : [2001]
 - (a) acetylsalicylic acid
 - (b) phenyl salicylate
 - (c) methyl salicylate
 - (d) none of the above
14. Aldehydes and ketones can be distinguished by:
 - (a) Ammonia
 - (b) H₂SO₄
 - (c) Alkaline KMnO₄
 - (d) Fehling solution



The above reaction is [2001]

- (a) Clemmensen reduction
- (b) Rosenmund reduction
- (c) Birch reduction
- (d) Walf-Kishner reduction

16. The intermediate formed in aldol condensation is [2002]

- (a) aldol
- (b) carbanion
- (c) alcohol
- (d) α -hydrogen ester

17. The compound most suitable for the preparation of cyanohydrin is [2002]

- (a) $\text{C}_2\text{H}_5\text{COOH}$
- (b) $\text{C}_6\text{H}_5\text{NH}_2$
- (c) $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$
- (d) $\text{C}_2\text{H}_5-\text{C}_2\text{H}_5$

18. Action of acetylene on dilute H_2SO_4 gives [2002]

- (a) acetic acid
- (b) acetaldehyde
- (c) acetone
- (d) acetoacetic ester

19. CH_3COCH_3 can be converted to $\text{CH}_3\text{CH}_2\text{CH}_3$ by the action of [2002]

- (a) HIO_3
- (b) HNO_3
- (c) HI
- (d) H_3PO_3

20. Among the following the strongest acid is [2003]

- (a) CH_3COOH
- (b) $\text{C}_6\text{H}_5\text{COOH}$
- (c) $m\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$
- (d) $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$

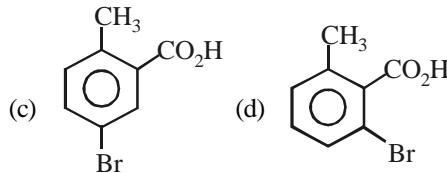
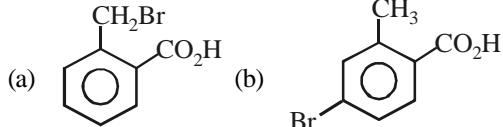
21. At higher temperature, iodoform reaction is given by the dilute solution of [2003]

- (a) $\text{CH}_3\text{CO}_2\text{CH}_3$
- (b) $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$
- (c) $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$
- (d) $\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$

22. The reagent used for the separation of acetaldehyde from acetophenone is [2004]

- (a) NaHSO_3
- (b) $\text{C}_6\text{H}_5\text{NHNH}_2$
- (c) NH_2OH
- (d) $\text{NaOH} + \text{I}_2$

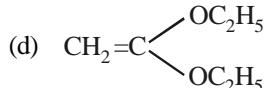
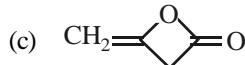
23. *o*-Toluic acid on reaction with $\text{Br}_2 + \text{Fe}$ gives [2004]



24. $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B. Compound B is : [2005]

- (a) $\text{CH}_3\text{COCH}_2\text{COOH}$

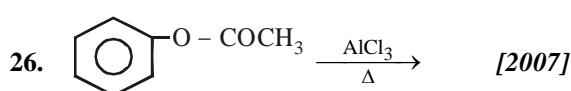
- (b) CH_3COCH_3



25. Isopropylbenzene on air oxidation in the presence of dilute acid gives: [2006]

- (a) $\text{C}_6\text{H}_5\text{COOH}$
- (b) $\text{C}_6\text{H}_5\text{COCH}_3$

- (c) $\text{C}_6\text{H}_5\text{CHO}$
- (d) $\text{C}_6\text{H}_5\text{OH}$



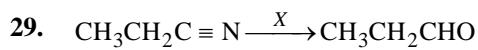
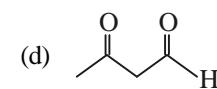
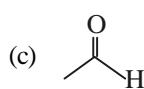
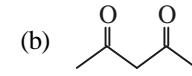
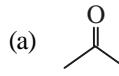
The product obtained is/are

- (a) *o*-product
- (b) *m*-product
- (c) *o*- and *p*-products
- (d) *o*-, *m*- and *p*-products

27. Benzoic acid is treated with lithium aluminium hydride. The compound obtained is [2007]

- (a) benzaldehyde
- (b) benzyl alcohol
- (c) toluene
- (d) benzene.

28. Maximum enol content is in [2008]



The compound X is

- (a) $\text{SnCl}_2/\text{HCl}/\text{H}_2\text{O}$, boil

- (b) $\text{H}_2/\text{Pd}-\text{BaSO}_4$

- (c) LiAlH_4 /ether

- (d) NaBH_4 /ether / H_3O^+

[2008]

- 40.** Carbonyl compounds undergo nucleophilic addition because of [2012]
- electronegativity difference of carbon and oxygen atoms
 - electromeric effect
 - more stable anion with negative charge on oxygen atom and less stable carbonium ion
 - none of the above
- 41.** Which of the following is correct order of acidity? [2012]
- $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{ClCH}_2\text{COOH} > \text{C}_2\text{H}_5\text{COOH}$
 - $\text{ClCH}_2\text{COOH} > \text{HCOOH} > \text{CH}_3\text{COOH} > \text{C}_2\text{H}_5\text{COOH}$
 - $\text{CH}_3\text{COOH} > \text{HCOOH} > \text{ClCH}_2\text{COOH} > \text{C}_2\text{H}_5\text{COOH}$
 - $\text{C}_2\text{H}_5\text{COOH} > \text{CH}_3\text{COOH} > \text{HCOOH} > \text{ClCH}_2\text{COOH}$
- 42.** Which is not true about acetophenone? [2012]
- It reacts with 2,4-dinitrophenylhydrazine to form 2, 4-dinitrophenylhydrazone
 - It reacts with Tollen's reagent to form silver mirror
 - It reacts with I_2/NaOH to form iodoform
 - On oxidation with alkaline KMnO_4 followed by hydrolysis it gives benzoic acid
- 43.** Which of the following products is formed when benzaldehyde is treated with CH_3MgBr and the addition product so obtained is subjected to acid hydrolysis? [2013]
- A secondary alcohol
 - A primary alcohol
 - Phenol
 - tert-Butyl alcohol
- 44.** Ethanoic acid on heating with ammonia forms compound A which on treatment with bromine and sodium hydroxide gives compound B. Compound B on treatment with $\text{NaNO}_2/\text{dil. HCl}$ gives compound C. The compounds A, B and C respectively are [2014]
- ethanamide, methanamine, methanol
 - propanamide, ethanamine, ethanol
 - N-ethylpropanamide, methaneisonitrile, methanamine
 - ethanamine, bromoethane, ethanediazonium chloride
- 45.** The final product (III) obtained in the reaction sequence –
- $$\text{CH}_3 - \text{CH}_2 - \text{COOH} \xrightarrow{\text{PCl}_3} \text{I}$$
- $$\xrightarrow{\text{C}_6\text{H}_6/\text{AlCl}_3} \text{II} \xrightarrow[\text{base/heat}]{\text{NH}_2 - \text{NH}_2} \text{III}$$
- [2014]
- (a)
- (b)
- (c)
- (d)
- 46.** + $\text{CH}_3\text{CHO} \xrightarrow{\text{Dil. NaOH}} \text{A}_{(\text{Major})} .$
- (A) will be –
- [2014]
- (a)
- (b)
- (c)
- (d) Both (b) & (c)
- 47.** Which of the following represents the correct order of the acidity in the given compounds? [2015]
- $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$
 - $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 - $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
 - $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$

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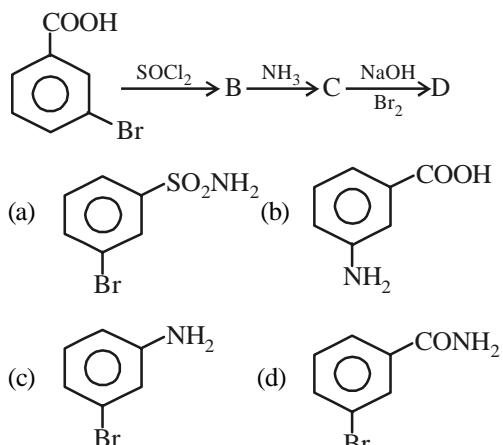
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48. An ester (A) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (B). Ozonolysis of (B) gave a ketone with molecular formula C_8H_8O which shows positive iodoform test. The structure of (A) is

[2015]

- (a) $C_6H_5COOC_2H_5$
- (b) $C_2H_5COOC_6H_5$
- (c) $H_3COCH_2COC_6H_5$
- (d) $p-H_3CO-C_6H_4-COCH_3$

49. In a set of reactions *m*-bromobenzoic acid gave a product D. Identify the product D. [2015]



50. Aldehydes that do not undergo aldol condensation are

- 1. propanal
- 2. trichloroethanal
- 3. methanal
- 4. ethanal
- 5. benzaldehyde

[2016]

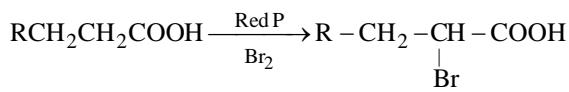
- (a) 3 and 4 only
- (b) 3 and 5 only
- (c) 1, 2 and 3 only
- (d) 2, 3 and 5 only

51. Aldol condensation will not be observed in

- (a) chloral
- (b) phenylacetaldehyde
- (c) hexanal
- (d) nitromethane

[2017]

52. The reaction



is called as

[2013, 2017]

- (a) Reimer-Tiemann reaction
- (b) Hell-volhard Zelinsky reaction
- (c) Cannizzaro reaction
- (d) Sandmeyer reaction

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 53-58) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

53. **Assertion :** Acetaldehyde on treatment with alkali gives aldol.

Reason : Acetaldehyde molecule contains α -hydrogen atom. [1997]

54. **Assertion :** Acetylene on treatment with alkaline $KMnO_4$ produces acetaldehyde.

Reason : Alkaline $KMnO_4$ is a reducing agent. [2000]

55. **Assertion :** Hydroxyketones are not directly used in Grignard reaction.

Reason : Grignard reagents react with hydroxyl group. [2003]

56. **Assertion :** Isobutanal does not give iodoform test.

Reason : It does not have α -hydrogen [2004]

57. **Assertion :** The pK_a of acetic acid is lower than that of phenol.

Reason : Phenoxide ion is more resonance stabilised. [2004]

58. **Assertion :** Acetamide has more polar $\text{C}=\text{O}$ group than ethyl acetoacetate.

Reason : $\ddot{\text{N}}\text{H}_2$ is more electron donating than $\ddot{\text{O}}\text{C}_2\text{H}_5$. [2007]

Directions for (Qs.59-69) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- 59. Assertion :** RCOCl , $(\text{RCO})_2\text{O}$ and RCOOR' all react with Grignard reagents to form 3° alcohols.
Reason : RCOCl reacts with R_2Cd to form ketones but $(\text{RCO})_2\text{O}$ and RCOOR' do not react at all. [2009]
- 60. Assertion :** Protonation of a carbonyl group increases its electrophilic character.
Reason : Protonation of a carbonyl group involves addition of an electrophile on nucleophilic oxygen. [2009]
- 61. Assertion :** Nitration of benzoic acid gives *m*-nitrobenzoic acid.
Reason : Carboxyl group increases the electron-density at *meta*-position. [2009]
- 62. Assertion :** β -Keto carboxylic acids lose CO_2 when heated at about 370 K.
Reason : An enol is first formed by loss of CO_2 , but it readily tautomerises to the more stable ketone. [2010]
- 63. Assertion :** The acetate ion is resonance stabilized.
Reason : Acetate ion is more basic than the methoxide ion. [2011]

64. Assertion : CH_3COCl is converted to CH_3CONH_2 on reaction with NH_3 .

Reason : Cl is a stronger nucleophile and better leaving group. [2011]

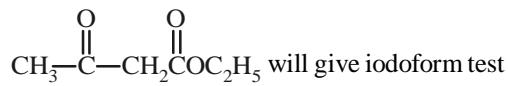
65. Assertion : Aldol condensation can be catalysed both by acids and bases.

Reason : β -Hydroxyaldehydes or ketones readily undergo acid-catalysed dehydration. [2011]

66. Assertion : 2, 2-Dimethylpropanal undergoes Cannizzaro reaction with conc. NaOH .

Reason : Cannizzaro reaction is a disproportionation reaction. [2012]

67. Assertion : Acetoacetic ester,



Reason : It does not contain $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-$ group. [2013]

68. Assertion : Benzaldehyde is more reactive than ethanol towards nucleophilic attack.

Reason : The overall effect of $-I$ and $+R$ effect of phenyl group decreases the electron density on the carbon atom of $> \text{C} = \text{O}$ group in benzaldehyde. [2014, 2015]

69. Assertion : The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

Reason : There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. [2016]

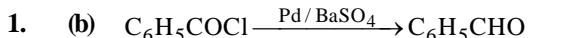
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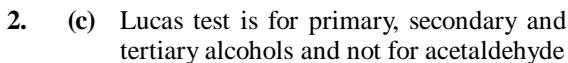
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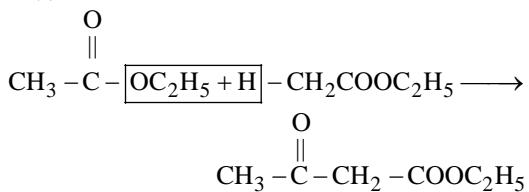
Type A : Multiple Choice Questions



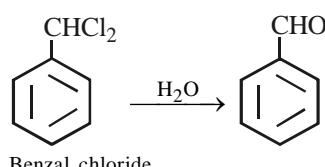
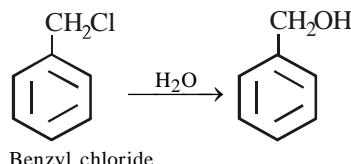
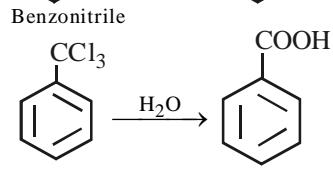
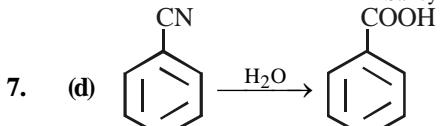
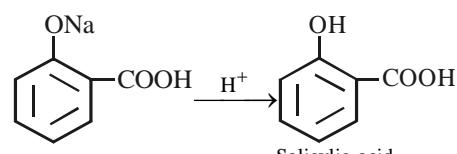
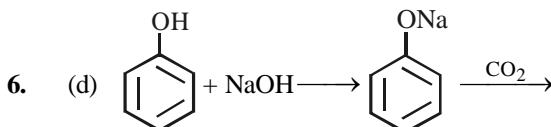
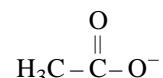
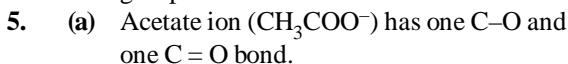
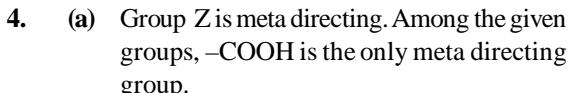
This reaction is known as Rosenmund's reduction.



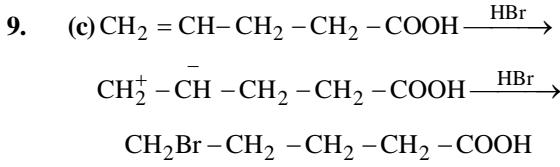
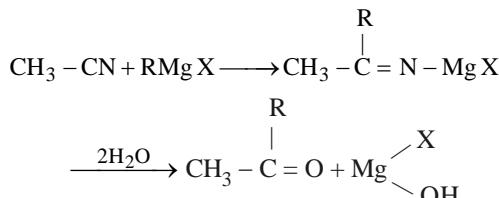
3. (a)



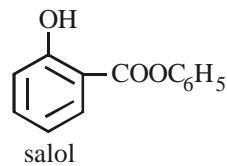
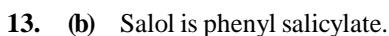
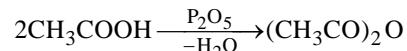
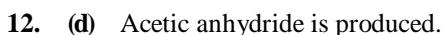
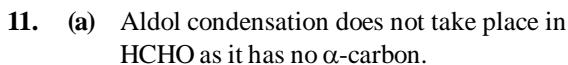
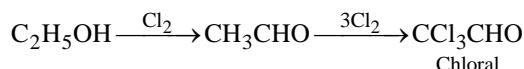
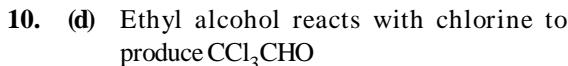
Self condensation of ester takes place in presence of strong base such as $\text{C}_2\text{H}_5\text{O}^-$. The reaction is known as Claisen condensation.



8. (a)



So, the addition is anti-Markovnikov.

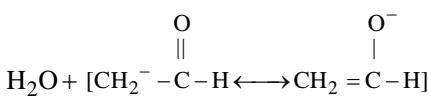
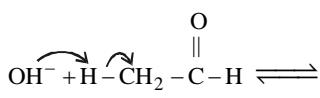


It is used as intestinal antiseptic.

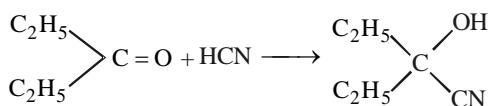
14. (d) Aldehydes and ketones can be distinguished by Fehling solution. Aldehydes can reduce it, whereas ketones cannot reduce it.

15. (b)

16. (b) Aldol condensation is carried out on aldehydes or ketones having α -hydrogen atom in presence of base which abstracts α - H atom from aldehyde/ketone to form corresponding carbanion which is stabilised by resonance.

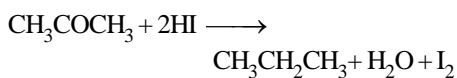


17. (c) Ketones reacts with HCN to form addition product, known as cyanohydrin compounds.



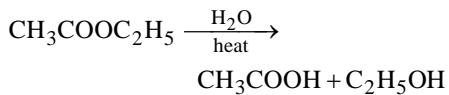
18. (b) Acetylene is hydrolysed by dil. H_2SO_4 to form acetaldehyde.

19. (c) CH_3COCH_3 can be reduced by HI to alkanes. HI is very strong reducing agent.

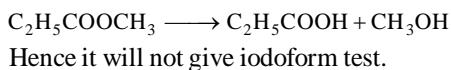


20. (b) Benzoic acid is the strongest acid. Benzoate ion is stabilised by resonance. +I effect of $-\text{CH}_3$ or $-\text{OCH}_3$ group reduces the possibility of ionisation of H^+ from COOH.

21. (b) Formation of iodoform is commonly used as a test for alcohols having $-\text{CH}(\text{OH})\text{CH}_3$ grouping, acetaldehyde and ketones having at least one alkyl group as methyl group, i.e. **for detecting the presence of $-\text{CHOHCH}_3$; $-\text{COCH}_3$ and CH_3CHO** . The esters (as given in the options) are hydrolysed into alcohols or acids.

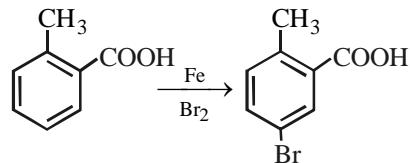


Ethyl alcohol, so formed, will give iodoform test.

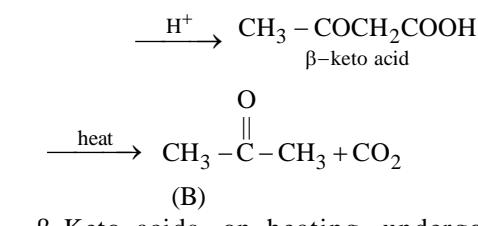
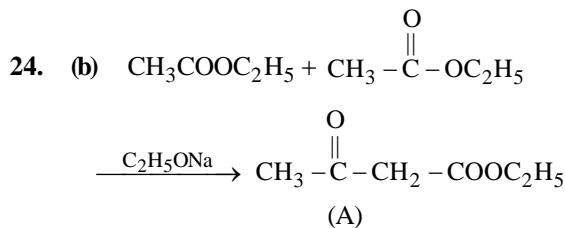


22. (a) NaHSO_3 does not react with acetophenone due to steric hindrance but it forms addition product with acetaldehyde.

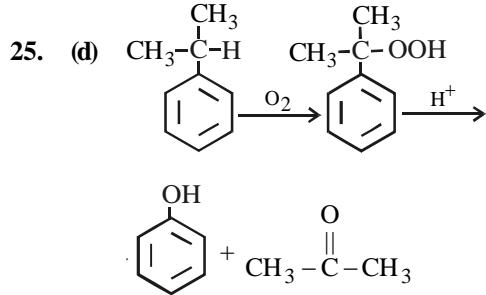
23. (c) In *o* - toluic acid, $-\text{CH}_3$ group is *ortho-para* directing



and $-\text{COOH}$ group is *meta*-directing. So, the resulting product will be (c) in which Br is attached at *para* to $-\text{CH}_3$ and *meta* to $-\text{COOH}$ group.



β -Keto acids, on heating, undergo decarboxylation.

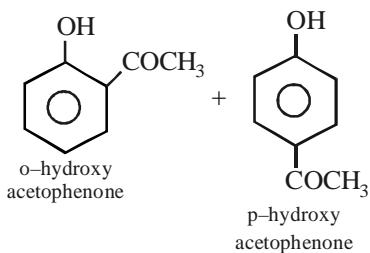
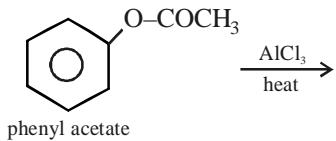


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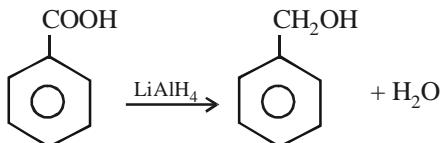
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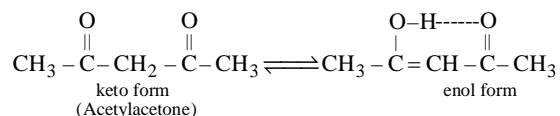
26. (c) The phenyl esters on treatment with AlCl_3 (anhy.) undergoes rearrangement to give *o*- and *p*- hydroxyketones (Fries rearrangement).



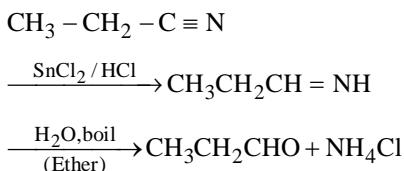
27. (b) When benzoic acid is treated with LiAlH_4 it reduces the $-\text{COOH}$ group of benzoic acid to $-\text{CH}_2\text{OH}$.



28. (b) Maximum enol content is in structure (b) because here the enol form is stabilised by H-bonding.

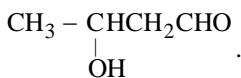


29. (a) Completing the given reaction

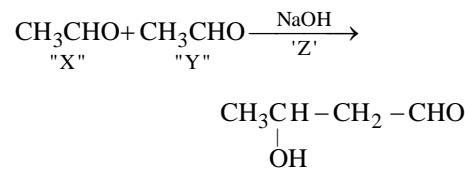


It is Stephen's reduction.

30. (d) The product obtained is

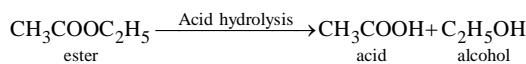


This product is obtained when 2 molecules of CH_3CHO are heated with concentrated alkali (NaOH)

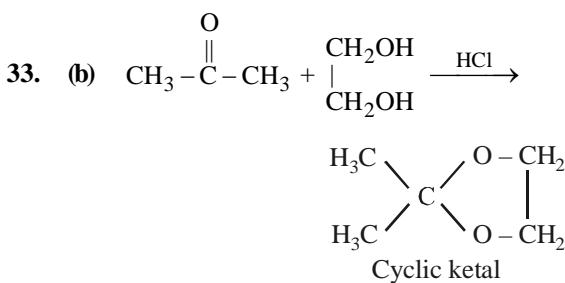


[Note : The aldehydes having α -hydrogen atom on heating with concentrated alkali give brown resinous mass; aldol condensation]

31. (c)

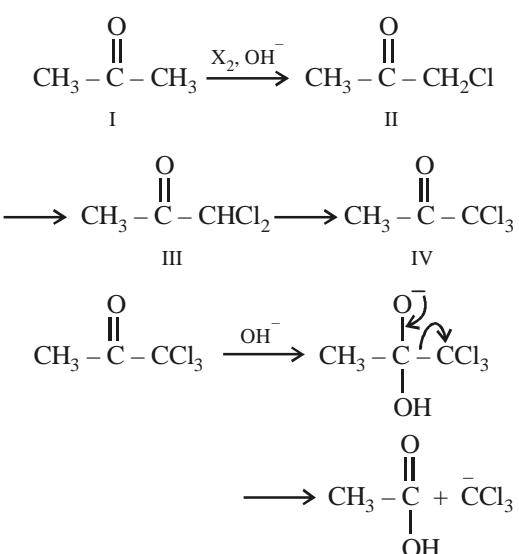


32. (a) In general, aldehydes containing no α -H atom undergo Cannizzaro's reaction. It follows the familiar pattern of carbonyl compounds i.e. nucleophilic addition and involves two successive additions. In step (i), a hydroxide ion is added to give intermediate compound (a). The presence of negative charge on compound (a) aids in loss of hydride ion.



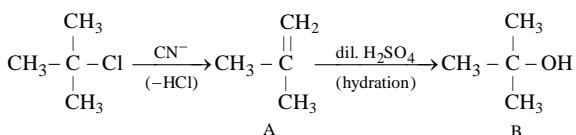
34. (c) Aldol condensation is given by the compounds which contain α -hydrogen atom.

35. (d) If we observe the haloform reaction carefully, we see that $-\text{COCH}_3$ group is first halogenated to the trihalo $-\text{COCX}_3$ through monohalogeno and dihalogeno compound. It is the $-\text{COCX}_3$ part which then undergoes nucleophilic addition. The product easily loses $-\text{CX}_3$ since it is a very good leaving group.

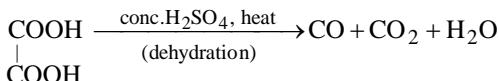


Thus all compounds (I to IV) are ultimately converted to CHCl_3 (chloroform).

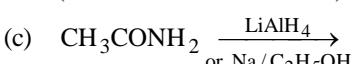
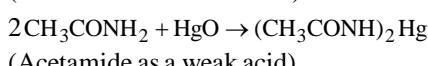
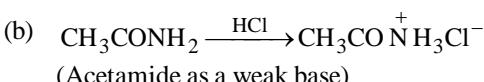
- 36. (b)** CN^- is a strong base and since the substrate is a *tert*-halide, it mainly undergoes elimination reaction forming alkene (A). In presence of dil. H_2SO_4 , alkenes undergo hydration in Markovnikov's way.



- 37. (d)**



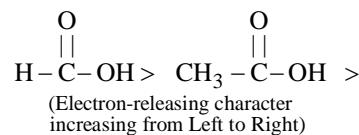
- 38. (d) (a)** $\text{H} - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{Cl} \rightarrow \text{CO} + \text{HCl}$



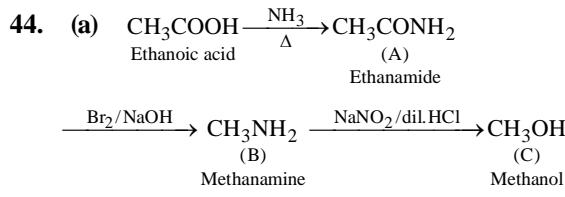
Thus all the three are correct.

- 39. (c)**
40. (c)
41. (b)

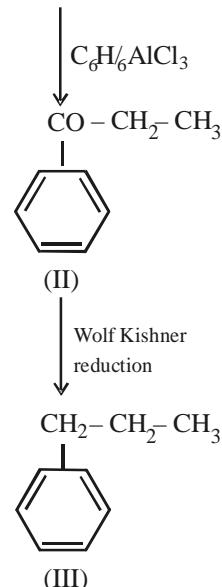
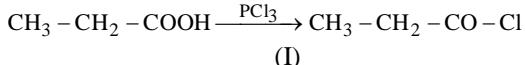
Recall that presence of electron-withdrawing group increases, while presence of electron-releasing group decreases the acidity of carboxylic acids.



- 42. (b)** Acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) being a ketone, does not reduce Tollen's reagent.
43. (a) Aldehydes, other than formaldehyde, when treated with RMgX give 2° alcohols



- 45. (a)**



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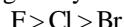
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46. (b) Aldol formed in aromatic aldehydes itself loses water molecule without heating because double bond formed is more stable due to conjugation with benzene ring.

$C_6H_5CH=CHCHO$ is commonly known as cinnamaldehyde.

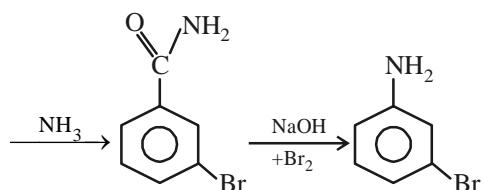
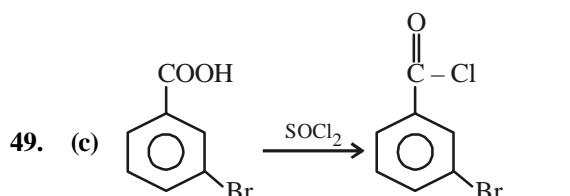
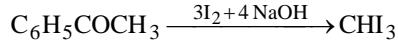
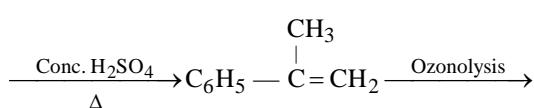
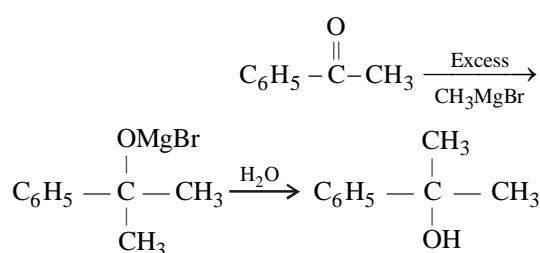
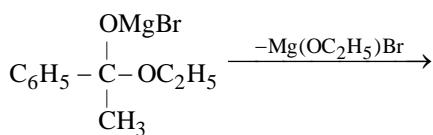
47. (c) Electron withdrawing substituent (like halogen, $-NO_2$, C_6H_5 etc.) would disperse the negative charge and hence stabilise the carboxylate ion and thus increase acidity of the parent acid. On the other hand, electron-releasing substituents would intensify the negative charge, destabilise the carboxylate ion and thus decrease acidity of the parent acid.

Electronegativity decreases in order

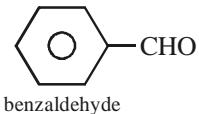
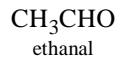
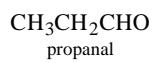


and hence $-I$ effect also decreases in the same order, therefore the correct option is
 $[FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH]$

48. (a) $C_6H_5COOC_2H_5 \xrightarrow{CH_3MgBr} \dots$

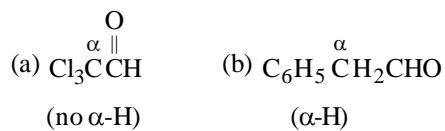


50. (d) Structures of given aldehydes



Trichloroethanal, methanal and benzaldehyde do not undergo aldol condensation. Aldol condensation is not given by aldehydes and ketones which do not contain α -hydrogen atom(s).

51. (a) only those compounds which have α -H give Aldol condensation



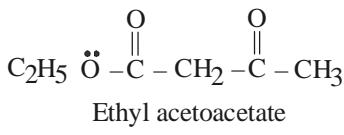
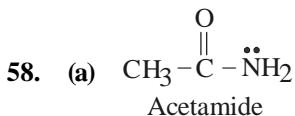
52. (b)

Type B : Assertion Reason Questions

53. (a) Acetaldehyde gives aldol condensation reaction because it contains α -hydrogen.
 54. (d) Both are false. $KMnO_4$ is an oxidising agent and acetylene on treatment with alkaline $KMnO_4$ produces oxalic acid



55. (a) Grignard reagents are highly reactive, so react with the hydroxyl group.
 56. (c) Isobutanal does not give iodoform test because it does not have $-\text{COCH}_3$ group.
 57. (c) Low pK_a value corresponds to more acidic compound. Acetic acid ($pK_a = 4.0$) is more acidic than phenol ($pK_a = 9.0$). It is due to the fact that carboxylate ion is more stabilized due to resonance because its resonating structures are equivalent.



As $-\text{NH}_2$ is more basic than RO^- hence acetamide has more polar $\text{C}=\text{O}$ group than OC_2H_5 group in ethyl acetoacetate.

Hence assertion and reason both are true and reason is correct explanation of assertion.

59. (b) RCOCl , $(\text{RCO})_2\text{O}$ and RCOOR' all add two molecules of Grignard reagents to give 3° alcohols.
 60. (b) Both assertion and reason are true and reason is not the correct explanation of assertion.
 61. (c) The correct reason : Carboxyl group only marginally decreases the electron density at *m*-position relative to *o*- and *p*-positions.
 62. (b)
 63. (c) Assertion is correct as conjugate base of a strong acid is weak. Since CH_3COOH is a stronger acid than CH_3OH , CH_3COO^- is a weaker base than OCH_3^- .
 64. (c)
 65. (b) **Correct explanation :** Both carbanion (formed in presence of a base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.
 66. (b) Aldehydes which do not contain α -hydrogen undergo Cannizzaro reaction.
 67. (d)
 68. (d) Benzaldehyde is less reactive than ethanol towards nucleophilic attack. The combined effect of $-I$ and $+R$ effect of phenyl group is electron donating which increases the electron density on the carbon atom of the $>\text{C}=\text{O}$ in benzaldehyde.
 69. (a)

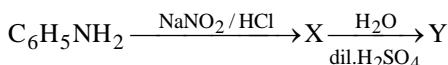
Chapter

27

Amines

TYPE A : MULTIPLE CHOICE QUESTIONS

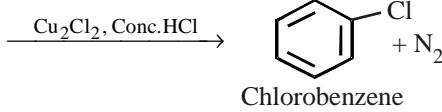
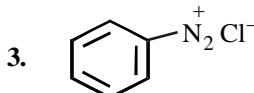
1. Identify Y in the reaction : [1998]



- (a) $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ (b) $\text{C}_6\text{H}_5\text{OH}$
 (c) $\text{C}_6\text{H}_5\text{NHOH}$ (d) C_6H_6

2. Dynamite is a mixture of: [1998]

- (a) Nitroglycerine + raw dust
 (b) Nitroglycerine + HCl
 (c) Hydrogen bomb + H_2SO_4
 (d) Glycerine + H_2SO_4



Above reaction is known as: [2000]

- (a) Strecker's reaction
 (b) Sandmeyer's reaction
 (c) Wohl-Ziegler reaction
 (d) Stephen's reaction

4. Reduction of nitrobenzene with Sn/HCl produces: [2001]

- (a) azobenzene (b) azoxybenzene
 (c) nitrobenzene (d) aniline

5. Hinsberg's reagent is : [2001]

- (a)
- $$\begin{array}{c} \text{COOC}_2\text{H}_5 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}$$
- (b) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$
 (c) $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$
 (d) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$

6. The product formed by the reaction of acetamide with bromine in presence of NaOH is : [2001]

- (a) CH_3CN (b) CH_3CHO
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) CH_3NH_2

7. Primary amine reacts with carbon disulphide and HgCl_2 to produce alkyl isothiocyanate. This reaction is : [2001]

- (a) Carbylamine reaction
 (b) Hoffmann bromamide reaction
 (c) Perkin reaction
 (d) Hoffmann mustard oil reaction

8. Which of the following is involved in Sandmeyer's reaction? [2002]

- (a) ferrous salt
 (b) diazonium salt
 (c) ammonium salt
 (d) cuprammonium salt

9. In the reaction :



The compound, $\text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$ is known as [2002]

- (a) aldol (b) Schiff's base
 (c) Schiff's reagent (d) Benedict's reagent

10. The ortho/para directing group among the following is : [2003]

- (a) COOH (b) CN
 (c) COCH_3 (d) NHCONH_2

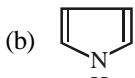
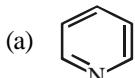
11. Among the following, the weakest base is [2003]

- (a) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_3$
 (c) $\text{O}_2\text{N}.\text{CH}_2\text{NH}_2$ (d) CH_3NHCHO

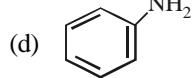
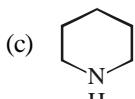
12. Nitrobenzene gives N-phenylhydroxylamine by :

- (a) Sn/HCl (b) $\text{H}_2/\text{Pd-C}$ [2003]
 (c) Zn/NaOH (d) Zn/ NH_4Cl

13. The strongest base among the following is



[2004]



14. Aromatic nitriles (ArCN) are not prepared by reaction : [2004]

- (a) ArX + KCN
- (b) ArN₂⁺ + CuCN
- (c) ArCONH₂ + P₂O₅
- (d) ArCONH₂ + SOCl₂

15. Melting points are normally highest for :

- (a) tertiary amides (b) secondary amides
- (c) primary amides (d) amines [2004]

16. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Tragedy"? [2005]

- (i) Methylamine (ii) Phosgene
- (iii) Phosphine (iv) Dimethylamine
- (a) (i) and (iii) (b) (iii) and (iv)
- (c) (i) and (ii) (d) (ii) and (iv)

17. Among the following which one does not act as an intermediate in Hofmann rearrangement?

- (a) RNCO (b) RCON [2005]
- (c) RCO^{..}NHBr (d) RNC

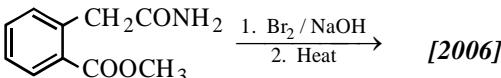
18. Pyridine is less basic than triethylamine because : [2005]

- (a) pyridine has aromatic character
- (b) nitrogen in pyridine is *sp*²-hybridised
- (c) pyridine is a cyclic system
- (d) in pyridine, lone pair of electrons on nitrogen is delocalised

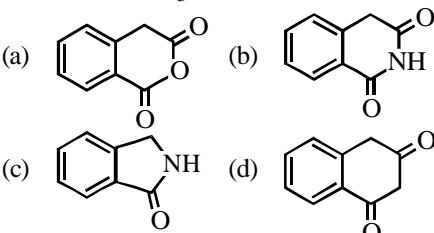
19. C₆H₅CONHCH₃ can be converted into C₆H₅CH₂NHCH₃ by : [2005]

- (a) NaBH₄ (b) H₂-Pd/C
- (c) LiAlH₄ (d) Zn-Hg/HCl

20. The following sequence of reactions on A gives



[2006]



21. Nitrobenzene on treatment with zinc dust and aqueous ammonium chloride gives: [2006]

- (a) C₆H₅N = NC₆H₅
- (b) C₆H₅NH₂
- (c) C₆H₅NO
- (d) C₆H₅NHOH

22. Which of the following statement is true? [2007]

- (a) Trimethyl amine forms a soluble compound with Hinsberg reagent and KOH.
- (b) Dimethyl amine reacts with KOH and phenol to form an azo dye.
- (c) Methyl amine reacts with nitrous acid and liberates N₂ from aq. solution.
- (d) None of these.

23. Which of the following amines will not give N₂ gas on treatment with nitrous acid (NaNO₂ + HCl)? [2007]

- (a) C₂H₅NH₂ (b) CH₃NH₂
- (c) (CH₃)₂CHNH₂ (d) All will give N₂.

24. The compound which gives an oily nitrosoamine on reaction with nitrous acid at low temperature, is [2008]

- (a) CH₃NH₂ (b) (CH₃)₂CHNH₂
- (c) CH₃-NH-CH₃ (d) (CH₃)₃N

25. Diethyl oxalate is used for distinguishing primary, secondary and tertiary [2009]

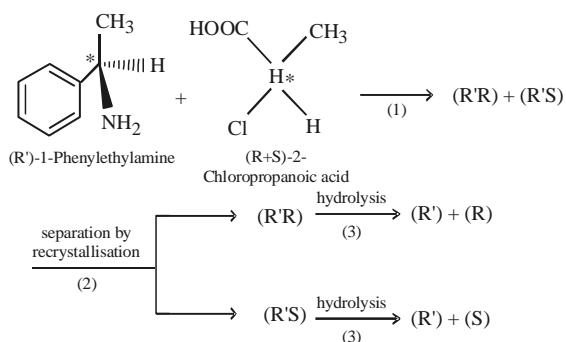
- (a) alcohols
- (b) amines
- (c) alkyl halides
- (d) hydrogens in hydrocarbons

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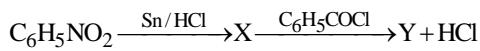
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26. Observe the following reaction : [2009]



Which statement is not correct about the above observation ?

- (a) The product mixture of step-1 is optically active
 - (b) The product R'R and R'S have identical structural formula
 - (c) R'R is nonsuperimposable on R'S
 - (d) R'R and R'S have same solubility in water
27. Fluorescein is an example of [2009]
- (a) azo dyes
 - (b) phthalein dyes
 - (c) triphenylmethane dyes
 - (d) nitro dyes
28. Urea upon hydrolysis yields: [2010]
- (a) acetamide
 - (b) carbonic acid
 - (c) ammonium hydroxide
 - (d) NO_2
29. Benzamide and benzyl amine can be distinguished by [2011]
- (a) cold dil. NaOH
 - (b) cold dil. HCl
 - (c) both a & b
 - (d) NaNO_2 , HCl , 0°C , then β -naphthol
30. The basic character of ethyl amine, diethyl amine and triethyl amine in chlorobenzene is [2011]
- (a) $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < (\text{C}_2\text{H}_5)_3\text{N}$
 - (b) $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$
 - (c) $(\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$
 - (d) $(\text{C}_2\text{H}_5)_3\text{N} < \text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$
31. Consider the following reaction [2012]



What is Y?

- (a) Acetanilide
- (b) Benzylaniline
- (c) Azobenzene
- (d) Hydrazobenzene

32. Which of the following gives primary amine on reduction? [2013]

- (a) $\text{CH}_3\text{CH}_2\text{NO}_2$
- (b) $\text{CH}_3\text{CH}_2-\text{O}-\text{N}=\text{O}$
- (c) $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$
- (d) $\text{CH}_3\text{CH}_2\text{NC}$

33. Which of the following compound will not undergo azo coupling reaction with benzene diazonium chloride. [2016]

- (a) Aniline
- (b) Phenol
- (c) Anisole
- (d) Nitrobenzene

34. Which of the following are intermediates in Sandmeyer reaction ? [2017]

- (i) $\text{C}_6\text{H}_5\text{N}^+ \equiv \text{NCl}^-$
- (ii) $\text{C}_6\text{H}_5\text{N}^+ \equiv \text{N}$
- (iii) $\dot{\text{C}}_6\text{H}_5$
- (iv) $\text{C}_6\text{H}_5\text{Cl}$
- (a) (ii) and (iii)
- (b) (i) and (iv)
- (c) (ii) and (iv)
- (d) (i) and (ii)

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 35-41) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.

35. **Assertion :** Amines are basic in nature

- Reason :** Presence of lone pair of electrons on nitrogen atom. [1999]

36. **Assertion :** Benzene diazonium chloride does not give test for nitrogen.

- Reason :** Loss of N_2 gas takes place during heating. [1999]

37. **Assertion :** $p\text{-O}_2\text{N.C}_6\text{H}_4\text{COCH}_3$ is prepared by Friedel Craft's acylation of nitrobenzene.
Reason : Nitrobenzene easily undergoes electrophilic substitution reaction. [2005]
38. **Assertion :** Alkyl isocyanides in acidified water give alkyl formamides.
Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile. [2005]
39. **Assertion :** Anilinium chloride is more acidic than ammonium chloride.
Reason : Anilinium ion is resonance stabilized. [2006]
40. **Assertion :** Benzene diazonium salt on boiling with water forms phenol.
Reason : C – N bond is polar. [2007]
41. **Assertion :** Nitrobenzene is used as a solvent in Friedel-Craft's reaction.
Reason : Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of *o*-and *p*-nitrophenols. [2008]
- Directions for (Qs.42-46) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
42. **Assertion :** Nitration of aniline can be conveniently done by protecting the amino group by acetylation.
Reason : Acetylation increases the electron-density in the benzene ring. [2010]
43. **Assertion :** Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N-methylcarbamate.
Reason : Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate. [2014]
44. **Assertion :** Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.
Reason : Acyl group sterically hinders the approach of further acyl groups [2016]
45. **Assertion :** Aniline does not undergo Friedel-Crafts reaction.
Reason : $-\text{NH}_2$ group of aniline reacts with AlCl_3 (Lewis acid) to give acid-base reaction.
46. **Assertion :** Aniline is better nucleophile than anilinium ion.
Reason : Anilinium ion have +ve charge.

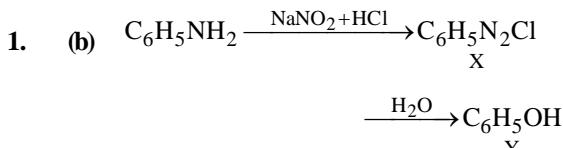
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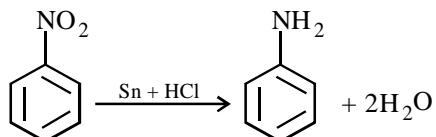
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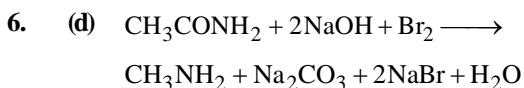
Type A : Multiple Choice Questions



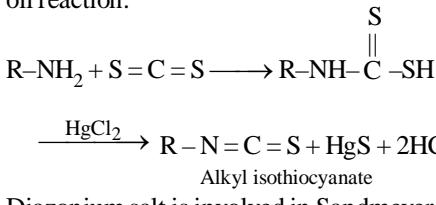
2. (a) Dynamite is a mixture of nitroglycerine and raw dust.
 3. (b) The given reaction is known as Sandmeyer's reaction.
 4. (d) Reduction of nitrobenzene with Sn/HCl produces aniline.



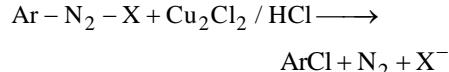
5. (b) Hinsberg's reagent is $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ which is used to distinguish primary, secondary and tertiary amines.



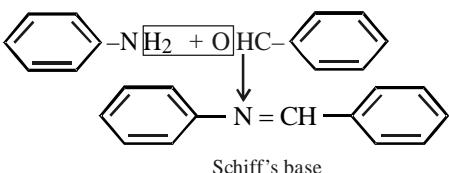
7. (d) The reaction is known as Hoffmann mustard oil reaction.



8. (b) Diazonium salt is involved in Sandmeyer's reaction.

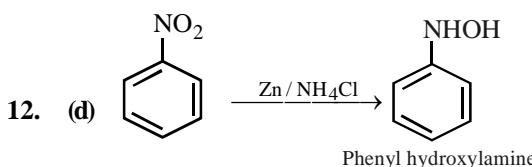


9. (b) Primary amines react with aldehydes or ketones to form compound known as Schiff's base



10. (d) $-\text{NH}-\text{CONH}_2$ group is ortho para directing. Nitrogen shares its lone pair with benzene ring and makes this group ortho para directing.

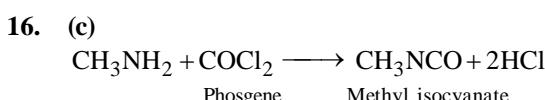
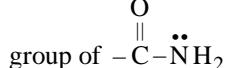
11. (c) As $-\text{NO}_2$ is strong electron withdrawing group.



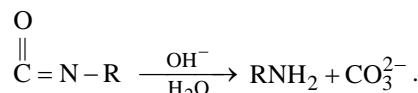
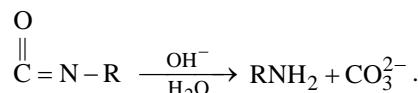
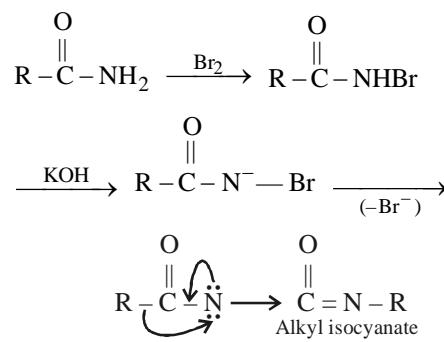
13. (c) The lone pair of electrons on nitrogen is not involved in the formation of π -electron cloud of the ring.

14. (a) Aryl halide (ArX) does not undergo nucleophilic substitution because they have strong C—X bond due to resonance.

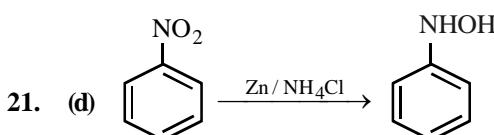
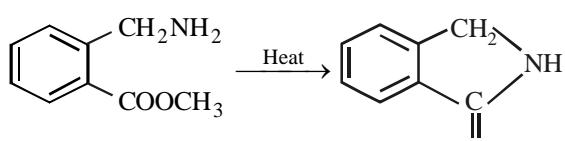
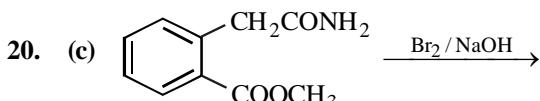
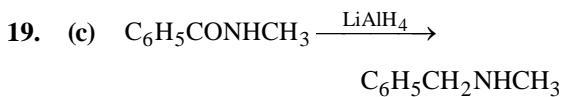
15. (d) Although amines as well as amides form intermolecular H-bonding, H-bonding in amides is less prominent because of $\text{O} \parallel \text{C} -$



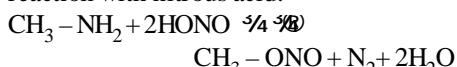
17. (d) Hofmann rearrangement



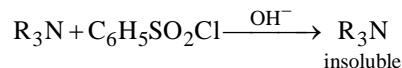
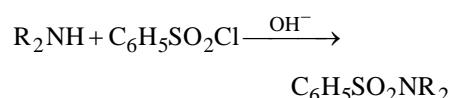
- 18. (b)** Pyridine is less basic because nitrogen in pyridine is sp^2 hybridised, and sp^2 hybridised orbital is more acidic in character than sp^3 hybridised orbital in $(C_2H_5)_2N$.



22. (c) Among the given statements only (c) is true. As methyl amine liberates N_2 on reaction with nitrous acid.



While dimethyl amine and trimethyl amine form insoluble compound with Hinsberg reagent and KOH.

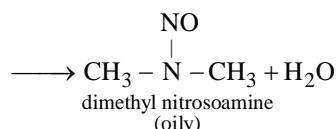


Azo dyes are not formed by secondary amines

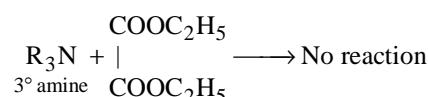
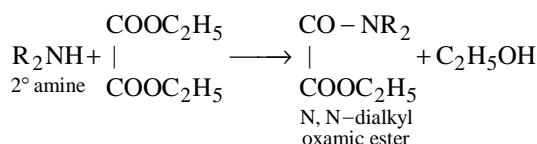
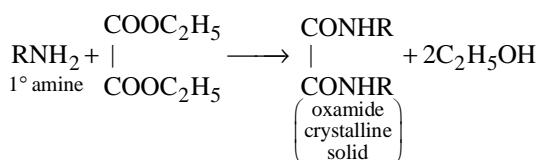
23. (d) All aliphatic primary amines liberate N_2 on treatment with nitrous acid ($NaNO_2 + HCl$)



24. (c) Out of primary, secondary and tertiary amines, the secondary amines, on reaction with HNO_2 , produce yellow oily compounds called *nitrosoamines*.



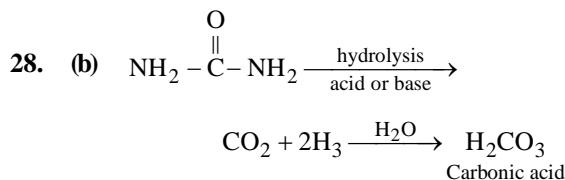
25. (b) Diethyl oxalate is used for distinguishing 1° , 2° and 3° amines as three amines react differently as discussed below.
The 1° amine forms corresponding substituted oxamide which is a crystalline solid; while 2° amine forms a diethyl oxamic ester which is a liquid and 3° amine does not react with diethyl oxalate since it does not contain a replacable hydrogen atom.



26. (d) R'R and R'S are diastereomers and have different physical properties like water solubility, B.P., M.P. etc.

Mixture of diastereomers is optically active hence the product mixture in step 1 is optically active.

27. (b) Fluorescein also called resorcinol-phthalein is an example of phthalein dye. It is prepared by heating phthalic anhydride and resorcinol over a zinc catalyst, and it crystallizes as a deep red powder.



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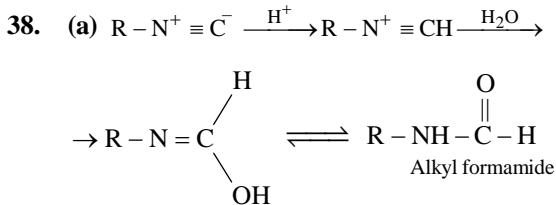
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- Note: The enzyme urease (occurs in soyabean) brings about the same change.
- 29. (b)** Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $C_6H_5CH_2NH_2$.
- 30. (a)** In presence of chlorobenzene, hydrogen bonding is not possible between the protonated amine and the solvent and thus the stabilization factor (solvation effect) is absent. Hence basicity is explained on the basis of the number of electron releasing groups in an amine.
- 31. (b) 32. (a) 33. (d) 34. (a)**

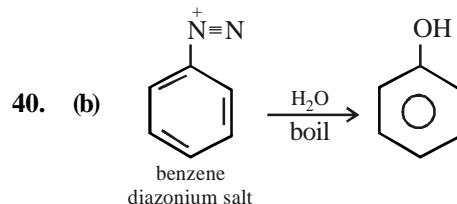
Type B : Assertion Reason Questions

- 35. (a)** Amines are basic in nature due to presence of a lone pair of electrons on nitrogen.
- 36. (a)** Benzene diazonium chloride does not give test of nitrogen as nitrogen gas is evolved on heating.
- 37. (d)** Nitrobenzene undergoes electrophilic substitution reaction with difficulty because NO_2 group is electron withdrawing & therefore, it deactivates the benzene ring.



In the first step due to partial negative charge on carbon it acts as nucleophile and therefore attacked by H^+ of the acid. Once it acquires positive charge, it becomes electrophile as is shown in the next step.

- 39. (c)** Anilinium chloride is more acidic than ammonium chloride because it liberates aniline (resonance stabilized) when heated with strong base. Anilinium ions does not show resonance because charge dispersion at ring may involve pentavalent nitrogen structure.



Although C–N bond is polar but it is not exact reason for the substitution.

- 41. (b)** Nitrobenzene is used as a solvent in Friedel-Craft's reaction because its $-NO_2$ group deactivates benzene ring for electrophilic substitution. Although the given statement of the reason is correct, it is not correct explanation of the given statement.
- 42. (c)** Acetylation decreases the electron density in the benzene ring thereby preventing oxidation.
- 43. (a) 44. (c) 45. (a)**
- 46. (a)** It is fact that aniline is better nucleophile than anilium ion. Anilium ion contain +ve charge, which reduces the tendency to donate lone pair of electron $C_6H_5NH_3^+$ (Anilium ion).

Chapter

28

Biomolecules

MULTIPLE CHOICE QUESTIONS

1. Which one of the following statements is true for protein synthesis (translation)? [2005]
 - (a) Amino acids are directly recognized by m-RNA
 - (b) The third base of the codon is less specific
 - (c) Only one codon codes for an amino acid
 - (d) Every t-RNA molecule has more than one amino acid attachment
2. The pair in which both species have iron is : [2006]
 - (a) Nitrogenase, cytochromes
 - (b) Carboxypeptidase, haemoglobin
 - (c) Haemocyanin, nitrogenase
 - (d) Haemoglobin, cytochromes
3. Lysine is least soluble in water in the pH range:
 - (a) 3 to 4
 - (b) 5 to 6 [2006]
 - (c) 6 to 7
 - (d) 8 to 9
4. Thymine is : [2006]
 - (a) 5-Methyluracil
 - (b) 4-Methyluracil
 - (c) 3-Methyluracil
 - (d) 1-Methyluracil
5. Which of the following statement is not correct? [2008]
 - (a) Chlorophyll is responsible for the synthesis of carbohydrates in plants
 - (b) The compound formed by the addition of oxygen to haemoglobin is called oxyhaemoglobin
 - (c) Acetylsalicylic acid is known as aspirin
 - (d) The metal ion present in vitamin B₁₂ is Mg²⁺
6. The beta and alpha glucose have different specific rotations. When either is dissolved in water, their rotation changes until the same fixed value results. This is called [2008]
 - (a) epimerisation
 - (b) racemisation
 - (c) anomerisation
 - (d) mutarotation
7. If one strand of DNA has the sequence ATCGTATG the sequence in the complementary strand would be: [2009]
 - (a) TAGCTTAC
 - (b) TCACATAC
 - (c) TAGCATAAC
 - (d) TACGATAC
8. Fructose on reduction gives a mixture of two alcohols which are related as [2011]
 - (a) diastereomers
 - (b) epimers
 - (c) both (a) and (b)
 - (d) anomers.
9. α -Amino acids are [2011]
 - (a) acidic due to -COOH group and basic due to -NH₂ group
 - (b) acidic due to -NH₃⁺ group and basic due to -COO⁻ group.
 - (c) neither acidic nor basic.
 - (d) none is true.
10. Denaturation of proteins leads to loss of its biological activity by [2012]
 - (a) Formation of amino acids
 - (b) Loss of primary structure
 - (c) Loss of both primary and secondary structures
 - (d) Loss of both secondary and tertiary structures
11. Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is [2013]
 - (a) three
 - (b) two
 - (c) one
 - (d) four
12. For osazone formation, the effective structural unit necessary is [2014]

(a) $\begin{array}{c} \text{CH}_2\text{OCH}_3 \\ \\ \text{CO} \end{array}$	(b) $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CO} \end{array}$
(c) $\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{CHOCH}_3 \end{array}$	(d) $\begin{array}{c} \text{CHO} \\ \\ \text{CHOCH}_3 \end{array}$

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- 13.** Which of the statements about "Denaturation" given below are correct? [2015]
- (A) Denaturation of proteins causes loss of secondary and tertiary structures of the protein.
 - (B) Denaturation leads to the conversion of double strand of DNA into single strand
 - (C) Denaturation affects primary structure which gets distorted
- Options :
- (a) (B) and (C)
 - (b) (A) and (C)
 - (c) (A) and (B)
 - (d) (A), (B) and (C)
- 14.** Which one of the following statements is correct? [2016]
- (a) All amino acids except lysine are optically active
 - (b) All amino acids are optically active
 - (c) All amino acids except glycine are optically active
 - (d) All amino acids except glutamic acids are optically active
- 15.** α -D-(+)-glucose and β -D-(+)-glucose are [2017]
- (a) conformers
 - (b) epimers
 - (c) anomers
 - (d) enantiomers
- TYPE B : ASSERTION REASON QUESTIONS**
- Directions for (Qs. 16-25) :** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.
- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
 - (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
 - (c) If the Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
 - (e) If the Assertion is incorrect but the Reason is correct.
- 16.** **Assertion :** Hydrolysis of sucrose is known as inversion of cane sugar.
Reason : Sucrose is a disaccharide. [1997]
- 17.** **Assertion :** Proteins on hydrolysis produce amino acids.
Reason : Amino acids contain $-\text{NH}_2$ and $-\text{COOH}$ groups. [1998]
- 18.** **Assertion :** Sucrose undergoes mutarotation.
Reason : Sucrose is a disaccharide. [2000]
- 19.** **Assertion :** DNA as well as RNA molecules are found in the nucleus of a cell.
Reason : On heating, the enzymes do not lose their specific activity. [2002]
- 20.** **Assertion :** Haemoglobin is an oxygen carrier.
Reason : Oxygen binds as O_2^- to Fe of haemoglobin. [2003]
- 21.** **Assertion :** Glycosides are hydrolyzed in acidic conditions
Reason : Glycosides are acetals. [2003]
- 22.** **Assertion :** Carboxypeptidase is an exopeptidase.
Reason : It cleaves the N-terminal bond. [2004]
- 23.** **Assertion :** Sucrose is a non-reducing sugar.
Reason : It has glycosidic linkage. [2004]
- 24.** **Assertion :** Maltose is a reducing sugar which gives two moles of D-glucose on hydrolysis.
Reason : Maltose has 1,4- β -glycosidic linkage [2005]
- 25.** **Assertion :** Alpha (α)-amino acids exist as internal salt in solution as they have amino and carboxylic acid groups in near vicinity.
Reason : H^+ ion given by carboxylic group ($-\text{COOH}$) is captured by amino group ($-\text{NH}_2$) having lone pair of electrons. [2007]
- Directions for (Qs.26-31) :** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.
- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.

- (c) If Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
- 26.** **Assertion :** Disruption of the natural structure of a protein is called denaturation.
Reason : The change in colour and appearance of egg during cooking is due to denaturation.
[2008]
- 27.** **Assertion :** Proteins are made up of α -amino acids.
Reason : During denaturation, secondary and tertiary structures of proteins are destroyed.
[2011]
- 28.** **Assertion :** At isoelectric point, the amino group does not migrate under the influence of electric field.
Reason : At isoelectric point, amino acid exists as a zwitterion.
[2012, 2013]
- 29.** **Assertion :** Treatment of D-glucose with dilute alkali affords an equilibrium mixture consisting of D-mannose, D-fructose and starting substance D-glucose.
Reason : The reaction involves an intermediate in which hybridisation of C₂ changes from sp^3 to sp^2 .
[2013]
- 30.** **Assertion :** Glucose and fructose give the same osazone.
Reason : During osazone formation stereochemistry only at C₁ and C₂ is destroyed.
[2014]
- 31.** **Assertion :** Vitamin D cannot be stored in our body
Reason : Vitamin D is fat soluble vitamin and is excreted from the body in urine.
[2016]

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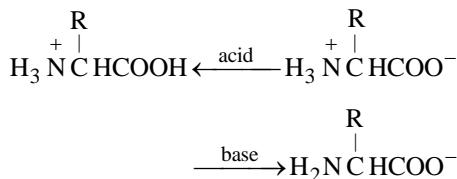
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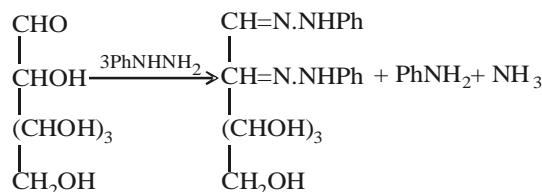
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Type A : Multiple Choice Questions

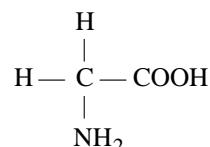
1. (b) The triplet of nucleotides having a specific sequence of bases is known as codon. More than one codon can specify same amino acid. Specificity of a codon is determined by first two bases, the third base of a codon is not very important.
2. (d) Haemoglobin and cytochromes.
3. (c) $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{NH}_2}{\underset{|}{\text{C}}}\text{HCOOH}$, Lysine is least soluble in water in the pH range 6–7.
4. (a) Thymine is 5-methyluracil.
5. (d) The statement is wrong or not correct. The metal ion present in vitamin B_{12} (cyanocobalamin) is cobalt. All other statements are correct.
6. (d) This type of change in optical rotation is called mutarotation.
7. (c) One strand of DNA : ATCGTATG Complementary strand : TAGCATAC
8. (c) Ketoses on reduction produce a new chiral carbon leading to the formation of two isomeric alcohols which are diastereomeric as well as C-2 epimers.
9. (b) Amino acids exist as Zwitterions in which acidic character is due to $-\text{NH}_3^+$ and basic due to $-\text{COO}^-$ group.



10. (d)
11. (a)



12. (b)
13. (c) When the proteins are subjected to the action of heat, mineral acids or alkali, the water soluble form of globular protein changes to water insoluble fibrous protein. This is called denaturation of proteins. During denaturation secondary and tertiary structures of protein destroyed but primary structures remains intact.
14. (c) With the exception of glycine all the 19 other common amino acids have a uniquely different functional group on the central tetrahedral alpha carbon.



Glycine

15. (c) Anomers are those diastereomers that differ in configuration at C-1 atom. Since α -D-(+)-glucose and β -D-(+)-glucose differ in configuration at C-1 atom so they are anomers.

Type B : Assertion Reason Questions

16. (b) Sucrose is a disaccharide with specific rotation of $+66.5^\circ$. On hydrolysis, it gives 1 mole of D-(+)-glucose and 1 mole of D-(-)-fructose. The hydrolysate is laevorotatory hence hydrolysis is known as inversion of sucrose.
17. (b) Proteins are polyamides so, on hydrolysis, give amino acids. Further it is a fact that amino acids contain both $-\text{NH}_2$ as well as $-\text{COOH}$ group. So assertion and reason, although both are correct but reason is not correct explanation of assertion.
18. (b) Sucrose which is a disaccharide undergoes mutarotation because it is converted into glucose and fructose on hydrolysis and the products have different optical activity from that of the reactant.
19. (d) DNA is found mainly in the nucleus of the cell and RNA occurs mainly in the

cytoplasm of the cell. So assertion given is false.

Enzymes are very good biological catalysts in certain temperature range but they lose their specific activity on heating.

Hence reason is also a wrong statement.

20. (c) The assertion is correct but the reason is incorrect because oxygen binds as O_2^- (and not as O_2^-) to Fe of haemoglobin.

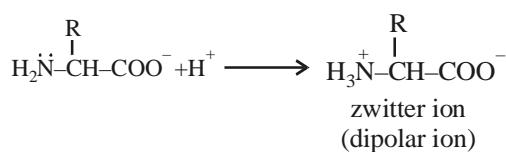
21. (d) Glycosides are formed by treating glucose with methanol in presence of dry HCl gas. They cannot be hydrolysed in acidic conditions. They are not acetals but they are hemiacetals.

22. (c) It is true that carboxypeptidase is an exopeptidase because it cleaves the peptide chain at carboxy terminal amino acids.

23. (a) Sucrose is a non-reducing sugar because it has glycosidic linkage which has no free aldehyde or ketonic group

24. (c) The two glucose units of maltose are linked through α -glycosidic linkage between C-1 of one glucose unit and C-4 of the other.

25. (a) All α -amino acids have $-NH_2$ and $-COOH$ groups. Since $-NH_2$ group is basic and $-COOH$ group is acidic, in neutral solution it exists as internal salt which is also called as zwitter ion. This zwitter ion is formed due to reason that proton of $-COOH$ group is transferred to $-NH_2$ group.



Hence assertion and reason both are true and reason is the correct explanation of assertion.

26. (b) During denaturation, the protein molecule uncoils, form a more random conformation and ultimately precipitates from the solution. Further during denaturation, a protein molecule loses its biological activity. Thus, reason is correct but it is not the correct explanation of assertion.

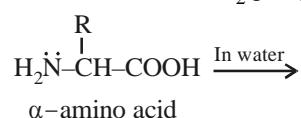
27. (c) **Correct explanation :** During formation of proteins, $-NH_2$ group of one amino acid condenses with $-CO_2H$ of the other with elimination of a water molecule to form a peptide bond.

28. (a) Reason is the correct explanation of Assertion.

29. (a) Reason is the correct explanation of Assertion.

30. (a) Reason is the correct explanation of Assertion.

31. (d) Vitamin D is a fat soluble vitamin and can be stored in the body since it is not excreted out of the body.



Chapter

29

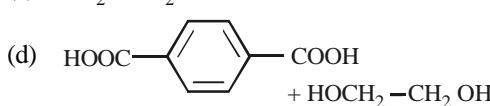
Polymers

TYPE A : MULTIPLE CHOICE QUESTIONS

1. Which of the following is a polymer containing nitrogen? [2008]
 - (a) Polyvinyl chloride
 - (b) Bakelite
 - (c) Nylon
 - (d) Terylene

2. Synthetic detergents are more effective in hard water than soaps because [2009]
 - (a) they are non-ionic
 - (b) their Ca^{++} and Mg^{++} salts are insoluble in water
 - (c) their Ca^{++} and Mg^{++} salts are water soluble
 - (d) they are highly soluble in water

3. Teflon, styron and neoprene are all [2012]
 - (a) Copolymers
 - (b) Condensation polymers
 - (c) Homopolymers
 - (d) Monomers

4. Which compound/set of compounds is used in the manufacture of nylon-66? [2014]
 - (a) $\text{HOOC}(\text{CH}_2)_4\text{COOH} + \text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$
 - (b) $\text{CH}_2=\text{CH}-\text{C}(\text{CH})=\text{CH}_2$
 - (c) $\text{CH}_2=\text{CH}_2$
 - (d)
 

5. The repeating unit present in Nylon 6 is [2016]
 - (a) $-\text{[NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO]}-$
 - (b) $-\text{[CO}(\text{CH}_2)_5\text{NH]}-$
 - (c) $-\text{[CO}(\text{CH}_2)_6\text{NH]}-$
 - (d) $-\text{[CO}(\text{CH}_2)_4\text{NH]}-$

6. Which one of the following is not a condensation polymer? [2017]
 - (a) Melamine
 - (b) Glyptal
 - (c) Dacron
 - (d) Neoprene

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs.7-8) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
7. **Assertion :** Bakelite is a thermosetting polymer.
Reason : Bakelite can be melted again and again without any change. [2015, 2016]
 8. **Assertion :** In vulcanisation of rubber, sulphur cross links are introduced.
Reason : Vulcanisation is a free radical initiated chain reaction. [2017]

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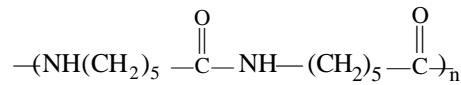
Type A : Multiple Choice Questions

1. (c) Nylon is a polymer of adipic acid and hexamethylenediamine thus it contains nitrogen. Polyvinyl chloride is a polymer of vinyl chloride. It does not contain nitrogen.
Bakelite is a resin of formaldehyde and phenol. It does not contain nitrogen.
Terylene is a polymer of ethylene glycol and terephthalic acid. It does not contain nitrogen. It is also called *dacron*.
2. (c) Structural features of soaps and detergents are almost same except that the polar end in detergents is $-\text{OSO}_3^-\text{Na}^+$ while in soaps polar end is $-\text{COO}^-\text{Na}^+$. Detergents have an advantage over soaps that its polar end sulphate and sulphonate retain their efficiency in hard water, since the corresponding Ca and Mg salts are soluble. Being salts of strong acids, they yield neutral solution, in contrast, to the soaps, which being salts of weak acids yield slightly alkaline solutions.

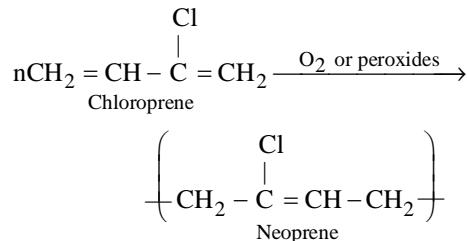
3. (c)

4. (a)

5. (b) Nylon 6 is



6. (d) Neoprene is an addition polymer of isoprene.



Type B : Assertion Reason Questions

7. (c) Bakelite can be heated only once.
8. (b) Vulcanisation is a process of treating natural rubber with sulphur or some compounds of sulphur under heat so as to modify its properties. This cross-linking give mechanical strength to the rubber.

Chapter

30

Chemistry in Everyday Life

MULTIPLE CHOICE QUESTIONS

9. Which of the following compounds is not an antacid? [2017]

- (a) Phenelzine
 - (b) Ranitidine
 - (c) Aluminium hydroxide
 - (d) Cimetidine

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Q. 10) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

(e) If the Assertion is incorrect but the Reason is correct.

10. Assertion : Activity of an enzyme is pH-dependent.

Reason : Change in pH affects the solubility of enzyme in water. [2003]

Directions for (Qs.11-14) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.

11. **Assertion :** Penicillin is an antibiotic.

Reason : The drugs which act on the central nervous system and help in reducing anxiety are called antibiotics. [2010]

12. **Assertion :** The addition of BHA to butter increases its storage life from months to years.

Reason : Butylated hydroxy anisole (BHA) is an antioxidant. [2014]

13. **Assertion :** Tetracycline is a broad spectrum antibiotic.

Reason : Tetracycline is effective against a number of types of bacteria, large viruses and typhus fever. [2016]

14. **Assertion :** Sedatives are given to patients who are mentally agitated and violent.

Reason : Sedatives are used to suppress the activities of central nervous system.

[2017]

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HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (c) Arsenicals are mainly used for the treatment of syphilis.
2. (b) Procaine is the only drug among the given options that is used as a local anaesthetic. Chloramphenicol and penicillin-G, both are antibiotics. Diazepam is a sedative.
3. (c)
4. (d) Ozone layer acts as a shield and does not allow ultraviolet radiation from sun to reach earth. It does not prevent infra-red radiation from sun to reach earth, thus option (d) is wrong statement and so it is the correct answer.
5. (d)
6. (c)
7. (d)
8. (a)
9. (a) Phenelzine is an antidepressant, while others are antacids.

Type B : Assertion Reason Questions

10. (b) The assertion that activity of an enzyme is pH dependent is true because with change in pH the enzymes are denatured. The statement that change in pH affects solubility of enzyme in water is also true.
11. (c) Assertion is true but Reason is false. The drugs which act on the central nervous system and help in reducing anxiety are called tranquilizers.
12. (a) Antioxidants are the compounds that retard the action of oxygen on the food and thereby help its preservation.
13. (a) Broad spectrum antibiotics are those medicines which are effective against several different types of harmful micro organisms.
14. (a) A small quantity of sedative produces a feeling of relaxation, calmness and drowsiness.

Chapter

31

Analytical Chemistry

TYPE A : MULTIPLE CHOICE QUESTIONS

- (a) CaCl_2 (b) BaCl_2
 (c) CuCl_2 (d) None of these

TYPE B : ASSERTION REASON QUESTIONS

Directions for (Qs. 9-17) : These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.

(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.

(c) If the Assertion is correct but Reason is incorrect.

(d) If both the Assertion and Reason are incorrect.

(e) If the Assertion is incorrect but the Reason is correct.

9. **Assertion :** Potassium can be used in Lassaigne test

Reason : Potassium reacts vigorously. [1997]

10. **Assertion :** During test for nitrogen with Lassaigne extract on adding FeCl_3 solution, sometimes a red precipitate is obtained.

Reason : Sulphur is also present [2001]

11. **Assertion :** Sb (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.

Reason : The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation. [2004]

12. **Assertion :** Borax bead test is not suitable for Al(III).

Reason : Al_2O_3 is insoluble in water [2005]

13. **Assertion :** In the iodometric titration, starch is used as an indicator.

Reason : Starch is a polysaccharide. [2006]

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- 14.** **Assertion :** $K_2Cr_2O_7$ is used as a primary standard in volumetric analysis.

Reason : It has a good solubility in water.

[2006]

- 15.** **Assertion :** Sb_2S_3 , is not soluble in yellow ammonium sulphide.

Reason : The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3

[2006]

- 16.** **Assertion :** Fe^{3+} can be used for coagulation of As_2S_3 sol.

Reason : Fe^{3+} reacts with As_2S_3 to give Fe_2S_3

[2006]

- 17.** **Assertion :** Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.

Reason : Change in colour is due to the complexation of alcohol with potassium dichromate.

[2006]

Directions for (Q.18) : Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
 - (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
 - (c) If Assertion is correct but Reason is incorrect.
 - (d) If both the Assertion and Reason are incorrect.
- 18.** **Assertion :** Cu^{2+} and Cd^{2+} are separated from each other by first adding KCN solution and then passing H_2S gas.

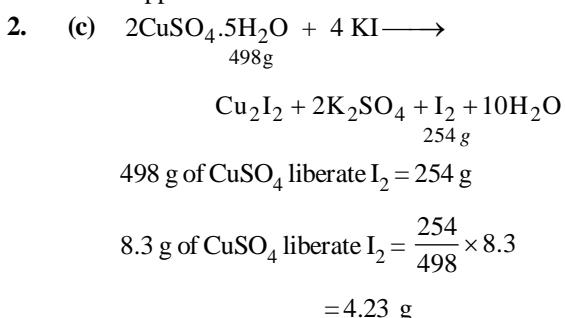
Reason : KCN reduces Cu^{2+} to Cu^+ and forms a complex with it.

[2013]

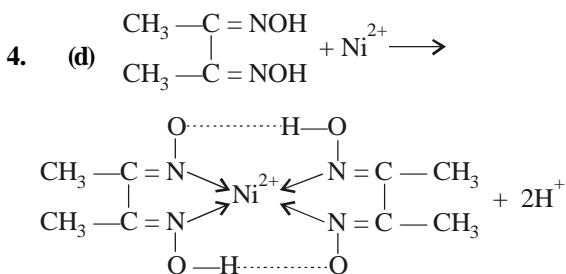
HINTS & SOLUTIONS

Type A : Multiple Choice Questions

1. (d) Beilstein test is used for the detection of halogens. A green or blue colour in flame indicates the presence of halogen. The colour is produced due to the formation of copper halides

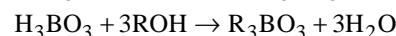
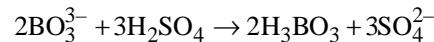


3. (a) Gravimetrically, Cu^{2+} ions are estimated as $\text{Cu}(\text{SCN})_2$, copper thiocyanate.



The reaction indicates that protons are released during reaction. Hence a basic medium is needed to facilitate the reaction. Thus the best pH range is 9-11. If medium is kept acidic then nitrogen atom of the ligand will start donating lone pair to H^+ ion of the acid and not to central metal ion.

5. (a) In the qualitative analysis of BO_3^{3-} , mixture is heated with conc. H_2SO_4 and little alcohol when trialkyl borate, R_3BO_3 or $\text{B}(\text{OR})_3$ is formed.



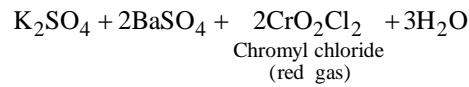
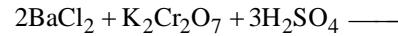
The vapours of trialkyl borate, $B(OMe)_3$ impart green colour to the burner flame.

6. (c) Nessler's reagent ($K_2[HgI_4]$) is used for the detection and quantitative

determination of ammonia (or NH_4^+) in solution. It gives a yellow colour or brown precipitate of oxydimeric ammonium iodide $\left(\text{O}-\begin{array}{c} \text{Hg} \\ | \\ \text{Hg} \\ | \\ \text{NH}_2\text{I} \end{array}\right)$ even with concentration as low as 1 part per million of NH_3 .

7. (b) Hot HCl will produce precipitate of AgCl with Ag^+ only. PbCl_2 will not precipitate because it is soluble in hot solution.

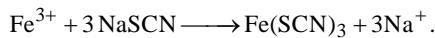
8. (b) The reagent is BaCl_2 which imparts green colour to flame. BaCl_2 forms chromyl chloride (which is red in colour), when treated with $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 .



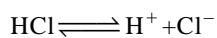
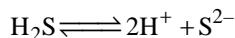
Type B : Assertion Reason Questions

9. (e) Potassium is not used in Lassaigne's test because of its higher reactivity.

10. (a) Due to presence of sulphur, sodium thiocyanate is produced which produces blood red coloured precipitate with Fe^{3+} ion.



11. (d) Sb (III), placed in II group of qualitative analysis is precipitated as Sb_2S_3 by passing H_2S in presence of HCl which decreases ionisation of H_2S (due to common ion effect). This is done to avoid precipitation of metals of higher groups.



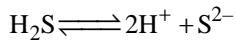
Thus when Sb(III) is precipitated by low concentration of H_2S , it will easily be

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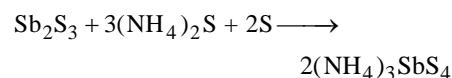
precipitated when concentration of S^{2-} is high, i.e., by H_2S in presence of alkali.



Thus here both assertion and reason are false.

12. (b) Metals form coloured compound (metaborates) with borax. On the basis of colour of metaborates, we can identify the metal. Aluminium does not form coloured metaborate, so this test is not valid for Al^{3+} ion. Al_2O_3 is insoluble in water but it is not explanation of A
13. (b) Starch is used as an indicator because it forms blue coloured complex with iodine. Starch is a polysaccharide but this is not explanation of A.
14. (c) $K_2Cr_2O_7$ is used as primary standard in volumetric analysis because its standard solution can be prepared. A is true but R is wrong.
15. (d) Antimony sulphide (Sb_2S_3) is soluble in yellow ammonium sulphide forming

ammonium thioantimonate.



The common ion effect due to S^{2-} ion does not reduce the solubility of Sb_2S_3 . So both A as well as R, are false.

16. (c) Fe^{3+} can be used to coagulate As_2S_3 as sol of As_2S_3 is negatively charged due to adsorption of S^{2-} ions. The positive charge of Fe^{3+} ion neutralises the negative charge of sol particles. Reason as given in the question does not explain A.
17. (c) A is true but R is wrong because change in colour of potassium dichromate is due to oxidation of alcohol by dichromate.
- $$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
- $$C_2H_5OH + O \longrightarrow CH_3COOH$$
18. (b) KCN forms complexes with Cu^+ and Cd^{2+} as $K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$ respectively. On passing H_2S , only Cd^{2+} complex is decomposed to give yellow CdS precipitate.