



**33**  
Years

**NTA NEET**

Chapterwise & Topicwise  
SOLVED PAPERS

**CHEMISTRY**

**2020-1988**

## DISHA PUBLICATION

45, 2nd Floor, Maharishi Dayanand Marg,  
Corner Market, Malviya Nagar, New Delhi - 110017  
Tel : 49842349 / 49842350

No part of this publication may be reproduced in any form without prior permission of the publisher. The author and the publisher do not take any legal responsibility for any errors or misrepresentations that might have crept in. We have tried and made our best efforts to provide accurate up-to-date information in this book.

All Right Reserved

© Copyright  
Disha

By:  
**Kalpana Bhargav**



[www.dishapublication.com](http://www.dishapublication.com)  
Books &  
ebooks for  
School &  
Competitive  
Exams



[www.mylearninggraph.com](http://www.mylearninggraph.com)  
Etests  
for  
Competitive  
Exams



Write to us at [feedback\\_disha@aiets.co.in](mailto:feedback_disha@aiets.co.in)

# CONTENTS

<b>1. Some Basic Concepts of Chemistry</b>	<b>1-10</b>	
Topic 1 : Significant Figures, Laws of Chemical Combinations and Mole Concept		
Topic 2: Percent Composition and Empirical Formula		
Topic 3: Stoichiometric Calculations		
<b>2. Structure of Atom</b>	<b>11-20</b>	
Topic 1 : Atomic Models and Dual Nature of Electromagnetic Radiation		
Topic 2 : Bohr's model for Hydrogen Atom (Emission and Absorption Spectra)		
Topic 3: Dual Behaviour of Matter and Heisenberg Uncertainty Principle		
Topic 4 : Quantum Mechanical Model of Atom		
<b>3. Classification of Elements and Periodicity in Properties</b>	<b>21-27</b>	
Topic 1: Modern Periodic Table		
Topic 2: Periodic Trends in Properties of Elements		
<b>4. Chemical Bonding and Molecular Structure</b>	<b>28-48</b>	
Topic 1: Electrovalent, Covalent and Co-ordinate Bonding		
Topic 2: Octet rule, Resonance and Hydrogen Bonding		
Topic 3: Dipole Moment and Bond Polarity		
Topic 4: VSEPR Theory and Hybridisation		
Topic 5: Valence Bond and Molecular Orbital Theory		
<b>5. States of Matter</b>	<b>49-57</b>	
Topic 1: Gas laws and Ideal gas Equation		
Topic 2: Kinetic Theory of Gases and Molecular Speeds		
Topic 3 : van der Waal's Equation and liquefaction of Gases		
Topic 4: Liquid State		
<b>6. Thermodynamics</b>	<b>58-69</b>	
Topic 1: First Law and Basic Fundamentals of Thermodynamics		
Topic 2: Laws of Thermochemistry		
Topic 3: Entropy and Second Law of Thermodynamics		
Topic 4: Spontaneity and Gibb's Free Energy		
<b>7. Equilibrium</b>	<b>70-89</b>	
Topic 1: Law of Mass Action, Equilibrium Constant ( $K_c$ and $K_p$ ) and its Application		
Topic 2: Relation between $K$ , $Q$ and $G$ and Factors Effecting Equilibrium		
Topic 3: Theories of Acids and Bases, Ionic Product of Water and pH Scale		
Topic 4: Ionisation of Weak Acids and Bases and Relation between $K_a$ and $K_b$		
Topic 5: Common Ion Effect, Salt Hydrolysis, Buffer Solutions and Solubility Product		
<b>8. Redox Reactions</b>	<b>90-93</b>	
Topic 1: Oxidation and Reduction Reactions		
Topic 2: Oxidation Number		
Topic 3: Disproportionation and Balancing of Redox Reactions		
Topic 4: Electrode Potential and Oxidising, Reducing Agents		
<b>9. Hydrogen</b>	<b>94-97</b>	
Topic 1: Preparation and Properties of Hydrogen		
Topic 2: Preparation and Properties of Water		
Topic 3: Preparation and Properties of Hydrogen Peroxide		
<b>10. The s-Block Elements</b>	<b>98-104</b>	
Topic 1: Preparation and Properties of Alkali Metals and their Compounds		
Topic 2: Some Important Compounds of Sodium		
Topic 3: Preparation and Properties of Alkaline Earth Metals and their Compounds		
Topic 4: Some Important Compounds of Calcium		
<b>11. The p-Block Elements (Group 13 &amp; 14)</b>	<b>105-109</b>	
Topic 1: Boron Family		
Topic 2: Carbon Family		
<b>12. Organic Chemistry - Some Basic Principles and Techniques</b>	<b>110-122</b>	
Topic 1: Classification and Nomenclature of Organic Compounds		
Topic 2: Isomerism in Organic Compounds		
Topic 3: Concept of Reaction Mechanism in Organic Compounds		

<b>13. Hydrocarbons</b>	<b>123-141</b>	
Topic 1: Alkanes		
Topic 2: Alkenes		
Topic 3: Alkynes		
Topic 4: Aromatic Hydrocarbons		
<b>14. Environmental Chemistry</b>	<b>142-144</b>	
Topic 1: Air Pollution		
Topic 2: Water and Soil Pollution		
<b>15. The Solid State</b>	<b>145-151</b>	
Topic 1: Properties and Types of Solids		
Topic 2: Crystal Structure of Solids		
Topic 3: Cubic System and Bragg's Equation		
Topic 4: Imperfection in Solids		
<b>16. Solutions</b>	<b>152-162</b>	
Topic 1: Solubility and Concentration of Solutions		
Topic 2: Vapour Pressure, Laws of Solutions and Ideal, Non-ideal Solutions		
Topic 3: Colligative Properties and Abnormal Molecular Masses		
<b>17. Electrochemistry</b>	<b>163-174</b>	
Topic 1: Conductance and Conductivity		
Topic 2: Electrolysis and Types of Electrolysis		
Topic 3: Cells and Electrode Potential, Nernst Equation		
Topic 4: Commercial Cells and Corrosion		
<b>18. Chemical Kinetics</b>	<b>175-187</b>	
Topic 1: Rate of Reaction, Rate Laws and Rate Constant		
Topic 2: Order of Reaction and Half Life Period		
Topic 3: Theories of Rate of Reaction		
<b>19. Surface Chemistry</b>	<b>188-192</b>	
Topic 1: Adsorption		
Topic 2: Catalysis and Theories of Catalysis		
Topic 3: Colloids and Emulsions		
<b>20. General Principles and Processes of Isolation of Elements</b>	<b>193-195</b>	
Topic 1: Occurrence of Metals		
Topic 2: Metallurgical Processes		
Topic 3: Purification and Uses of Metals		
<b>21. The p-Block Elements (Group 15, 16, 17 and 18)</b>	<b>196-209</b>	
Topic 1: Nitrogen Family		
Topic 2: Oxygen Family		
Topic 3: Halogen Family		
Topic 4: Noble Gases		
<b>22. The d-and f-Block Elements</b>	<b>210-222</b>	
Topic 1: Characteristics of d-Block Elements		
Topic 2: Compounds of Transition Metals		
Topic 3: Lanthanoids and Actinoids		
<b>23. Coordination Compounds</b>	<b>223-240</b>	
Topic 1: Coordination Number, Nomenclature and Isomerism of Coordination Compounds		
Topic 2: Magnetic Moment, Valence Bond Theory and Crystal Field Theory		
Topic 3: Organometallic Compounds		
<b>24. Haloalkanes and Haloarenes</b>	<b>241-254</b>	
Topic 1: Preparation and Properties of Haloalkanes		
Topic 2: Preparation and Properties of Haloarenes		
Topic 3: Some Important Polyhalogen Compounds		
<b>25. Alcohols, Phenols and Ethers</b>	<b>255-268</b>	
Topic 1: Preparation and Properties of Alcohols		
Topic 2: Preparation and Properties of Phenols		
Topic 3: Preparation and Properties of Ethers		
<b>26. Aldehydes, Ketones and Carboxylic Acids</b>	<b>269-290</b>	
Topic 1: Methods of Preparation of Carbonyl Compounds		
Topic 2: Properties of Carbonyl Compounds		
Topic 3: Preparation and Properties of Carboxylic Acids		
<b>27. Amines</b>	<b>291-304</b>	
Topic 1: Aliphatic and Aromatic+ Amines		
Topic 2: Amides, Cyanides and Isocyanides		
Topic 3: Nitrocompounds, Alkyl Nitrites and Diazonium Salts		
<b>28. Biomolecules</b>	<b>305-315</b>	
Topic 1: Carbohydrates and Lipids		
Topic 2: Amino Acids and Proteins		
Topic 3: Nucleic Acid and Enzymes		
Topic 4: Vitamins and Hormones		
<b>29. Polymers</b>	<b>316-322</b>	
Topic 1: Classification of Polymers		
Topic 2: Preparation and Properties of Polymers		
Topic 3: Uses of Polymers		
<b>30. Chemistry in Everyday Life</b>	<b>323-324</b>	
<b>31. Nuclear Chemistry</b>	<b>325-328</b>	

# What you should know about NEET

## NEET ALL INDIA MERIT LIST

AIR will include the rank numbers and names of all the candidates who appear for NEET. It will not take into account the candidate's category or their stance towards the AIQ reservation.

- With the help of all the merit list, candidates can check the overall positions of all the candidates who have appeared for NEET.
- In this merit list, the factors like qualifying status and the state from which a candidate belongs will not be considered while making this merit list.
- NTA will provide the All India Rank and AIQ Merit List along with the other required information to DGHS.
- State medical councils prepare their own merit lists for counselling based on factors such as the applicant's eligibility on the basis of their domicile requirement.
- A state merit list will be released by the state medical councils and it will depict the state rank of candidates on a comparative scale with applicants from the same state.

## MERIT LIST FOR 15% OF ALL INDIA QUOTA SEATS

NTA will prepare the merit list for 15% of the All India Quota (AIQ) admissions by numbering the candidates who qualify NEET 2020 by scoring equal to or more marks equivalent to the cutoff.

- The merit list will have equal number of names as seats under All India Quota.
- For such candidates, counselling will be done on the basis of their All India Quota Rank and not their state rank.
- There will also be a waiting list equal to 4 times the merit list or so if required by the DGHS (Director General of Health Services)
- Andhra Pradesh and Telangana will now participate in 15% All India Quota Counselling and do not require a self declaration form anymore.
- Candidates from Jammu and Kashmir still need to produce the self declaration form for participating in All India Quota Counselling.

## **NEET**

- Merit List 85% of Seats
- For the remaining 85% of the seats, NTA will forward the results to DGHS, to be forwarded to the state medical councils and mandated authorities.
- Admitting authorities will invite candidates for counselling and a separate merits list will be released on the basis of All India rank.
- State counselling will be conducted by the respective counselling authorities. Candidates must check their websites to stay updated.
- Deemed private universities will conduct their own counselling procedure
- Candidates who wish to take admission in AFMC must apply separately on their website since they will hold a second screening process.

### **NEET TIE-BREAKING CRITERIA**

If two or more candidates score equal marks, than the following process of comparison shall be followed to resolve the situation:

- Candidate with higher marks in Zoology and Botany will be prioritized.
- Candidate with a better score in Chemistry shall be preferred.
- Candidate with lesser incorrect answers shall be prioritized.
- As the last resort to, if the tie persists, candidate older in age will be preferred.

### **ELIGIBILITY CRITERIA FOR NEET 2021**

As per NTA, candidates willing to appear in NEET 2021 should qualify the eligibility criteria mentioned below.

- Age Limit – Candidates must attain 17 years of age by December 31, 2021 to sit for NEET 2021. There is no upper age limit for NEET 2021 as per an interim order of the Supreme Court. However, the candidature of aspirants more than 25 years of age is subject to the Supreme Courts' orders.
- Educational Qualification – Candidates who have completed or appearing in class 12th with minimum 5 subjects including English, Chemistry, Physics as compulsory subjects can apply. Candidates of distance learning or private students and those who have biology as an additional subject are also eligible for the exam.
- Minimum Percentage Required – General candidates should score a minimum 50%, general PwD – 45%, OBC/SC/ST – 45% and OBC/SC/ST PWD – 40%.
- Number of Attempts – There is no limit on the number of attempts for NEET 2021. Candidates can appear for the exam as many times as they want.

## NEET 2021 – NEXT YEAR PLAN

- CBSE has decided to reduce the syllabus up to 30% from Class IX to XII. The syllabus has been reduced from all the subjects including physics, Chemistry, and Biology which are major subjects for NEET. This could affect the preparation of the candidates as they will not be able to understand the basics of the topics and will also not be able to solve the questions which are interrelated to curtailed topics. Read More Syllabus reduction impact on NEET 2021
- With the reduction in the syllabus by CBSE, there are speculations that the syllabus for NEET 2021 could also be revised but no official announcement has been made yet by the respective authorities.
- The official notification of NEET 2021 is expected to release in the month of December 2020.

## REASONS THAT COULD AFFECT NEET 2021 EXAM DATE

- Due to COVID-19 schools are closed and because of the high strength of students in the schools, we can expect that the school could be the last place to open after the lockdown is over.
- However, all the students are attending the classes in the online mode but still to complete the whole syllabus online is the biggest challenge.
- This may lead to the delay in the final exams of class 12 which could further lead to the delay of NEET 2021.

## MAJOR CHANGES IN NEET

The NEET 2020 will be experiencing few major striking changes in its pattern and conducting nature with the focus being on more accuracy of identification of applicants to ensure 100% transparency in its examining procedure. Applicants now have to upload Class X certificates, left-hand thumb impressions and also provide their roll numbers for Class XII Board Exams along with the standard signature and scanned photograph - both in passport and postcard sizes.

- One Exam for all Medical Aspirants: The merger of AIIMS and JIPMER will only see all of 1207 AIIMS MBBS and 200 JIPMER MBBS seats in the respective institutes to be contested for, in a single analysis of NEET-UG performance of candidates.

## NEET

- UT applicants need to self-declare their contesting consideration: With the new formation of Union Territories of India, the likes of Kashmir and Ladakh have thought of pulling off from the 15% allocation of the All India Quota Scheme. Therefore, aspirants from these UTs need to fill in the form for self-declaration for seat allotment under AIQ.
- Application Fee Hike: The fee for application has been hiked to ₹ 1500 for general candidates with respect to ₹ 1400 from last year and applicants can now even upload live photographs while they fill out their form. The amount respects to ₹ 1400 for General-EWS applicants and ₹ 800 for reserved category applicants for 2020.
- Flexible Edit Window: As the maximum of Class 12 medical students will get their admit cards for board exam after the registration for NEET is over. Thus, the edit window will be re-opened by the authority for NEET Application form 2020 for the students of Class 12 to punch in their roll numbers.
- More Exam Centres: This year, the exam of NEET 2020 will be conducted across the nation in exactly 155 cities in India with the inclusion of the union territory of Ladakh as the latest entry.
- Upper Age Limit Relaxation: For NEET 2020, the upper age limit is capped at 25 years as on 31st December 2019, while the lower age limit is capped at 17 years as on 31st December 2019. There is a relaxation of flat 5 years for reserved category candidates in the upper age limit.

However, general applicants above the 25-age mark can appear for the NEET 2020 test with their candidature being considered or not, is still in a turmoil for the awaiting verdict of the Supreme Court regarding the same.

An aspirant who applies for NEET has to meet the eligibility criteria of NEET which specifies the academic qualifications, age limit, pass percentage, nationality etc that are mandatory to appear for the exam. The NEET eligibility criteria are based on regulations of Graduate Medical Education 1997 Act. Candidates must meet the NEET eligibility as given failing which they will not be allowed to appear for the exam. It should be noted that merely fulfilling the eligibility criteria of NEET is not sufficient for admissions. NEET admission criteria and cutoff for MBBS, BDS and other medical courses will be separate for All India and state counselling.

1

# **Some Basic Concepts of Chemistry**



## Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Significant figures, law of chemical combinations and mole concept	mole concept	1	E	1	E	1	E				
Stoichiometric calculations	stoichiometric calculations					1	A				
LOD - Level of Difficulty	E - Easy	A - Average		D - Difficult		Qns - No. of Questions					

## Topic 1 : Significant Figures, Laws of Chemical Combinations and Mole Concept



5. The number of water molecules is maximum in :  
 [2015 RS]

6. If Avogadro number  $N_A$ , is changed from  $6.022 \times 10^{23} \text{ mol}^{-1}$  to  $6.022 \times 10^{20} \text{ mol}^{-1}$  this would change : **[2015 RSJ]**

  - (a) the definition of mass in units of grams
  - (b) the mass of one mole of carbon
  - (c) the ratio of chemical species to each other in a balanced equation.
  - (d) the ratio of elements to each other in a compound

7. When 22.4 litres of  $\text{H}_2(\text{g})$  is mixed with 11.2 litres of  $\text{Cl}_2(\text{g})$ , each at S.T.P., the moles of  $\text{HCl}(\text{g})$  formed is equal to : **[2014]**

  - (a) 1 mole of  $\text{HCl}(\text{g})$
  - (b) 2 moles of  $\text{HCl}(\text{g})$
  - (c) 0.5 moles of  $\text{HCl}(\text{g})$
  - (d) 1.5 moles of  $\text{HCl}(\text{g})$

8. 1.0 g of magnesium is burnt with 0.56 g O<sub>2</sub> in a closed vessel. Which reactant is left in excess and how much? **[2014]**  
 (At. wt. Mg = 24; O = 16)  
 (a) Mg, 0.16 g      (b) O<sub>2</sub>, 0.16 g  
 (c) Mg, 0.44 g      (d) O<sub>2</sub>, 0.28 g
9. Which has the maximum number of molecules among the following? **[2011 M]**  
 (a) 44 g CO<sub>2</sub>      (b) 48 g O<sub>3</sub>  
 (c) 8 g H<sub>2</sub>      (d) 64 g SO<sub>2</sub>
10. The number of atoms in 0.1 mol of a triatomic gas is: **[2010]**  
 ( $N_A = 6.02 \times 10^{23}$  mol<sup>-1</sup>)  
 (a)  $6.026 \times 10^{22}$       (b)  $1.806 \times 10^{23}$   
 (c)  $3.600 \times 10^{23}$       (d)  $1.800 \times 10^{22}$
11. What volume of oxygen gas (O<sub>2</sub>) measured at 0°C and 1 atm, is needed to burn completely 1L of propane gas (C<sub>3</sub>H<sub>8</sub>) measured under the same conditions? **[2008]**  
 (a) 7 L      (b) 6 L  
 (c) 5 L      (d) 10 L
12. Number of moles of MnO<sub>4</sub><sup>-</sup> required to oxidize one mole of ferrous oxalate completely in acidic medium will be: **[2008]**  
 (a) 0.6 moles      (b) 0.4 moles  
 (c) 7.5 moles      (d) 0.2 moles
13. Volume occupied by one molecule of water (density = 1 g cm<sup>-3</sup>) is: **[2008]**  
 (a)  $9.0 \times 10^{-23}$  cm<sup>3</sup>      (b)  $6.023 \times 10^{-23}$  cm<sup>3</sup>  
 (c)  $3.0 \times 10^{-23}$  cm<sup>3</sup>      (d)  $5.5 \times 10^{-23}$  cm<sup>3</sup>
14. The number of moles of KMnO<sub>4</sub> that will be needed to react with one mole of sulphite ion in acidic solution is **[2007]**  
 (a) 4/5      (b) 2/5  
 (c) 1      (d) 3/5
15. An element, X has the following isotopic composition: **[2007]**  
 $^{200}X$ : 90%       $^{199}X$ : 8.0%       $^{202}X$ : 2.0%  
 The weighted average atomic mass of the naturally occurring element X is closest to  
 (a) 201 amu      (b) 202 amu  
 (c) 199 amu      (d) 200 amu
16. The number of moles of KMnO<sub>4</sub> reduced by one mole of KI in alkaline medium is: **[2005]**  
 (a) one      (b) two  
 (c) five      (d) one fifth
17. The maximum number of molecules is present in  
 (a) 15 L of H<sub>2</sub> gas at STP      **[2004]**  
 (b) 5 L of N<sub>2</sub> gas at STP
18. (c) 0.5 g of H<sub>2</sub> gas  
 (d) 10 g of O<sub>2</sub> gas
18. Which has maximum number of molecules? **[2002]**  
 (a) 7 g N<sub>2</sub>      (b) 2 g H<sub>2</sub>  
 (c) 16 g NO<sub>2</sub>      (d) 16 g O<sub>2</sub>
19. Specific volume of cylindrical virus particle is  $6.02 \times 10^{-2}$  cc/g whose radius and length are 7 Å & 10 Å respectively. If  $N_A = 6.02 \times 10^{23}$ , find molecular weight of virus **[2001]**  
 (a)  $3.08 \times 10^3$  kg/mol      (b)  $3.08 \times 10^4$  kg/mol  
 (c)  $1.54 \times 10^4$  kg/mol      (d) 15.4 kg/mol
20. Assuming fully decomposed, the volume of CO<sub>2</sub> released at STP on heating 9.85 g of BaCO<sub>3</sub> (Atomic mass, Ba = 137) will be **[2000]**  
 (a) 2.24 L      (b) 4.96 L  
 (c) 1.12 L      (d) 0.84 L
21. Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. wt. of Fe is 56) present in one molecule of haemoglobin are **[1998]**  
 (a) 1      (b) 6  
 (c) 4      (d) 2
22. The number of significant figures for the three numbers 161 cm, 0.161 cm, 0.0161 cm are **[1998]**  
 (a) 3, 4 and 5 respectively  
 (b) 3, 4 and 4 respectively  
 (c) 3, 3 and 4 respectively  
 (d) 3, 3 and 3 respectively
23. The weight of one molecule of a compound C<sub>60</sub>H<sub>122</sub> is **[1995]**  
 (a)  $1.2 \times 10^{-20}$  gram      (b)  $1.4 \times 10^{-21}$  gram  
 (c)  $5.025 \times 10^{23}$  gram      (d)  $6.023 \times 10^{23}$  gram
24. In the final answer of the expression  

$$\frac{(29.2 - 20.2)(1.79 \times 10^5)}{1.37}$$
  
 the number of significant figures is: **[1994]**  
 (a) 1      (b) 2  
 (c) 3      (d) 4
25. If  $N_A$  is Avogadro's number then number of valence electrons in 4.2g of nitride ions (N<sup>3-</sup>) is **[1994]**  
 (a)  $2.4 N_A$       (b)  $4.2 N_A$   
 (c)  $1.6 N_A$       (d)  $3.2 N_A$
26. The molecular weight of O<sub>2</sub> and SO<sub>2</sub> are 32 and 64 respectively. At 15°C and 150 mm Hg pressure, one litre of O<sub>2</sub> contains 'N' molecules. The number of molecules in two litres of SO<sub>2</sub> under the same conditions of temperature and pressure will be: **[1990]**

## **Some Basic Concepts of Chemistry –**



## Topic 2: Percent Composition and Empirical Formula



35. Percentage of Se in peroxidase anhydride enzyme is 0.5% by weight (at. wt. = 78.4) then minimum molecular weight of peroxidase anhydride enzyme is **[2001]**  
 (a)  $1.568 \times 10^3$       (b) 15.68  
 (c)  $2.136 \times 10^4$       (d)  $1.568 \times 10^4$

36. An organic compound containing C, H and O gave on analysis C – 40% and H – 6.66%. Its empirical formula would be **[1999, 94]**  
 (a)  $C_3H_6O$       (b)  $CHO$   
 (c)  $CH_2O$       (d)  $CH_4O$

37. An organic compound containing C, H and N gave the following analysis :  
 $C = 40\%$ ;  $H = 13.33\%$ ;  $N = 46.67\%$   
 Its empirical formula would be **[1998]**  
 (a)  $C_2H_7N_2$       (b)  $CH_5N$   
 (c)  $CH_4N$       (d)  $C_2H_7N$

38. The percentage weight of Zn in white vitriol  $[ZnSO_4 \cdot 7H_2O]$  is approximately equal to ( $Zn = 65, S = 32, O = 16$  and  $H = 1$ ) **[1995]**  
 (a) 33.65 %      (b) 32.56 %  
 (c) 23.65 %      (d) 22.65 %

39. A metal oxide has the formula  $Z_2O_3$ . It can be reduced by hydrogen to give free metal and water. 0.1596 g of the metal oxide requires 6 mg of hydrogen for complete reduction. The atomic weight of the metal is **[1989]**  
 (a) 27.9      (b) 159.6  
 (c) 79.8      (d) 55.8

### Topic 3: Stoichiometric Calculations

40. A mixture of 2.3 g formic acid and 4.5 g oxalic acid is treated with conc.  $H_2SO_4$ . The evolved gaseous mixture is passed through KOH pellets. Weight (in g) of the remaining product at STP will be **[2018]**  
 (a) 1.4      (b) 3.0  
 (c) 4.4      (d) 2.8

41. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample ? **[2015 RSJ]**  
 (a) 75      (b) 96  
 (c) 60      (d) 84

42. What is the mass of precipitate formed when 50 mL of 16.9% solution of  $AgNO_3$  is mixed with 50 mL of 5.8% NaCl solution ? **[2015 RSJ]**  
 $(Ag = 107.8, N = 14, O = 16, Na = 23, Cl = 35.5)$   
 (a) 28 g      (b) 3.5 g  
 (c) 7 g      (d) 14 g

ANSWER KEY

<b>1</b>	(c)	<b>7</b>	(a)	<b>13</b>	(c)	<b>19</b>	(d)	<b>25</b>	(a)	<b>31</b>	(a)	<b>37</b>	(c)	<b>43</b>	(c)	<b>49</b>	(c)
<b>2</b>	(c)	<b>8</b>	(a)	<b>14</b>	(b)	<b>20</b>	(c)	<b>26</b>	(c)	<b>32</b>	(d)	<b>38</b>	(d)	<b>44</b>	(a)	<b>50</b>	(c)
<b>3</b>	(a)	<b>9</b>	(c)	<b>15</b>	(d)	<b>21</b>	(c)	<b>27</b>	(a)	<b>33</b>	(a)	<b>39</b>	(d)	<b>45</b>	(d)	<b>51</b>	(c)
<b>4</b>	(a)	<b>10</b>	(b)	<b>16</b>	(b)	<b>22</b>	(d)	<b>28</b>	(a)	<b>34</b>	(a)	<b>40</b>	(d)	<b>46</b>	(b)	<b>52</b>	(d)
<b>5</b>	(d)	<b>11</b>	(c)	<b>17</b>	(a)	<b>23</b>	(b)	<b>29</b>	(b)	<b>35</b>	(d)	<b>41</b>	(d)	<b>47</b>	(d)	<b>53</b>	(a)
<b>6</b>	(b)	<b>12</b>	(b)	<b>18</b>	(b)	<b>24</b>	(c)	<b>30</b>	(c)	<b>36</b>	(c)	<b>42</b>	(c)	<b>48</b>	(c)	<b>54</b>	(a)

# Hints & Solutions

1. (c) Number of atoms

$$= \frac{W}{\text{Molar mass}} \times N_A \times \text{atomicity}$$

- (a) Number of Mg atoms =  $\frac{1}{24} \times N_A \times 1$   
 (b) Number of O atoms =  $\frac{1}{32} \times N_A \times 2$   
 (c) Number of Li atoms =  $\frac{1}{7} \times N_A \times 1$   
 (d) Number of Ag atoms =  $\frac{1}{108} \times N_A \times 1$

2. (c)  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

$$1 \text{ Mol NH}_3 = \frac{3}{2} \text{ mol H}_2$$

$$20 \text{ mol NH}_3 = \frac{3}{2} \times 20 \text{ mol H}_2 = 30 \text{ mol H}_2$$

$\therefore$  30 moles of  $\text{H}_2$  are required.

3. (a) (1) Mass of water =  $18 \times 1 = 18 \text{ g}$   
 Molecules of water = mole  $\times N_A$

$$= \frac{18}{18} N_A = N_A$$

- (2) Molecules of water = mole  $\times N_A$

$$= \frac{0.18}{18} N_A = 10^{-2} N_A$$

- (3) Molecules of water = mole  $\times N_A = 10^{-3} N_A$

- (4) Moles of water =  $\frac{0.00224}{22.4} = 10^{-4}$

$$\text{Molecules of water} = \text{mole} \times N_A = 10^{-4} N_A$$

4. (a) Ratio of weight of gases =  $w_{\text{H}_2} : w_{\text{O}_2} = 1 : 4$

$$\text{Ratio of moles of gases} = n_{\text{H}_2} : n_{\text{O}_2} = \frac{1}{2} : \frac{4}{32}$$

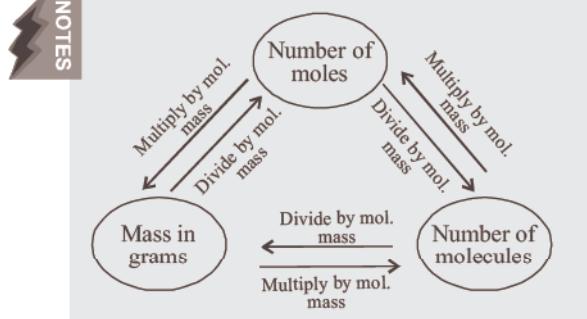
$$\therefore \text{Molar Ratio} = \frac{1}{2} \times \frac{32}{4} = 4 : 1$$

5. (d) No. of moles of water

In 1.8 g of  $\text{H}_2\text{O}$  = 0.1 moles

In 18 g of  $\text{H}_2\text{O}$  = 1 moles

1 mole contains  $6.022 \times 10^{23}$  molecules of water  
 therefore maximum number of molecules is in 18  
 moles of water.



6. (b) If  $6.022 \times 10^{23}$  changes to  $6.022 \times 10^{20}/\text{mol}$  then this would change mass of one mole of carbon.

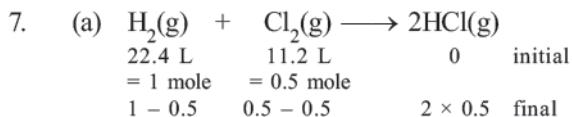


Mass of  $^{12}\text{C}$  carbon is used to define the atomic mass unit. In this system,  $^{12}\text{C}$  is assigned a mass of exactly 12 a.m.u.

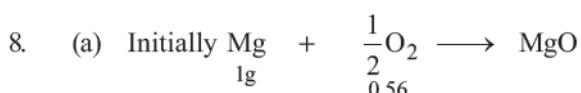
Earlier one mole was defined as the amount of substance that contains as many particles as there are atoms in exactly 12 g of the  $^{12}\text{C}$  isotope. From November 2018, one mole is defined as exactly  $6.02214076 \times 10^{23}$  constitutive particles, which may be atoms, molecules, ions or electrons.

Hence, if we change the value of  $N_A$  from  $6.022 \times 10^{23} \text{ mol}^{-1}$  to  $6.022 \times 10^{20} \text{ mol}^{-1}$  then mass of one mole of carbon will also change.

The definition of mass is independent of Avogadro number  $N_A$ .



Moles of  $\text{HCl}$  formed =  $2 \times 0.5 = 1$



$$\text{or } \begin{array}{ll} \frac{1}{24} \text{ mole} & \frac{0.56}{32} \text{ mole} \\ 0.0417 \text{ mole} & 0.0175 \text{ mole} \\ (0.0417 - 2 \times 0.0175) & 0 \text{ mole} \\ = 0.0067 \text{ mole} & \end{array}$$

$$\therefore \text{Mass of Mg} = 0.0067 \times 24 = 0.16\text{g}$$

9. (c) **No. of molecules**

$$\text{Moles of CO}_2 = \frac{44}{44} = 1, N_A$$

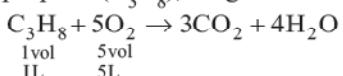
$$\text{Moles of O}_3 = \frac{48}{48} = 1, N_A$$

$$\text{Moles of H}_2 = \frac{8}{2} = 4, 4N_A$$

$$\text{Moles of SO}_2 = \frac{64}{64} = 1, N_A$$

10. (b) The number of atoms in 0.1 mol of a triatomic gas =  $0.1 \times 3 \times 6.023 \times 10^{23}$   
 $= 1.806 \times 10^{23}$

11. (c) Writing the equation of combustion of propane ( $C_3H_8$ ), we get



From the above equation we find that we need 5 L of oxygen at N.T.P. to completely burn 1 L of propane at N.T.P.

If we change the conditions for both the gases from N.T.P. to same conditions of temperature and pressure. The same results are obtained.  
*i.e.* 5 L is the correct answer.

12. (b)  $5\begin{matrix} COO^- \\ | \\ COO^- \end{matrix} + 2 MnO_4^- + 16 H^+ \rightarrow 2 Mn^{2+} + 10CO_2 + 8H_2O$

From above equation 2 moles of  $MnO_4^-$  required to oxidise 5 moles of oxalate.

Thus number of moles of  $MnO_4^-$  required to oxidise one mole of oxalate =  $2 \times 2/5 = 0.4$  moles

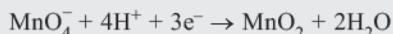
**NOTES**  
In  $KMnO_4$  the oxidation state of Mn is +7. In acidic medium Mn takes up five electrons and making it an oxidizing agent. In strongly alkaline solution it takes up only 1 electrons and making it much weaker oxidising agent. In neutral medium it gives up 3 electrons to form  $MnO_2$ .

Acidic medium:



Alkaline medium:  $MnO_4^- + e^- \rightarrow MnO_4^{2-}$

Neutral medium:



13. (c)  $\therefore$  Volume occupied by 1 gram water = 1 cm<sup>3</sup>  
or Volume occupied by

$$\frac{6.023 \times 10^{23}}{18} \text{ molecules of water} = 1 \text{ cm}^3$$

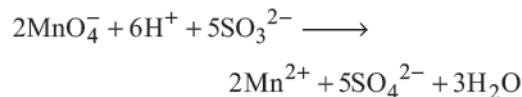
$$[\therefore 1 \text{ g water} = \frac{1}{18} \text{ moles of water}]$$

Thus, volume occupied by 1 molecule of water

$$= \frac{1 \times 18}{6.023 \times 10^{23}} \text{ cm}^3 = 3.0 \times 10^{-23} \text{ cm}^3$$

i.e. the correct answer is option (c).

14. (b) The balance chemical equation is :



From the equation it is clear that

Moles of  $MnO_4^-$  require to oxidise 5 moles of  $SO_3^{2-}$  are 2

Moles of  $MnO_4^-$  require to oxidise 1 mole of  $SO_3^{2-}$  are 2/5.

15. (d) Average isotopic mass of

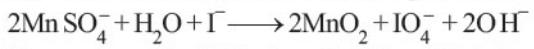
$$X = \frac{200 \times 90 + 199 \times 8 + 202 \times 2}{90 + 8 + 2}$$

$$= \frac{18000 + 1592 + 404}{100}$$

$$= \frac{19996}{100} = 199.96 \simeq 200 \text{ amu}$$

**NOTES**  
Average atomic mass  
= (Mass of isotope A  $\times$  % natural abundance) +  
(Mass of isotope B  $\times$  % natural abundance) +  
.....  
(% Natural abundance of A + % natural abundance  
of B) + .....

16. (b) In weak alkaline medium, the equation is:



Hence, one mole of KI reduce, 2 moles of  $KMnO_4$ .

17. (a) No. of molecules in different cases

(a)  $\because$  22.4 litre at STP contains

$$= 6.023 \times 10^{23} \text{ molecule of H}_2$$

$$\therefore 15 \text{ litre at STP contains} = \frac{15}{22.4} \times 6.023 \times 10^{23}$$

(b)  $\because$  22.4 litre at STP contains

$$= 6.023 \times 10^{23} \text{ molecule of N}_2$$

$$\therefore 5 \text{ litre at STP contains} = \frac{5}{22.4} \times 6.023 \times 10^{23}$$

(c)  $\because$  2 g of  $H_2$  =  $6.023 \times 10^{23}$  molecules of  $H_2$

$$\therefore 0.5 \text{ g of } H_2 = \frac{0.5}{2} \times 6.023 \times 10^{23}$$

(d) Similarly 10 g of  $O_2$  gas

$$= \frac{10}{32} \times 6.023 \times 10^{23} \text{ molecules}$$

Thus (a) will have maximum number of molecules

18. (b) 2g of H<sub>2</sub> means one mole of H<sub>2</sub>, hence contains  $6.023 \times 10^{23}$  molecules. Others have less than one mole, so have less no. of molecules.

19. (d) Specific volume (volume of 1 g) of cylindrical virus particle =  $6.02 \times 10^{-2}$  cc/g  
Radius of virus (r) =  $7 \text{ \AA} = 7 \times 10^{-8} \text{ cm}$   
Length of virus =  $10 \times 10^{-8} \text{ cm}$   
Volume of virus =

$$\pi r^2 l = \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8}$$

$$= 154 \times 10^{-23} \text{ cc}$$

$$\text{Wt. of one virus particle} = \frac{\text{volume}}{\text{specific volume}}$$

$$\text{Mol. wt. of virus} = \text{Wt. of } N_A \text{ particle}$$

$$= \frac{154 \times 10^{-23}}{6.02 \times 10^{-2}} \times 6.02 \times 10^{23}$$

$$= 15400 \text{ g/mol} = 15.4 \text{ kg/mol}$$

20. (c)  $BaCO_3 \rightarrow BaO + CO_2$   
 $197 \text{ g}$

As 197 g of BaCO<sub>3</sub> will release 22.4 litre of CO<sub>2</sub> at STP

∴ 1 g of BaCO<sub>3</sub> will release

$$= \frac{22.4}{197} \text{ litre of CO}_2$$

And 9.85 g of BaCO<sub>3</sub> will release carbon dioxide

$$= \frac{22.4}{197} \times 9.85 = 1.12 \text{ litre of CO}_2$$

21. (c) Given : Percentage of the iron = 0.334%; Molecular weight of the haemoglobin = 67200 and atomic weight of iron = 56. We know that the number of iron atoms

$$= \frac{\text{Molecular wt. of haemoglobin} \times \% \text{ of iron}}{100 \times \text{Atomic weight of iron}}$$

$$= \frac{67200 \times 0.334}{100 \times 56} = 4$$

22. (d) Number 161 cm, 0.161 cm and 0.0161 cm have 3, 3 and 3 significant figures respectively.



All non-zero digits are significant and the zeros at the beginning of a number are not significant.

23. (b) Molecular weight of C<sub>60</sub>H<sub>122</sub>  
=  $(12 \times 60) + 122 = 842$ .

Therefore, weight of one molecule

$$= \frac{\text{Molecular weight of C}_60\text{H}_{122}}{\text{Avogadro's number}}$$

$$= \frac{842}{6.023 \times 10^{23}} = 1.36 \times 10^{-21} \text{ g} \approx 1.4 \times 10^{-21} \text{ g}$$

24. (c)  $\frac{(29.2 - 20.2)(1.79 \times 10^5)}{1.37}$

As the least precise number contains 3 significant figures therefore, answers should also contain 3 significant figures.

25. (a) No of moles of nitride ion

$$= \frac{4.2}{14} = 0.3 \text{ mol} = 0.3 \times N_A \text{ nitride ions.}$$

$$\text{Valence electrons} = 8 \times 0.3 N_A = 2.4 N_A$$



Nitride ion has seven protons in the nucleus and ten electrons surrounding the nucleus. Therefore total no. of electrons is 10. Number of valence electrons is  $(5 + 3) = 8$ .

26. (c) According to Avogadro's law "equal volumes of all gases contain equal numbers of molecules under similar conditions of temperature and pressure". Thus if 1 L of one gas contains N molecules, 2 L of any gas under the same conditions will contain 2N molecules.

27. (a) Average atomic mass =  $\frac{19 \times 10 + 81 \times 11}{100} = 10.81$

28. (a) 1 mol of CO<sub>2</sub> = 44 g of CO<sub>2</sub>

$$4.4 \text{ g CO}_2 = \frac{4.4}{44} = 0.1 \text{ mol CO}_2$$

$$= 6 \times 10^{22} \text{ molecules}$$

=  $2 \times 6 \times 10^{22}$  atoms or  $1.2 \times 10^{23}$  atoms of oxygen.

29. (b)  $6.02 \times 10^{23}$  molecules of CO = 1 mole of CO  
 $6.02 \times 10^{24}$  CO molecules = 10 moles of CO  
= 10 g atoms of O = 5 g molecules of O<sub>2</sub>

30. (c)  $C_2H_4 + 3 O_2 \longrightarrow 2CO_2 + 2H_2O$   
28 kg 96 kg

As 28 kg of C<sub>2</sub>H<sub>4</sub> undergo complete combustion by 96 kg of O<sub>2</sub>

∴ 2.8 kg of C<sub>2</sub>H<sub>4</sub> undergo complete combustion by 9.6 kg of O<sub>2</sub>.

31. (a)  $C_p/C_v = 1.4$  shows that the gas is diatomic.  
22.4 litre at NTP ≈  $6.02 \times 10^{23}$  molecules  
11.2 L at NTP =  $3.01 \times 10^{23}$  molecules  
No. of atoms in gas =  $3.01 \times 10^{23} \times 2$  atoms  
=  $6.02 \times 10^{23}$  atoms



$r = \frac{C_p}{C_v} = 1 + \frac{2}{F}$ , where F = degree of freedom of the gas molecules

For mono atomic gas, F = 3

$$\therefore \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{3} = \frac{5}{3} = 1.67$$

For diatomic gas, F = 5

$$\therefore \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{5} = \frac{7}{5} = 1.40$$

For triatomic gas, F = 6 or 7 (depending upon the nature of the gas)

$$\therefore \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{6} = 1.33$$

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{7} = 1.29$$

32. (d) At NTP, 22400 cc of  $\text{N}_2\text{O}$

$$= 6.02 \times 10^{23} \text{ molecules}$$

$\therefore 1 \text{ cc of } \text{N}_2\text{O} \text{ contain}$

$$= \frac{6.02 \times 10^{23}}{22400} \text{ molecules}$$

$$= \frac{3 \times 6.02 \times 10^{23}}{22400} = \frac{1.8}{224} \times 10^{22} \text{ atoms}$$

( $\because \text{N}_2\text{O}$  molecule has 3 atoms)

No. of electrons in a molecule of  $\text{N}_2\text{O}$

$$= 7 + 7 + 8 = 22$$

Hence, no. of electrons

$$= \frac{6.02 \times 10^{23}}{22400} \times 22 = \frac{1.32 \times 10^{23}}{224} \text{ electrons}$$

33. (a) 1 mol  $\text{CCl}_4$  vapour =  $12 + 4 \times 35.5$

$$= 154 \text{ g} \equiv 22.4 \text{ L at STP}$$

$$\therefore \text{Density} = \frac{154}{22.4} \text{ gL}^{-1} = 6.875 \text{ gL}^{-1}$$

34. (a)

Element	%	Atomic weight	Atomic ratio	Simple ratio
C	38.71	12	$\frac{38.71}{12} = 3.23$	$\frac{3.23}{3.23} = 1$
H	9.67	1	$\frac{9.67}{1} = 9.67$	$\frac{9.67}{3.23} = 3$
O	$100 - (38.71 + 9.67)$ $= 51.62$	16	$\frac{51.62}{16} = 3.23$	$\frac{3.23}{3.23} = 1$

Thus, empirical formula is  $\text{CH}_3\text{O}$ .

35. (d) Suppose the mol. wt. of enzyme =  $x$

Given 100 g of enzyme wt of Se = 0.5 g

$$\therefore \text{In } x \text{ g of enzyme wt. of Se} = \frac{0.5}{100} \times x$$

$$\text{Hence } 78.4 = \frac{0.5 \times x}{100}$$

$$\therefore x = 15680 = 1.568 \times 10^4$$

36. (c) Table for empirical formula :

Element	%	At. wt	Relative number	Ratio
C	40	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$
H	6.66	1	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{3.33} = 2$
O	53.34	16	$\frac{53.34}{16} = 3.33$	$\frac{3.33}{3.33} = 1$

(% of O in organic compound

$$= 100 - (40 + 6.66) = 53.34\%$$

$\therefore$  Empirical formula of organic compound =  $\text{CH}_2\text{O}$ .

37. (c) As the sum of the percentage of C, H & N is 100. Thus, it does not contains O atom.

#### Table for empirical formula

Element	%	At. wt.	Relative Number	Ratio
C	40.00	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$
H	13.33	1	$\frac{13.33}{1} = 13.33$	$\frac{13.33}{3.33} = 4$
N	46.67	14	$\frac{46.67}{14} = 3.33$	$\frac{3.33}{3.33} = 1$

Hence, empirical formula =  $\text{CH}_4\text{N}$

38. (d) Molecular weight of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$   
 $= 65 + 32 + (4 \times 16) + 7(2 \times 1 + 16) = 287$ .

$\therefore$  percentage mass of zinc (Zn)

$$= \frac{65}{287} \times 100 = 22.65\%$$

39. (d) The reaction can be given as



0.1596 g of  $\text{Z}_2\text{O}_3$  react with  $\text{H}_2 = 6 \text{ mg} = 0.006 \text{ g}$

$\therefore 1 \text{ g of H}_2$  react with

$$= \frac{0.1596}{0.006} = 26.6 \text{ g of } \text{Z}_2\text{O}_3$$

$\therefore$  Eq. wt. of  $\text{Z}_2\text{O}_3 = 26.6$

(from the definition of eq. wt.)

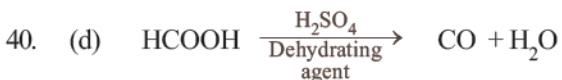
Eq. wt. of Z + Eq. wt. of O (8) = 26.6

$$\Rightarrow \text{Eq. wt. of Z} = 26.6 - 8 = 18.6$$

Valency of metal in  $\text{Z}_2\text{O}_3 = 3$

$$\text{Eq. wt. of metal} = \frac{\text{Atomic wt.}}{\text{valency}}$$

$$\therefore \text{At. wt. of } Z = 18.6 \times 3 = 55.8$$



$$\begin{array}{l} \text{At start} = \frac{2.3}{46} = \frac{1}{20} \\ \text{(moles)} \end{array}$$

$$\begin{array}{rccccc} & & \text{[H}_2\text{O absorbed by H}_2\text{SO}_4] & & & \\ \text{Final moles} & 0 & & 0 & & \end{array}$$

$$\begin{array}{rccccc} & & \frac{1}{20} & & \frac{1}{20} & \\ \text{H}_2\text{C}_2\text{O}_4 & \xrightarrow{\text{H}_2\text{SO}_4} & \text{CO} & + & \text{CO}_2 & + \text{H}_2\text{O} \\ & & \text{[H}_2\text{O absorbed by H}_2\text{SO}_4] & & & \end{array}$$

$$\begin{array}{l} \text{At start} = \frac{4.5}{90} = \frac{1}{20} \\ \text{(moles)} \end{array}$$

$$\begin{array}{rccccc} & & \frac{1}{20} & & \frac{1}{20} & \\ \text{Final moles} & 0 & & 0 & & \frac{1}{20} \end{array}$$

$\text{CO}_2$  is absorbed by KOH.

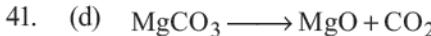
So, the remaining product is only CO.

Moles of CO formed from both reactions

$$= \frac{1}{20} + \frac{1}{20} = \frac{1}{10}$$

Left mass of CO = moles  $\times$  molar mass

$$= \frac{1}{10} \times 28 = 2.8 \text{ g}$$

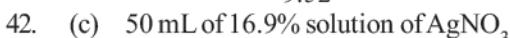


84 g of  $\text{MgCO}_3$  form 40 g of MgO

$$\therefore 20 \text{ g of } \text{MgCO}_3 \text{ form } \frac{40 \times 20}{84} \text{ g of MgO} = 9.52 \text{ g of MgO}$$

Since 8.0 g of MgO is formed

$$\text{Purity of sample} = \frac{8}{9.52} \times 100 = 84.0\%$$



$$\left( \frac{16.9}{100} \times 50 \right) = 8.45 \text{ g of AgNO}_3$$

$$n_{\text{mole}} = \frac{8.45 \text{ g}}{(107.8 + 14 + 16 \times 3) \text{ g/mol}}$$

$$= \left( \frac{8.45 \text{ g}}{169.8 \text{ g/mol}} \right) = 0.0497 \text{ moles}$$

50 mL of 5.8% solution of NaCl contain

$$\text{NaCl} = \left( \frac{5.8}{100} \times 50 \right) = 2.9 \text{ g}$$

$$n_{\text{NaCl}} = \frac{2.9 \text{ g}}{(23 + 35.5) \text{ g/mol}} = 0.0495 \text{ moles}$$

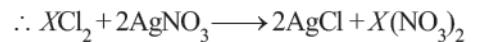


$$\begin{array}{ccc} 1 \text{ mole} & 1 \text{ mole} & 1 \text{ mole} \\ \therefore 0.049 \text{ mole} & 0.049 \text{ mole} & 0.049 \text{ mole of AgCl} \end{array}$$

$$\begin{aligned} n &= \frac{w}{M} \rightarrow w = (n_{\text{AgCl}}) \times \text{Molecular Mass} \\ &= (0.049) \times (107.8 + 35.5) = 7.02 \text{ g} \end{aligned}$$

43. (c) Millimoles of solution of chloride  
 $= 0.05 \times 10 = 0.5$

Millimoles of  $\text{AgNO}_3$  solution  $= 10 \times 0.1 = 1$   
 So, the millimoles of  $\text{AgNO}_3$  are double than the chloride solution.



$$44. \quad \text{(a) } M = \frac{6.02 \times 10^{20} \times 1000}{100 \times 6.02 \times 10^{23}} = \frac{6.02 \times 10^{21}}{6.02 \times 10^{23}}$$

$$= 0.01 \text{ M}$$

$$45. \quad \text{(d) No. of milli equivalent of HCl}$$

$$= 20 \times 0.05 = 1.0$$

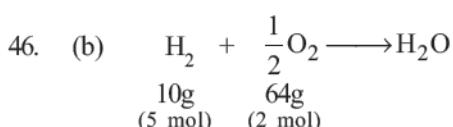
$$\text{No. of milli equivalent of Ba(OH)}_2$$

$$= 30 \times 0.1 \times 2 = 6.0$$

After neutralization, no. of milli equivalents in 50 mL of solution  $= (6 - 1) = 5$

Total volume of the solution  $= 20 + 30 = 50 \text{ mL}$   
 $\therefore$  No. of equivalent of  $\text{OH}^-$  in 50 mL is

$$[\text{OH}^-] = \frac{5 \times 1000}{50} \times 10^{-3} = 0.1 \text{ M}$$



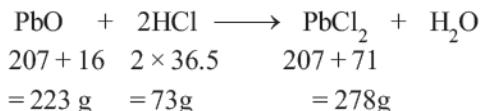
In this reaction oxygen is the limiting agent.  
 Hence, amount of  $\text{H}_2\text{O}$  produced depends on the amount of  $\text{O}_2$  taken.

$\therefore 0.5 \text{ mole of O}_2$  gives  $\text{H}_2\text{O} = 1 \text{ mol}$

$\therefore 2 \text{ mole of O}_2$  gives  $\text{H}_2\text{O} = 4 \text{ mol}$

 When there is not enough of one reactant in a chemical reaction, the reaction stops. To find the amount of product produced, we must determine reactant that will limit the chemical reaction (the limiting reagent) we can find the limiting reagent by calculating the amount of product that can be formed by each reactant, the one that produces less product is the limiting reagent.

47. (d) Writing the equation for the reaction, we get



From this equation we find 223 g of PbO reacts with 73 g of HCl to form 278 g of PbCl<sub>2</sub>.

If we carry out the reaction between 3.2 g HCl and 6.5 g PbO.

Amount of PbO that reacts with 3.2 g HCl

$$= \frac{223}{73} \times 3.2 = 9.77 \text{ g.}$$

Since amount of PbO present is only 6.5 g so PbO is the limiting reagent.

Amount of PbCl<sub>2</sub> formed by 6.5 g of PbO

$$= \frac{278}{223} \times 6.5 \text{ g}$$

Number of moles of PbCl<sub>2</sub> formed

$$= \frac{278}{223} \times \frac{6.5}{278} \text{ moles} = 0.029 \text{ moles.}$$

48. (c) Molarity of H<sub>2</sub>SO<sub>4</sub> solution

$$= \frac{98 \times 1000}{98 \times 100} \times 1.80 = 18.0$$

Suppose  $V$  mL of this H<sub>2</sub>SO<sub>4</sub> is used to prepare 1 lit. of 0.1M H<sub>2</sub>SO<sub>4</sub>

$$\therefore V \times 18.0 = 1000 \times 0.1$$

$$\text{or } V = \frac{1000 \times 0.1}{18.0} = 5.55 \text{ mL.}$$

49. (c) 2Al<sub>2</sub>O<sub>3</sub> + 3C  $\longrightarrow$  Al + 3CO<sub>2</sub>

Gram equivalent of Al<sub>2</sub>O<sub>3</sub>  $\equiv$  g equivalent of C

$$\text{Now equivalent weight of Al} = \frac{27}{3} = 9$$

Equivalent weight of C

$$= \frac{12}{4} = 3 \text{ (C} \rightarrow \text{C}^{+4}\text{O}_2)$$

$$\begin{aligned} \text{No. of gram equivalent of Al} &= \frac{270 \times 10^3}{9} \\ &= 30 \times 10^3 \end{aligned}$$

Hence,

$$\text{No. of gram equivalent of C} = 30 \times 10^3$$

Again,

No. of gram equivalent of C

$$= \frac{\text{mass in gram}}{\text{gram equivalent weight}}$$

$$\Rightarrow 30 \times 10^3 = \frac{\text{mass}}{3}$$

$$\Rightarrow \text{mass} = 90 \times 10^3 \text{ g} = 90 \text{ kg}$$

50. (c) N<sub>2</sub> + 3H<sub>2</sub>  $\rightarrow$  2NH<sub>3</sub>
- |          |          |          |
|----------|----------|----------|
| 1 vol.   | 3 vol.   | 2 vol.   |
| 10 litre | 30 litre | 20 litre |

It is given that only 50% of the expected product is formed hence, only 10 litre of NH<sub>3</sub> is formed.

N<sub>2</sub> used = 5 litres, left = 30 - 5 = 25 litres  
H<sub>2</sub> used = 15 litres, left = 30 - 15 = 15 litres

51. (c) According to Stoichiometry, they should react as follow:



Thus, for 1 mole of O<sub>2</sub> only 0.8 moles of NH<sub>3</sub> is consumed. Hence O<sub>2</sub> is consumed completely.

52. (d) 2C<sub>6</sub>H<sub>6</sub> + 15O<sub>2</sub>(g)  $\longrightarrow$  12CO<sub>2</sub>(g) + 6H<sub>2</sub>O(g)

$\because$  156 g of benzene, required oxygen  
 $= 15 \times 22.4$  litre

$\therefore$  1 g of benzene, required oxygen

$$= \frac{15 \times 22.4}{156} \text{ litre}$$

$\therefore$  39 g of benzene, required oxygen

$$= \frac{15 \times 22.4 \times 39}{156} = 84.0 \text{ litre}$$

53. (a) 5 M H<sub>2</sub>SO<sub>4</sub> = 10 N H<sub>2</sub>SO<sub>4</sub>,  
 $(\because$  Basicity of H<sub>2</sub>SO<sub>4</sub> = 2)

$$\begin{aligned} N_1 V_1 &= N_2 V_2, \\ 10 \times 1 &= N_2 \times 10 \text{ or } N_2 = 1 \text{ N} \end{aligned}$$

54. (a) Mg<sup>2+</sup> + Na<sub>2</sub>CO<sub>3</sub>  $\longrightarrow$  MgCO<sub>3</sub> + 2Na<sup>+</sup>

1 g eq. 1 g eq.

1 g eq. of Mg<sup>2+</sup> = 12 g of Mg<sup>2+</sup> = 12000 mg

= 1000 milli eq. of Na<sub>2</sub>CO<sub>3</sub>

$\therefore$  12 mg Mg<sup>2+</sup> = 1 milli eq. Na<sub>2</sub>CO<sub>3</sub>

# 2

# Structure of Atom

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Bohr's model for H atom	Absorption/emission spectra			1	E						
Dual behaviour of matter and Heisenberg uncertainty principle	uncertainty principle/orbital stability/de-Broglie wavelength							1	A		
Quantum mechanical model of atom	Quantum numbers					1	A			1	E
	orbital energy			1	A						

LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

### Topic 1 : Atomic Models and Dual Nature of Electromagnetic Radiation

- Calculate the energy in joule corresponding to light of wavelength 45 nm :  
(Planck's constant  $h = 6.63 \times 10^{-34}$  Js; speed of light  $c = 3 \times 10^8$  ms $^{-1}$ ) [2014]  
(a)  $6.67 \times 10^{15}$       (b)  $6.67 \times 10^{11}$   
(c)  $4.42 \times 10^{-15}$       (d)  $4.42 \times 10^{-18}$
- According to law of photochemical equivalence the energy absorbed (in ergs/mole) is given as ( $h = 6.62 \times 10^{-27}$  ergs,  $c = 3 \times 10^{10}$  cm s $^{-1}$ ,  $N_A = 6.02 \times 10^{23}$  mol $^{-1}$ ) [NEET Kar. 2013]  
(a)  $\frac{1.196 \times 10^{16}}{\lambda}$       (b)  $\frac{1.196 \times 10^8}{\lambda}$   
(c)  $\frac{2.859 \times 10^5}{\lambda}$       (d)  $\frac{2.859 \times 10^{16}}{\lambda}$
- The value of Planck's constant is  $6.63 \times 10^{-34}$  Js. The speed of light is  $3 \times 10^{17}$  nm s $^{-1}$ . Which value is closest to the wavelength in nanometer of a quantum of light with frequency of  $6 \times 10^{15}$  s $^{-1}$ ? [NEET 2013]  
(a) 25      (b) 50  
(c) 75      (d) 10

- The energies  $E_1$  and  $E_2$  of two radiations are 25 eV and 50 eV, respectively. The relation between their wavelengths i.e.,  $\lambda_1$  and  $\lambda_2$  will be: [2011]  
(a)  $\lambda_1 = \lambda_2$       (b)  $\lambda_1 = 2\lambda_2$   
(c)  $\lambda_1 = 4\lambda_2$       (d)  $\lambda_1 = \frac{1}{2}\lambda_2$
- The energy absorbed by each molecule ( $A_2$ ) of a substance is  $4.4 \times 10^{-19}$  J and bond energy per molecule is  $4.0 \times 10^{-19}$  J. The kinetic energy of the molecule per atom will be: [2009]  
(a)  $2.2 \times 10^{-19}$  J      (b)  $2.0 \times 10^{-19}$  J  
(c)  $4.0 \times 10^{-20}$  J      (d)  $2.0 \times 10^{-20}$  J
- The value of Planck's constant is  $6.63 \times 10^{-34}$  Js. The velocity of light is  $3.0 \times 10^8$  m s $^{-1}$ . Which value is closest to the wavelength in nanometers of a quantum of light with frequency of  $8 \times 10^{15}$  s $^{-1}$ ? [2003]  
(a)  $3 \times 10^7$       (b)  $2 \times 10^{-25}$   
(c)  $5 \times 10^{-18}$       (d)  $4 \times 10^1$
- If the energy of a photon is given as  $3.03 \times 10^{-19}$  J then, the wavelength ( $\lambda$ ) of the photon is :  
(a) 6.56 nm      (b) 65.6 nm [2000]  
(c) 656 nm      (d) 0.656 nm

8. In the photo-electron emission, the energy of the emitted electron is [1994]  
 (a) greater than the incident photon  
 (b) same as that of the incident photon  
 (c) smaller than the incident photon  
 (d) proportional to the intensity of incident photon.
9. The electron was shown experimentally to have wave properties by [1994]  
 (a) de Broglie  
 (b) Davisson and Germer  
 (c) N. Bohr  
 (d) Schrodinger.
10. Which of the following is never true for cathode rays ? [1994]  
 (a) They possess kinetic energy  
 (b) They are electromagnetic waves  
 (c) They produce heat  
 (d) They produce mechanical pressure.

### Topic 2 : Bohr's model for Hydrogen Atom (Emission and Absorption Spectra)

11. Which of the following series of transitions in the spectrum of hydrogen atom falls in visible region ? [2019]  
 (a) Lyman series      (b) Balmer series  
 (c) Paschen series      (d) Brackett series
12. Based on equation  $E = -2.178 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) J$ , certain conclusions are written. Which of them is not correct ? [NEET 2013]  
 (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 mean 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.
13. According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon? [2011 MJ]

- (a)  $n = 6$  to  $n = 1$       (b)  $n = 5$  to  $n = 4$   
 (c)  $n = 6$  to  $n = 5$       (d)  $n = 5$  to  $n = 3$
14. The energy of second Bohr orbit of the hydrogen atom is  $-328 \text{ kJ mol}^{-1}$ ; hence the energy of fourth Bohr orbit would be: [2005]  
 (a)  $-41 \text{ kJ mol}^{-1}$       (b)  $-82 \text{ kJ mol}^{-1}$   
 (c)  $-164 \text{ kJ mol}^{-1}$       (d)  $-1312 \text{ kJ mol}^{-1}$
15. The frequency of radiation emitted when the electron falls from  $n = 4$  to  $n = 1$  in a hydrogen atom will be (Given ionization energy of  $H = 2.18 \times 10^{-18} \text{ J atom}^{-1}$  and  $h = 6.625 \times 10^{-34} \text{ Js}$ ) [2004]  
 (a)  $1.54 \times 10^{15} \text{ s}^{-1}$       (b)  $1.03 \times 10^{15} \text{ s}^{-1}$   
 (c)  $3.08 \times 10^{15} \text{ s}^{-1}$       (d)  $2.00 \times 10^{15} \text{ s}^{-1}$
16. In hydrogen atom, energy of first excited state is  $-3.4 \text{ eV}$ . Find out KE of the same orbit of Hydrogen atom [2002]  
 (a)  $+3.4 \text{ eV}$       (b)  $+6.8 \text{ eV}$   
 (c)  $-13.6 \text{ eV}$       (d)  $+13.6 \text{ eV}$
17. According to Bohr's theory the energy required for an electron in the  $\text{Li}^{2+}$  ion to be emitted from  $n = 2$  state is (given that the ground state ionization energy of hydrogen atom is  $13.6 \text{ eV}$ ) [1999]  
 (a)  $61.2 \text{ eV}$       (b)  $13.6 \text{ eV}$   
 (c)  $30.6 \text{ eV}$       (d)  $10.2 \text{ eV}$
18. The Bohr orbit radius for the hydrogen atom ( $n = 1$ ) is approximately  $0.530 \text{ \AA}$ . The radius for the first excited state ( $n = 2$ ) orbit is (in  $\text{\AA}$ ) [1998]  
 (a) 0.13      (b) 1.06  
 (c) 4.77      (d) 2.12
19. The radius of hydrogen atom in the ground state is  $0.53 \text{ \AA}$ . The radius of  $\text{Li}^{2+}$  ion (atomic number = 3) in a similar state is [1995]  
 (a)  $0.17 \text{ \AA}$       (b)  $0.265 \text{ \AA}$   
 (c)  $0.53 \text{ \AA}$       (d)  $1.06 \text{ \AA}$
20. If ionization potential for hydrogen atom is  $13.6 \text{ eV}$ , then ionization potential for  $\text{He}^+$  will be  
 (a)  $54.4 \text{ eV}$       (b)  $6.8 \text{ eV}$  [1993]  
 (c)  $13.6 \text{ eV}$       (d)  $24.5 \text{ eV}$
21. The energy of an electron in the  $n^{\text{th}}$  Bohr orbit of hydrogen atom is [1992]  
 (a)  $-\frac{13.6}{n^4} \text{ eV}$       (b)  $-\frac{13.6}{n^3} \text{ eV}$   
 (c)  $-\frac{13.6}{n^2} \text{ eV}$       (d)  $-\frac{13.6}{n} \text{ eV}$

## **Topic 3: Dual Behaviour of Matter and Heisenberg Uncertainty Principle**

24. In hydrogen atom, the de-Broglie wavelength of an electron in the second Bohr orbit is [Given that Bohr radius,  $a_0 = 52.9 \text{ pm}$ ] **[NEET Odisha 2019]**

(a)  $105.8 \text{ pm}$       (b)  $211.6 \text{ pm}$   
 (c)  $211.6 \pi \text{ pm}$       (d)  $52.9 \pi \text{ pm}$

25. Which one is the wrong statement? **[2017]**

(a) The uncertainty principle is  $\Delta E \times \Delta t \geq h / 4\pi$   
 (b) Half filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement.  
 (c) The energy of  $2s$  orbital is less than the energy of  $2p$  orbital in case of Hydrogen like atoms  
 (d) de-Broglie's wavelength is given by  $\lambda = \frac{h}{mv}$ , where  $m$  = mass of the particle,  $v$  = group velocity of the particle

26. A  $0.66 \text{ kg}$  ball is moving with a speed of  $100 \text{ m/s}$ . The associated wavelength will be  $(h = 6.6 \times 10^{-34} \text{ Js})$ : **[2010]**

(a)  $1.0 \times 10^{-32} \text{ m}$       (b)  $6.6 \times 10^{-32} \text{ m}$   
 (c)  $6.6 \times 10^{-34} \text{ m}$       (d)  $1.0 \times 10^{-35} \text{ m}$

27. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to  $1 \times 10^{-18} \text{ g cm s}^{-1}$ . The uncertainty in electron velocity is, (mass of an electron is  $9 \times 10^{-28} \text{ g}$ ) **[2008]**

(a)  $1 \times 10^9 \text{ cm s}^{-1}$       (b)  $1 \times 10^6 \text{ cm s}^{-1}$   
 (c)  $1 \times 10^5 \text{ cm s}^{-1}$       (d)  $1 \times 10^{11} \text{ cm s}^{-1}$

28. If uncertainty in position and momentum are equal, then uncertainty in velocity is: **[2008]**

(a)  $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$       (b)  $\sqrt{\frac{h}{2\pi}}$   
 (c)  $\frac{1}{m}\sqrt{\frac{h}{\pi}}$       (d)  $\sqrt{\frac{h}{\pi}}$

29. Given : The mass of electron is  $9.11 \times 10^{-31}$  kg  
 Planck constant is  $6.626 \times 10^{-34}$  Js,  
 the uncertainty involved in the measurement of velocity within a distance of  $0.1$  Å is [2006]  
 (a)  $5.79 \times 10^7$  ms $^{-1}$       (b)  $5.79 \times 10^8$  ms $^{-1}$   
 (c)  $5.79 \times 10^5$  ms $^{-1}$       (d)  $5.79 \times 10^6$  ms $^{-1}$

30. The position of both, an electron and a helium atom is known within  $1.0$  nm. Further the momentum of the electron is known within  $5.0 \times 10^{-26}$  kg ms $^{-1}$ . The minimum uncertainty in the measurement of the momentum of the helium atom is [1998]  
 (a)  $50$  kg ms $^{-1}$       (b)  $80$  kg ms $^{-1}$   
 (c)  $8.0 \times 10^{-26}$  kg ms $^{-1}$       (d)  $5.0 \times 10^{-26}$  kg ms $^{-1}$

31. The momentum of a particle having a de Broglie wavelength of  $10^{-17}$  metres is [1996]  
 (Given  $h = 6.625 \times 10^{-34}$  Js)  
 (a)  $3.3125 \times 10^{-7}$  kg ms $^{-1}$   
 (b)  $26.5 \times 10^{-7}$  kg ms $^{-1}$   
 (c)  $6.625 \times 10^{-17}$  kg ms $^{-1}$   
 (d)  $13.25 \times 10^{-17}$  kg ms $^{-1}$

32. Uncertainty in position of an electron (mass =  $9.1 \times 10^{-28}$  g) moving with a velocity of  $3 \times 10^4$  cm/s accurate upto 0.001% will be (use  $h/4(\pi)$  in uncertainty expression where  $h = 6.626 \times 10^{-27}$  erg-second) [1995]  
 (a)  $1.93$  cm      (b)  $3.84$  cm  
 (c)  $5.76$  cm      (d)  $7.68$  cm

33. When an electron of charge ‘e’ and mass ‘m’ moves with a velocity ‘v’ about the nuclear charge ‘Ze’ in circular orbit of radius ‘r’, the potential energy of the electrons is given by [1994]  
 (a)  $Ze^2 / r$       (b)  $-Ze^2 / r$   
 (c)  $Ze^2 / r$       (d)  $mv^2 / r$

34. Which of the following statements do not form a part of Bohr’s model of hydrogen atom ? [1989]  
 (a) Energy of the electrons in the orbits are quantized  
 (b) The electron in the orbit nearest the nucleus has the lowest energy  
 (c) Electrons revolve in different orbits around the nucleus  
 (d) The position and velocity of the electrons in the orbit cannot be determined simultaneously.

## Topic 4 : Quantum Mechanical Model of Atom



42. The correct set of four quantum numbers for the valence electron of rubidium atom ( $Z=37$ ) is [2012]

(a) 5, 1, 1 + 1/2      (b) 6, 0, 0, + 1/2  
 (c) 5, 0, 0, + 1/2      (d) 5, 1, 0, + 1/2

43. Maximum number of electrons in a subshell with :  $l=3$  and  $n=4$  is : [2012]

(a) 14      (b) 16  
 (c) 10      (d) 12

44. If  $n = 6$ , the correct sequence for filling of electrons will be : [2011]

(a)  $ns \rightarrow (n-2)f \rightarrow (n-1)d \rightarrow np$   
 (b)  $ns \rightarrow (n-1)d \rightarrow (n-2)f \rightarrow np$   
 (c)  $ns \rightarrow (n-2)f \rightarrow np \rightarrow (n-1)d$   
 (d)  $ns \rightarrow np (n-1)d \rightarrow (n-2)f$

45. The total number of atomic orbitals in fourth energy level of an atom is : [2011]

(a) 8      (b) 16  
 (c) 32      (d) 4

46. Which of the following is **not** permissible arrangement of electrons in an atom? [2009]

(a)  $n=5, l=3, m=0, s=+1/2$   
 (b)  $n=3, l=2, m=-3, s=-1/2$   
 (c)  $n=3, l=2, m=-2, s=-1/2$   
 (d)  $n=4, l=0, m=0, s=-1/2$

47. Maximum number of electrons in a subshell of an atom is determined by the following: [2009]

(a)  $2l+1$       (b)  $4l-2$   
 (c)  $2n^2$       (d)  $4l+2$

48. Consider the following sets of quantum numbers:

$n$	$l$	$m$	$s$
(i) 3	0	0	+ 1/2
(ii) 2	2	1	+ 1/2
(iii) 4	3	-2	- 1/2
(iv) 1	0	-1	- 1/2
(v) 3	2	3	+ 1/2

Which of the following sets of quantum number is not possible? [2007]

(a) (i), (ii), (iii) and (iv)      (b) (ii), (iv) and (v)  
 (c) (i) and (iii)      (d) (ii), (iii) and (iv)

49. The orientation of an atomic orbital is governed by [2006]

(a) Spin quantum number  
 (b) Magnetic quantum number  
 (c) Principal quantum number  
 (d) Azimuthal quantum number

50. The ions  $O^{2-}$ ,  $F^-$ ,  $Na^+$ ,  $Mg^{2+}$  and  $Al^{3+}$  are isoelectronic. Their ionic radii show [2003]  
 (a) A decrease from  $O^{2-}$  to  $F^-$  and then increase from  $Na^+$  to  $Al^{3+}$   
 (b) A significant increase from  $O^{2-}$  to  $Al^{3+}$   
 (c) A significant decrease from  $O^{2-}$  to  $Al^{3+}$   
 (d) An increase from  $O^{2-}$  to  $F^-$  and then decrease from  $Na^+$  to  $Al^{3+}$
51. Which of the following is isoelectronic? [2002]  
 (a)  $CO_2$ ,  $NO_2$       (b)  $NO_2^-$ ,  $CO_2$   
 (c)  $CN^-$ ,  $CO$       (d)  $SO_2$ ,  $CO_2$
52. The following quantum numbers are possible for how many orbital (s)  $n = 3$ ,  $l = 2$ ,  $m = +2$ ? [2001]  
 (a) 1      (b) 3  
 (c) 2      (d) 4
53. Set of isoelectronic species is [2000]  
 (a)  $N_2$ ,  $CO_2$ ,  $CN^-$ ,  $O_2$  (b)  $N$ ,  $H_2S$ ,  $CO$   
 (c)  $N_2$ ,  $CO$ ,  $CN^-$ ,  $O_2^{+2}$  (d)  $Ca$ ,  $Mg$ ,  $Cl$
54. The ion that is isoelectronic with  $CO$  is [1997]  
 (a)  $CN^-$       (b)  $O_2^+$   
 (c)  $O_2^-$       (d)  $N_2^+$
55. The orbitals are called degenerate when [1996]  
 (a) they have the same wave functions  
 (b) they have the same wave functions but different energies  
 (c) they have different wave functions but same energy  
 (d) they have the same energy
56. If electron has spin quantum number  $+1/2$  and a magnetic quantum number  $-1$ , it cannot be present in [1994]  
 (a) d-orbital      (b) f-orbital  
 (c) p-orbital      (d) s-orbital.
57. For which one of the following sets of four quantum numbers, an electron will have the highest energy? [1994]
- | $n$   | $l$ | $m$ | $s$    |
|-------|-----|-----|--------|
| (a) 3 | 2   | 1   | $1/2$  |
| (b) 4 | 2   | -1  | $1/2$  |
| (c) 4 | 1   | 0   | $-1/2$ |
| (d) 5 | 0   | 0   | $-1/2$ |
58. Which of the following species has four lone pairs of electrons? [1993]  
 (a) I      (b)  $O^-$   
 (c)  $Cl^-$       (d) He
59. The order of filling of electrons in the orbitals of an atom will be [1991]  
 (a)  $3d$ ,  $4s$ ,  $4p$ ,  $4d$ ,  $5s$  (b)  $4s$ ,  $3d$ ,  $4p$ ,  $5s$ ,  $4d$   
 (c)  $5s$ ,  $4p$ ,  $3d$ ,  $4d$ ,  $5s$  (d)  $3d$ ,  $4p$ ,  $4s$ ,  $4d$ ,  $5s$
60. For azimuthal quantum number  $l = 3$ , the maximum number of electrons will be [1991]  
 (a) 2      (b) 6  
 (c) 0      (d) 14.
61. In a given atom no two electrons can have the same values for all the four quantum numbers. This is called [1991]  
 (a) Hund's Rule  
 (b) Aufbau principle  
 (c) Uncertainty principle  
 (d) Pauli's Exclusion principle.
62. An ion has 18 electrons in the outermost shell, it is [1990]  
 (a)  $Cu^+$       (b)  $Th^{4+}$   
 (c)  $Cs^+$       (d)  $K^+$
63. The total number of electrons that can be accommodated in all the orbitals having principal quantum number 2 and azimuthal quantum number 1 is [1990]  
 (a) 2      (b) 4  
 (c) 6      (d) 8
64. The maximum number of electrons in a subshell is given by the expression [1989]  
 (a)  $4l - 2$       (b)  $4l + 2$   
 (c)  $2l + 2$       (d)  $2n^2$
65. Number of unpaired electrons in  $N^{2+}$  is [1989]  
 (a) 2      (b) 0  
 (c) 1      (d) 34
66. The number of spherical nodes in  $3p$  orbitals are [1988]  
 (a) one      (b) three  
 (c) none      (d) two

## ANSWER KEY

1	(d)	8	(c)	15	(c)	22	(a)	29	(d)	36	(a)	43	(a)	50	(c)	57	(b)	64	(b)
2	(b)	9	(b)	16	(a)	23	(b)	30	(d)	37	(d)	44	(a)	51	(c)	58	(c)	65	(c)
3	(b)	10	(b)	17	(c)	24	(c)	31	(c)	38	(d)	45	(b)	52	(a)	59	(b)	66	(a)
4	(b)	11	(b)	18	(d)	25	(c)	32	(a)	39	(a)	46	(b)	53	(c)	60	(d)		
5	(d)	12	(c)	19	(a)	26	(d)	33	(b)	40	(c)	47	(d)	54	(a)	61	(d)		
6	(d)	13	(c)	20	(a)	27	(a)	34	(d)	41	(a)	48	(b)	55	(d)	62	(a)		
7	(c)	14	(b)	21	(c)	28	(a)	35	(d)	42	(c)	49	(b)	56	(d)	63	(c)		

## Hints &amp; Solutions

1. (d)  $E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3 \times 10^8}{45 \times 10^{-9}}$   
 $= 4.42 \times 10^{-18} \text{ J}$

2. (b)  $E = \frac{hc}{\lambda} \times N_A$   
 $= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10} \times 6.02 \times 10^{23}}{\lambda}$   
 $= \frac{1.19 \times 10^8}{\lambda} \text{ ergs mol}^{-1}$

**NOTES** Law of photochemical equivalence is the fundamental principle relating to chemical reactions induced by light which states that for every mole of a substance that reacts  $6.022 \times 10^{23}$  quanta of light are absorbed. The photochemical equivalence law is also sometimes called the stark-Einstein law.

3. (b)  $c = \nu \lambda$   
 $\lambda = \frac{c}{\nu} = \frac{3 \times 10^{17}}{6 \times 10^{15}} = 50 \text{ nm}$

4. (b) Given  $E_1 = 25 \text{ eV}$     $E_2 = 50 \text{ eV}$

$$E_1 = \frac{hc}{\lambda_1} \quad E_2 = \frac{hc}{\lambda_2} \quad \therefore \frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1}$$

$$\therefore \frac{\lambda_2}{\lambda_1} = \frac{25}{50} = \frac{1}{2} \quad \therefore \lambda_1 = 2\lambda_2$$

5. (d) K.E per atom

$$= \frac{(4.4 \times 10^{-19}) - (4.0 \times 10^{-19})}{2}$$

$$= \frac{0.4 \times 10^{-19}}{2} = 2.0 \times 10^{-20} \text{ J}$$

6. (d)  $E = h\nu = \frac{hc}{\lambda}$  or  $\lambda = \frac{c}{\nu}$   
 $\Rightarrow \lambda = \frac{3 \times 10^8}{8 \times 10^{15}} = 3.75 \times 10^{-8} \text{ m}$

In nanometer  $\lambda = 3.75 \times 10$  which is closest to  $4 \times 10^1$

7. (c) The energy of photon,

$$E = \frac{hc}{\lambda} = 3.03 \times 10^{-19}$$

$$\text{or } \lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3.03 \times 10^{-19}}$$

$$\text{or } \lambda = \frac{19.878}{3.03} \times 10^{-7} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$$

8. (c) K.E. of emitted electron is smaller than the incident photon.

**NOTES** K.E of emitted electron =  $hu - hu_0$   
where  $hu_0$  = work function.  
[work function is the minimum energy required to remove an electron from the surface of the material.]  
Energy of the incident photon =  $hu$   
maximum kinetic energy of the photoelectrons depend upon the frequency of the light not on the intensity of light.

9. (b) Wave nature of electron was shown by Davisson and Germer. Davisson and Germer demonstrated the physical reality of the wave nature of electrons by showing that a beam of electrons could also be diffracted by crystals just like light of x-rays.

10. (b) Cathode rays are not electromagnetic waves.

11. (b) Balmer series

12. (c) The electrons has more negative energy in lower orbits than in higher orbit and also the electrons are more tightly bound in the smallest allowed orbit.

**NOTES**

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.

13. (c) Energy of photon obtained from the transition  $n = 6$  to  $n = 5$  will have least energy.

$$\Delta E = 13.6Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

14. (b)  $E_n = E_1 \times \left( \frac{Z}{n} \right)^2$

$$E_2 = \frac{E_1}{2^2} = -328 \text{ kJ/mol}$$

$$E_4 = \frac{E_1}{4^2}$$

$$\Rightarrow \frac{E_4}{E_2} = \frac{2^2}{4^2} = \frac{1}{2^2}$$

$$\Rightarrow E_4 = \frac{E_2}{2^2} = \frac{-328}{4} \text{ kJ/mol} = -82 \text{ kJ/mol}$$

15. (c) I.E. =  $E_1 - E_{\infty}$

$$2.18 \times 10^{-18} = E_1 - 0$$

$$E_1 = 2.18 \times 10^{-18} \text{ J-atom}^{-1}$$

$$\Delta E = E_1 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Rightarrow h\nu = 2.18 \times 10^{-18} \left( \frac{1}{1^2} - \frac{1}{4^2} \right)$$

$$\Rightarrow 6.625 \times 10^{-34} \times \nu = 2.18 \times 10^{-18} \times \frac{15}{16}$$

$$\Rightarrow \nu = \frac{2.18 \times 10^{-18} \times 15}{6.625 \times 10^{-34} \times 16}$$

$$\Rightarrow \nu = 3.08 \times 10^{15} \text{ s}^{-1}$$

16. (a) Suppose the nucleus of hydrogen atom have charge of one proton  $+e$ . The electron revolves in an orbit of radius  $r$  around it.

Therefore the centripetal force is supplied by electrostatic force of attraction between the electron and nucleus i.e.

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

$$\text{or } mv^2 = \frac{Ze^2}{r}$$

$$\text{or } \frac{1}{2}mv^2 = \frac{1}{2} \frac{Ze^2}{r} = \text{K.E}$$

now total energy ( $E_n$ ) = K.E + P.E  
in first excited state

$$E = \frac{1}{2}mv^2 + \left[ -\frac{Ze^2}{r} \right]$$

$$= +\frac{1}{2} \frac{Ze^2}{r} - \frac{Ze^2}{r}$$

$$-3.4 \text{ eV} = -\frac{1}{2} \frac{Ze^2}{r}$$

$$\therefore \text{K.E.} = \frac{1}{2} \frac{Ze^2}{r} = +3.4 \text{ eV}$$

**SELON NOTES** For Bohr orbit, kinetic energy = -Total energy and Potential energy =  $2 \times$  Total energy.

17. (c) Energy of electron in 2nd orbit of  $\text{Li}^{+2}$

$$= -13.6 \frac{Z^2}{n^2}$$

$$= \frac{-13.6 \times (3)^2}{(2)^2} = -30.6 \text{ eV}$$

Energy required =  $0 - (-30.6) = 30.6 \text{ eV}$

18. (d) Radius of hydrogen atom =  $0.530 \text{ \AA}$ , Number of excited state ( $n$ ) = 2 and atomic number of hydrogen atom ( $Z$ ) = 1. We know that the Bohr radius.

$$(r) = \frac{n^2}{Z} \times \text{Bohr Radius of atom} = \frac{(2)^2}{1} \times 0.530 \\ = 4 \times 0.530 = 2.12 \text{ \AA}$$

19. (a) State of hydrogen atom ( $n$ ) = 1

(due to ground state)

Radius of hydrogen atom ( $r$ ) =  $0.53 \text{ \AA}$ . Atomic number of Li ( $Z$ ) = 3.

Radius of  $\text{Li}^{2+}$  ion

$$= r \times \frac{n^2}{Z} = 0.53 \times \frac{(1)^2}{3} = 0.17 \text{ \AA}$$

20. (a) The ionization energy of any hydrogen like species (having one electron only) is given by the equation

$$I.E = \frac{2\pi^2 Z^2 m e^4}{h^2} \text{ or } I.E \propto Z^2$$

Since the atomic number of H is 1 and that of He is 2, therefore, the I.E. of  $\text{He}^+$  is four times ( $2^2$ ) the I.E. of H i.e.,  $13.6 \times 4 = 54.4 \text{ eV}$



For H-like particles,

$$E_n = -\frac{21.8 \times 10^{-19}}{h^2} Z^2 \text{ J/atom}$$

$$= -\frac{1312}{n^2} Z^2 \text{ kJ/mol}$$

$$I.E = E_{a_0} - E_1 = 0 - (-I.E_H Z^2)$$

$$= Z^2 \times I.E_H$$

$$\text{Now for } \text{He}^+, Z = 2 \quad \therefore \quad I.E = 4 \times I.E_H$$

$$\text{for } \text{Li}^{2+}, Z = 3 \quad \therefore \quad I.E = 9 \times I.E_H$$

21. (c) Energy of an electron in Bohr's orbit is given

$$\text{by the relationship. } E_n = -\frac{13.6}{n^2} \text{ eV.}$$

22. (a) Radius of  $n^{\text{th}}$  orbit =  $r_1 n^2$ . (for H-atom)

23. (b) Both He and  $\text{Li}^+$  contain 2 electrons each, therefore their spectrum will be similar.

24. (c)  $n\lambda = 2\pi r$

$$\lambda = \frac{2\pi}{n} r$$

$$r_n = a_0 n^2$$

$$r_2 = 52.9 \times (2)^2 \text{ pm}$$

$$\therefore \lambda = \frac{2\pi}{2} \times 52.9 \times 4$$

$$\lambda = 211.6 \pi \text{ pm}$$

25. (c) For hydrogen like atoms energy of  $2s$ -orbital and  $2p$ -orbital is equal.

$$26. (d) \lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}}{0.66 \times 100} = 1 \times 10^{-35} \text{ m}$$

27. (a)  $\Delta p = m\Delta v$

Substituting the given values of  $\Delta x$  and  $m$ , we get  $1 \times 10^{-18} \text{ g cm s}^{-1} = 9 \times 10^{-28} \text{ g} \times \Delta v$

$$\text{or } \Delta v = \frac{1 \times 10^{-18}}{9 \times 10^{-28}}$$

$$= 1.1 \times 10^9 \text{ cm s}^{-1} \approx 1 \times 10^9 \text{ cm s}^{-1}$$

28. (a) We know  $\Delta p \cdot \Delta x \geq \frac{h}{4\pi}$

$$\text{or } m \cdot \Delta v \cdot \Delta x = \frac{h}{4\pi} \quad [\because \Delta p = m\Delta v]$$

since  $\Delta p = \Delta x$  (given)

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

$$\text{or } (\Delta v)^2 = \frac{h}{4\pi m^2}$$

$$\text{or } \Delta v = \sqrt{\frac{h}{4\pi m^2}} = \frac{1}{2m} \sqrt{\frac{h}{\pi}}$$

29. (d) We know that  $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

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

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

$$\Delta v = \frac{6.626 \times 10^{-34}}{4\pi \times 0.1 \times 10^{-10} \times 9.11 \times 10^{-31}} \\ = \frac{66}{4\pi \times 9} \times 10^7 = 5.79 \times 10^6 \text{ m/sec}$$

30. (d) By Heisenberg uncertainty Principle

$$\Delta x \times \Delta p = \frac{h}{4\pi} \text{ (which is constant)}$$

As  $\Delta x$  for electron and helium atom is same thus momentum of electron and helium will also be same and the uncertainty in momentum of helium atom is equal to  $5 \times 10^{-26} \text{ kg ms}^{-1}$ .

31. (c) Acc. to de-Broglie,

$$\lambda = \frac{h}{mv} \Rightarrow mv = \frac{h}{\lambda} = \frac{6.625 \times 10^{-34}}{10^{-17}}$$

$$\Rightarrow p = 6.625 \times 10^{-17} \text{ kg m/s}$$

32. (a) Given mass of an electron ( $m$ ) =  $9.1 \times 10^{-31} \text{ g}$ ; Velocity of electron ( $v$ ) =  $3 \times 10^4 \text{ cm/s}$ ;

$$\text{Accuracy in velocity} = 0.001\% = \frac{0.001}{100}; \\ \text{Actual velocity of the electron}$$

$$(\Delta v) = 3 \times 10^4 \times \frac{0.001}{100} = 0.3 \text{ cm/s.}$$

$$\text{Planck's constant } (h) = 6.626 \times 10^{-34} \text{ erg sec.}$$

∴ Uncertainty in the position of the electron

$$(\Delta x) = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-34} \times 7}{4 \times 22 \times (9.1 \times 10^{-31}) \times 0.3} = 1.93 \text{ cm}$$

33. (b) P.E. = work done =  $\int_{\infty}^r -\frac{Ze^2}{r^2} dr = -\frac{Ze^2}{r}$ .



Kinetic and potential energy of atoms results from the motion of electrons. When electrons are excited they move to a higher energy orbital farther away from the atom. The further the orbital is from the nucleus, the higher the potential energy of an electron at that energy level. When the electron returns to a low energy state, it releases potential energy in the form of kinetic energy.

34. (d) It is uncertainty principle which was given by Heisenberg and not Bohr's postulate.  
 35. (d) Total number of nodes =  $(n-1)$

$$3 = n - 1 \Rightarrow n = 4$$

Number of angular nodes =  $l = 3 \Rightarrow f$ -subshell

36. (a)  $5f \quad 5 + 3 = 8$   
 $6p \quad 6 + 1 = 7$   
 $5p \quad 5 + 1 = 6$   
 $4d \quad 4 + 2 = 6$   
 $5f > 6p > 5p > 4d$

37. (d) The correct configuration of 'N' is

$1s^2$	$2s^2$	$2p_x^1$	$2p_y^1$	$2p_z^1$
↑↓	↑↓	1	1	1

38. (d) Two electrons occupying the same orbital should have opposite spins i.e. they differ in spin quantum number.

39. (a) Given:  $n = 3, l = 1, m = 0$   
 Hence orbital is  $3p$

-1	0	+1

hence the number of orbital identified by  $m = 0$  can be one only.

40. (c)  $n = 3 \rightarrow 3^{\text{rd}}$  shell  
 $l = 1 \rightarrow p$  sub shell.  
 $m = -1$  is possible for two electrons present in an orbital.



$m = 0$  is fixed for  $P_z$  orbital but  $P_x$  and  $P_y$  orbital can take any value among  $\pm 1$ .

41. (a) Orbital angular momentum

$$= \frac{h}{2\pi} \sqrt{\ell(\ell+1)}$$

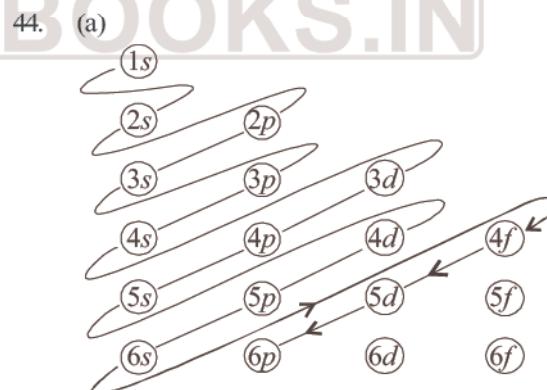
For  $p$  orbital  $\ell = 1$

$$\text{So, } = \frac{h}{2\pi} \sqrt{2} = \frac{h}{\sqrt{2}\pi}$$

42. (c) Electronic configuration of Rb = [Kr]  $5s^1$   
 Set of quantum numbers,  $n = 5$   
 $\ell = 0, \therefore s$ -orbital  
 $m = 0, s = +1/2$

The other possible answer is 5, 0, 0,  $-1/2$ . In any orbital any electron can take the value of  $\pm 1/2$  and the other electron of the same orbital, takes the value with opposite sign.

43. (a)  $(n = 4, l = 3) \Rightarrow 4f$  subshell  
 Since, maximum no. of electrons in a subshell  
 $= 2(2l+1)$   
 So, total no. of electron in  $4f$  subshell  
 $= 2(2 \times 3 + 1) = 14$  electrons.



When  $n = 6$ , the sequence of filling of electrons:

$$6s \longrightarrow 4f \longrightarrow 5d \longrightarrow 6p$$

or  $ns \longrightarrow (n-2)f \longrightarrow (n-1)d \longrightarrow np$

45. (b) Total no. of atomic orbital in a shell =  $n^2$ .  
 Given  $n = 4$ ; hence number of atomic orbitals in 4<sup>th</sup> shell will be 16.  
 46. (b)  $m = 2l + 1$ , thus for  $l = 2, m = 5$ , hence values of  $m$  will be  $-2, -1, 0, +1, +2$ .  
 Therefore for  $l = 2, m$  cannot have the value  $-3$ .  
 47. (d) The number of subshell is  $(2l + 1)$ . The maximum number of electrons in the sub shell is  $2(2l + 1) = (4l + 2)$

48. (b) (ii) is not possible for any value of  $n$  because  $l$  varies from 0 to  $(n - 1)$  thus for  $n = 2$ ,  $l$  can be only 0 and 1.  
 (iv) is not possible because for  $l = 0$ ,  $m = 0$ .  
 (v) is not possible because for  $l = 2$ ,  $m$  varies from  $-2$  to  $+2$ .
49. (b) Magnetic quantum no. represents the orientation of atomic orbitals in an atom. For example  $p_x$ ,  $p_y$  &  $p_z$  have orientation along X-axis, Y-axis & Z-axis.
50. (c) Amongst isoelectronic species, ionic radii of anion is more than that of cations. Further size of anion increases with increase in  $-ve$  charge and size of cation decreases with increase in  $+ve$  charge. Hence, ionic radii decreases from  $O^-$  to  $Al^{3+}$ .
51. (c) Both  $CN^-$  and CO have 14 electrons.
52. (a) Quantum number  $n=3$ ,  $l=2$ ,  $m=+2$  represent one of the  $3d$ -orbitals with
- $$s = \pm \frac{1}{2}$$
- which is possible only for one orbital.
53. (c) The molecule which contains same number of electrons are called isoelectronic. eg.  
 $N_2 = CO = CN^- = O_2^{+2} = 14e^-$
54. (a) We know that ions which have the same number of electrons are called isoelectronic. We also know that both CO and  $CN^-$  have 14 electrons, therefore these are isoelectronic.
55. (d) The orbitals which have same energy are called degenerate orbitals eg.  $p_x$ ,  $p_y$ ,  $p_z$ .
56. (d) For  $s$ -orbital;  $l=0$   
 Thus value of  $m$  must be zero, which is given as  $-1$  in the question. Hence, the electron can not be present in  $s$ -orbital.
57. (b) The sub-shell are  $3d$ ,  $4d$ ,  $4p$  and  $5s$ ,  $4d$  has highest energy as  $n + l$  value is maximum for this.
58. (c) Outer electronic configuration of  $Cl$   
 $= 3s^2 3p_x^2 3p_y^2 3p_z^1$   
 Outer electronic configuration of  
 $Cl^- = 3s^2 3p_x^2 3p_y^2 3p_z^2$   
 hence,  $Cl^-$  contains four lone pairs of electrons.
59. (b) The sub-shell with lowest value of  $(n + l)$  is filled up first. When two or more sub-shells have same  $(n + l)$  value the subshell with lowest value of ' $n$ ' is filled up first therefore the correct order is
- |         |       |       |       |       |       |
|---------|-------|-------|-------|-------|-------|
| orbital | $4s$  | $3d$  | $4p$  | $5s$  | $4d$  |
| $n + l$ | 4 + 0 | 3 + 2 | 4 + 1 | 5 + 0 | 4 + 2 |
| value   | = 4   | 5     | 5     | 5     | 6     |
60. (d)  $l = 3$  means f-subshell. Maximum no. of electrons  $= 4l + 2 = 4 \times 3 + 2 = 14$
61. (d) This is as per the definition of Pauli's Exclusion principle.
62. (a)  $Cu^+ = 29 - 1 = 28 e^-$   
 thus the electronic configuration of  $Cu^+$  is  

$$= 1s^2 2s^2 2p^6 \underbrace{3s^2 3p^6}_{18e^-} 3d^{10}$$
63. (c)  $n = 2$ ,  $l = 1$  means  $2p$ -orbital. Electrons that can be accommodated = 6 as  $p$  sub-shell has 3 orbitals and each orbital contains 2 electrons.
64. (b) No. of orbitals in a sub-shell  $= 2l + 1$   
 $\Rightarrow$  No. of electrons  $= 2(2l + 1) = 4l + 2$
65. (c)  $N(7) = 1s^2 2s^2 2p^3$   
 $N^{2+} = 1s^2, 2s^2 2p_x^1$   
 Unpaired electrons = 1.
66. (a) No. of radial nodes in  $3p$ -orbital  
 $= (n - l - 1)$   
 [for  $p$  orbital  $l = 1$ ]  
 $= 3 - 1 - 1 = 1$



There are two types of nodes, angular nodes and radial nodes. Angular nodes are typically flat plane. The quantum number  $l$  determines the number of angular nodes in an orbital. Radial nodes are spheres that occurs as the principal quantum number increases. Total nodes of an orbital is the sum of angular and radial nodes which is given by  $N = n - l - 1$

# 3

## Classification of Elements and Periodicity in Properties



Trend Analysis with Important Topics & Sub-Topics



Topic Name	Sub-Topic	2020		2019		2018		2017		2016	
		QNS.	LOD								
Modern periodic table	modern periodic table	2	E					1	E		
	Electronic configuration					1	A				
Periodic trends in properties of elements	I.E/ionic, atomic size/electron gain enthalpy trend					1	A			1	A
	Ionisation enthalpy trend			1	A						

LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

### Topic 1: Modern Periodic Table

- Identify the incorrect match. *[2020]*

Name	IUPAC Official Name
(A) Unnilunium	(i) Mendelevium
(B) Unniltrium	(ii) Lawrencium
(C) Unnilhexium	(iii) Seaborgium
(D) Unununnum	(iv) Darmstadtium
(a) (B), (ii)	(b) (C), (iii)
(c) (D), (iv)	(d) (A), (i)
- Match the following : *[2020]*

Oxide	Nature
(A) CO	(i) Basic
(B) BaO	(ii) Neutral
(C) Al <sub>2</sub> O <sub>3</sub>	(iii) Acidic
(D) Cl <sub>2</sub> O <sub>7</sub>	(iv) Amphoteric

Which of the following is correct option?

(A)	(B)	(C)	(D)
(a) (ii)	(i)	(iv)	(iii)
(b) (iii)	(iv)	(i)	(ii)
(c) (iv)	(iii)	(ii)	(i)
(d) (i)	(ii)	(iii)	(iv)

- The element Z= 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration ? *[2017]*
  - Carbon family, [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>2</sup>
  - Oxygen family, [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>4</sup>
  - Nitrogen family, [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>6</sup>
  - Halogen family, [Rn] 5f<sup>14</sup> 6d<sup>10</sup> 7s<sup>2</sup> 7p<sup>5</sup>
- An atom has electronic configuration 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>3</sup> 4s<sup>2</sup>, you will place it in which group? *[2002]*
  - Fifth
  - Fifteenth
  - Second
  - Third
- The element, with atomic number 118, will be *[1996]*
  - alkali
  - noble gas
  - lanthanide
  - transition element
- The electronic configuration of an element is 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>3</sup>. What is the atomic number of the element, which is just below the above element in the periodic table? *[1995]*
  - 33
  - 34
  - 36
  - 49
- If the atomic number of an element is 33, it will be placed in the periodic table in the *[1993]*
  - First group
  - Third group
  - Fifth group
  - Seventh group.

### Topic 2: Periodic Trends in Properties of Elements

8. Match the oxide given in column A with its property given in column B /NEET Odisha, 2019]
- | Column-A                     | Column-B       |
|------------------------------|----------------|
| (i) $\text{Na}_2\text{O}$    | (A) Neutral    |
| (ii) $\text{Al}_2\text{O}_3$ | (B) Basic      |
| (iii) $\text{N}_2\text{O}$   | (C) Acidic     |
| (iv) $\text{Cl}_2\text{O}_7$ | (D) Amphoteric |
- Which of the following options has all correct pairs?
- (i)-(B), (ii)-(D), (iii)-(A), (iv)-(C)
  - (i)-(B), (ii)-(A), (iii)-(D), (iv)-(C)
  - (i)-(C), (ii)-(B), (iii)-(A), (iv)-(D)
  - (i)-(A), (ii)-(D), (iii)-(B), (iv)-(C)
9. For the second period elements the correct increasing order of first ionisation enthalpy is :
- $\text{Li} < \text{Be} < \text{B} < \text{C} < \text{N} < \text{O} < \text{F} < \text{Ne}$  /2019]
  - $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$
  - $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{N} < \text{O} < \text{F} < \text{Ne}$
  - $\text{Li} < \text{Be} < \text{B} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$
10. The correct order of atomic radii in group 13 elements is /2018/
- $\text{B} < \text{Al} < \text{In} < \text{Ga} < \text{Tl}$
  - $\text{B} < \text{Al} < \text{Ga} < \text{In} < \text{Tl}$
  - $\text{B} < \text{Ga} < \text{Al} < \text{In} < \text{Tl}$
  - $\text{B} < \text{Ga} < \text{Al} < \text{Tl} < \text{In}$
11. In which of the following options the order of arrangement does not agree with the variation of property indicated against it ? /2016/
- $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$  (increasing ionic size)
  - $\text{B} < \text{C} < \text{N} < \text{O}$  (increasing first ionisation enthalpy)
  - $\text{I} < \text{Br} < \text{F} < \text{Cl}$  (increasing electron gain enthalpy)
  - $\text{Li} < \text{Na} < \text{K} < \text{Rb}$  (increasing metallic radius)
12. The species Ar,  $\text{K}^+$  and  $\text{Ca}^{2+}$  contain the same number of electrons. In which order do their radii increase ? /2015/
- $\text{Ca}^{2+} < \text{Ar} < \text{K}^+$
  - $\text{Ca}^{2+} < \text{K}^+ < \text{Ar}$
  - $\text{K}^+ < \text{Ar} < \text{Ca}^{2+}$
  - $\text{Ar} < \text{K}^+ < \text{Ca}^{2+}$
13. The formation of the oxide ion  $\text{O}^{2-}(\text{g})$ , from oxygen atom requires first an exothermic and then an endothermic step as shown below :
- $$\text{O}(\text{g}) + \text{e}^- \rightarrow \text{O}^-(\text{g}); \Delta_f H^\ominus = -141 \text{ kJ mol}^{-1}$$
- $$\text{O}^-(\text{g}) + \text{e}^- \rightarrow \text{O}^{2-}(\text{g}); \Delta_f H^\ominus = +780 \text{ kJ mol}^{-1}$$

Thus process of formation of  $\text{O}^{2-}$  in gas phase is unfavourable even though  $\text{O}^{2-}$  is isoelectronic with neon. It is due to the fact that /2015 RS/

- Electron repulsion outweighs the stability gained by achieving noble gas configuration
- $\text{O}^-$  ion has comparatively smaller size than oxygen atom
- Oxygen is more electronegative
- Addition of electron in oxygen results in larger size of the ion.

14. Which of the following orders of ionic radii is correctly represented ? /2014/

- $\text{H}^- > \text{H}^+ > \text{H}$
- $\text{Na}^+ > \text{F}^- > \text{O}^{2-}$
- $\text{F}^- > \text{O}^{2-} > \text{Na}^+$
- $\text{Al}^{3+} > \text{Mg}^{2+} > \text{N}^{3-}$

15. Which one of the following arrangements represents the correct order of least negative to most negative electron gain enthalpy for C, Ca, Al, F and O? /NEET Kar. 2013/

- $\text{Ca} < \text{Al} < \text{C} < \text{O} < \text{F}$
- $\text{Al} < \text{Ca} < \text{O} < \text{C} < \text{F}$
- $\text{Al} < \text{O} < \text{C} < \text{Ca} < \text{F}$
- $\text{C} < \text{F} < \text{O} < \text{Al} < \text{Ca}$

16. Identify the wrong statement in the following: /2012/

- Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius.
- Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius.
- Atomic radius of the elements increases as one moves down the first group of the periodic table.
- Atomic radius of the elements decreases as one moves across from left to right in the 2<sup>nd</sup> period of the periodic table.

17. What is the value of electron gain enthalpy of  $\text{Na}^+$  if  $\text{IE}_1$  of Na = 5.1 eV? /2011M/

- 5.1 eV
- 10.2 eV
- +2.55 eV
- +10.2 eV

18. Among the elements Ca, Mg, P and Cl, the order of increasing atomic radii is : /2010/

- $\text{Ca} < \text{Mg} < \text{P} < \text{Cl}$
- $\text{Mg} < \text{Ca} < \text{Cl} < \text{P}$
- $\text{Cl} < \text{P} < \text{Mg} < \text{Ca}$
- $\text{P} < \text{Cl} < \text{Ca} < \text{Mg}$

19. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl? /2005, 2010/

- $\text{Cl} < \text{F} < \text{O} < \text{S}$
- $\text{O} < \text{S} < \text{F} < \text{Cl}$
- $\text{F} < \text{S} < \text{O} < \text{Cl}$
- $\text{S} < \text{O} < \text{Cl} < \text{F}$

20. The correct order of the decreasing ionic radii among the following isoelectronic species are :  
 (a)  $\text{Ca}^{2+} > \text{K}^+ > \text{S}^{2-} > \text{Cl}^-$  [2010]  
 (b)  $\text{Cl}^- > \text{S}^{2-} > \text{Ca}^{2+} > \text{K}^+$   
 (c)  $\text{S}^{2-} > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$   
 (d)  $\text{K}^+ > \text{Ca}^{2+} > \text{Cl}^- > \text{S}^{2-}$
21. Amongst the elements with following electronic configurations, which one of them may have the highest ionization energy? [2009]  
 (a)  $\text{Ne}[3s^23p^2]$  (b)  $\text{Ar}[3d^{10}4s^24p^3]$   
 (c)  $\text{Ne}[3s^23p^1]$  (d)  $\text{Ne}[3s^23p^3]$
22. The stability of + 1 oxidation state increases in the sequence: [2009]  
 (a)  $\text{Ti} < \text{In} < \text{Ga} < \text{Al}$  (b)  $\text{In} < \text{Ti} < \text{Ga} < \text{Al}$   
 (c)  $\text{Ga} < \text{In} < \text{Al} < \text{Ti}$  (d)  $\text{Al} < \text{Ga} < \text{In} < \text{Ti}$
23. Which one of the following ionic species has the greatest proton affinity to form stable compound?  
 (a)  $\text{NH}_2^-$  (b)  $\text{F}^-$  [2007]  
 (c)  $\text{I}^-$  (d)  $\text{HS}^-$
24. Which of the following electronic configuration of an atom has the lowest ionisation enthalpy?  
 [2007]  
 (a)  $1s^2 2s^2 2p^3$  (b)  $1s^2 2s^2 2p^5 3s^1$   
 (c)  $1s^2 2s^2 2p^6$  (d)  $1s^2 2s^2 2p^5$
25. Identify the correct order of the size of the following:  
 (a)  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$  [2007]  
 (b)  $\text{Ar} < \text{Ca}^{2+} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$   
 (c)  $\text{Ca}^{2+} < \text{Ar} < \text{K}^+ < \text{Cl}^- < \text{S}^{2-}$   
 (d)  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{S}^{2-} < \text{Cl}^-$
26. Which one of the following oxides is expected to exhibit paramagnetic behaviour? [2005]  
 (a)  $\text{CO}_2$  (b)  $\text{SiO}_2$   
 (c)  $\text{SO}_2$  (d)  $\text{ClO}_2$
27. Ionic radii are [2004]  
 (a) inversely proportional to effective nuclear charge  
 (b) inversely proportional to square of effective nuclear charge  
 (c) directly proportional to effective nuclear charge  
 (d) directly proportional to square of effective nuclear charge
28. Among K, Ca, Fe and Zn, the element which can form more than one binary compound with chlorine is [2004]  
 (a) Fe (b) Zn  
 (c) K (d) Ca
29. Which of the following statements is true? [2002]  
 (a) Silicon exhibits 4 coordination number in its compound  
 (b) Bond energy of  $\text{F}_2$  is less than  $\text{Cl}_2$   
 (c) Mn(III) oxidation state is more stable than Mn(II) in aqueous state  
 (d) Elements of 15th group shows only +3 and +5 oxidation states
30. Which of the following order is wrong? [2002]  
 (a)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3$  – Acidic  
 (b)  $\text{Li} < \text{Be} < \text{B} < \text{C}$  – First IP  
 (c)  $\text{Al}_2\text{O}_3 < \text{MgO} < \text{Na}_2\text{O} < \text{K}_2\text{O}$  – Basic  
 (d)  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$  – Ionic radius
31. Correct order of first IP among following elements Be, B, C, N, O is [2001]  
 (a)  $\text{B} < \text{Be} < \text{C} < \text{O} < \text{N}$  (b)  $\text{B} < \text{Be} < \text{C} < \text{N} < \text{O}$   
 (c)  $\text{Be} < \text{B} < \text{C} < \text{N} < \text{O}$  (d)  $\text{Be} < \text{B} < \text{C} < \text{O} < \text{N}$
32. Of the given electronic configurations for the elements, which electronic configuration indicates that there will be abnormally high difference in the second and third ionization energy for the element? [1999]  
 (a)  $1s^2 2s^2 2p^6 3s^2$  (b)  $1s^2 2s^2 2p^6 3s^1$   
 (c)  $1s^2 2s^2 2p^6 3s^2 3p^1$  (d)  $1s^2 2s^2 2p^6 3s^2 3p^2$
33. The first ionization potentials (eV) of Be and B respectively are [1998]  
 (a) 8.29, 9.32 (b) 9.32, 9.32  
 (c) 8.29, 8.29 (d) 9.32, 8.29
34. Which of the following does not represent the correct order of the properties indicated [1997]  
 (a)  $\text{Ni}^{2+} > \text{Cr}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$  (size)  
 (b)  $\text{Sc} > \text{Ti} > \text{Cr} > \text{Mn}$  (size)  
 (c)  $\text{Mn}^{2+} > \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+}$  (unpaired electron)  
 (d)  $\text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$  (unpaired electron)
35. Which one of the following ions will be the smallest in size? [1996]  
 (a)  $\text{Na}^+$  (b)  $\text{Mg}^{2+}$   
 (c)  $\text{F}^-$  (d)  $\text{O}^{2-}$
36. Among the following oxides, the one which is most basic is [1994]  
 (a)  $\text{ZnO}$  (b)  $\text{MgO}$   
 (c)  $\text{Al}_2\text{O}_3$  (d)  $\text{N}_2\text{O}_5$
37. One of the characteristic properties of non-metals is that they [1993]  
 (a) Are reducing agents  
 (b) Form basic oxides  
 (c) Form cations by electron gain  
 (d) Are electronegative

38. Which electronic configuration of an element has abnormally high difference between second and third ionization energy? **[1993]**
- $1s^2, 2s^2, 2p^6, 3s^1$
  - $1s^2, 2s^2, 2p^6, 3s^1 3p^1$
  - $1s^2, 2s^2, 2p^6, 3s^2 3p^2$
  - $1s^2, 2s^2, 2p^6, 3s^2$
39. In the periodic table from left to right in a period, the atomic volume **[1993]**
- Decreases
  - Increases
  - Remains same
  - First decrease then increases
40.  $\text{Na}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  are isoelectronic. The order of their ionic size is **[1993]**
- $\text{Na}^+ > \text{Mg}^{++} < \text{Al}^{3+} < \text{Si}^{4+}$
  - $\text{Na}^+ < \text{Mg}^{++} > \text{Al}^{3+} > \text{Si}^{4+}$
  - $\text{Na}^+ > \text{Mg}^{++} > \text{Al}^{3+} > \text{Si}^{4+}$
  - $\text{Na}^+ < \text{Mg}^{++} > \text{Al}^{3+} < \text{Si}^{4+}$
41. One would expect proton to have very large **[1993]**
- Charge
  - Ionization potential
  - Hydration energy
  - Radius.
42. Which of the following sets has strongest tendency to form anions ? **[1993]**
- (a) Ga, In, Tl      (b) Na, Mg, Al  
 (c) N, O, F      (d) V, Cr, Mn
43. Elements of which of the following groups will form anions most readily ? **[1992]**
- Oxygen family
  - Nitrogen family
  - Halogens
  - Alkali metals
44. In the periodic table, with the increase in atomic number, the metallic character of an element **[1989]**
- Decreases in a period and increases in a group
  - Increases in a period and decreases in a group
  - Increases both in a period and the group
  - Decreases in a period and the group.
45. The electronic configuration of four elements are given below. Which element does not belong to the same family as others ? **[1989]**
- $[\text{Xe}]4f^{14}5d^{10}1s^2$
  - $[\text{Kr}]4d^{10}5s^2$
  - $[\text{Ne}]3s^23p^5$
  - $[\text{Ar}]3d^{10}4s^2$
46. Pauling's electronegativity values for elements are useful in predicting **[1989]**
- Polarity of the molecules
  - Position in the E.M.F. series
  - Coordination numbers
  - Dipole moments.

## ANSWER KEY

<b>1</b>	(c)	<b>6</b>	(a)	<b>11</b>	(b)	<b>16</b>	(a)	<b>21</b>	(d)	<b>26</b>	(d)	<b>31</b>	(a)	<b>36</b>	(b)	<b>41</b>	(c)	<b>46</b>	(a)
<b>2</b>	(a)	<b>7</b>	(c)	<b>12</b>	(b)	<b>17</b>	(a)	<b>22</b>	(d)	<b>27</b>	(a)	<b>32</b>	(a)	<b>37</b>	(a)	<b>42</b>	(c)		
<b>3</b>	(a)	<b>8</b>	(a)	<b>13</b>	(a)	<b>18</b>	(c)	<b>23</b>	(a)	<b>28</b>	(a)	<b>33</b>	(d)	<b>38</b>	(d)	<b>43</b>	(c)		
<b>4</b>	(a)	<b>9</b>	(b)	<b>14</b>	(N)	<b>19</b>	(b)	<b>24</b>	(b)	<b>29</b>	(b)	<b>34</b>	(a)	<b>39</b>	(d)	<b>44</b>	(a)		
<b>5</b>	(b)	<b>10</b>	(c)	<b>15</b>	(a)	<b>20</b>	(c)	<b>25</b>	(a)	<b>30</b>	(b)	<b>35</b>	(b)	<b>40</b>	(c)	<b>45</b>	(c)		

# Hints & Solutions

1. (c) Unununium ( $Z = 111$ ), it is Roentgenium (Rg) not Darmstadtium.
  2. (a) CO : Neutral oxide  
BaO : Basic oxide  
 $\text{Al}_2\text{O}_3$  : Amphoteric oxide  
 $\text{Cl}_2\text{O}_7$  : Acidic oxide
  3. (a) After  $^{86}\text{Rn}$  (Group 18), elements from atomic number 89 to 103 (actinides) are in group 3  
 $114 = 103 + 11$ . Thus, element with atomic number 114 will be in group (3 + 11) or group 14 (carbon family).  
 The outer shell configuration of group 14 is  $ns^2 = np^2$ .  
 Hence, only option (a) is correct.
  4. (a) The electronic configuration clearly suggest that it is a *d*-block element (having configuration  $(n-1)d^{1-10} ns^{0-2}$ ) which starts from group 3 and goes till group 12. Hence with  $d^5$  configuration it would be classified in the fifth group.
  5. (b) Electronic configuration of element with atomic number 118 will be  $[\text{Rn}]5f^{14}6d^{10}7s^27p^6$ . Since its electronic configuration in the outer most orbit ( $ns^2np^6$ ) resemble with that of inert or noble gases, therefore it will be noble gas element.
  6. (a) Atomic number of the given element is 15 and it belongs to 5th group. Therefore atomic number of the element below the above element =  $15 + 18 = 33$ .
  7. (c) Element with  $Z=33$   
 $(1s^22s^2p^63s^2p^6d^{10}4s^2p^3)$  lies in fifth (or 15th) group.
  8. (a)  $\text{Na}_2\text{O}$  basic oxide  
 $\text{Al}_2\text{O}_3$  amphoteric oxide  
 $\text{N}_2\text{O}$  neutral  
 $\text{Cl}_2\text{O}_7$  acidic oxide
  9. (b) Consider the stability of electronic configuration after loss of one electron.
  10. (c) Due to poor shielding effect of 3d electrons in Ga, the atomic radii of Ga  $<$  Al. Thus, the correct order of atomic radii is B  $<$  Ga  $<$  Al  $<$  In  $<$  Tl.  
 11. (b) The correct order is B  $<$  C  $<$  O  $<$  N  
 Generally ionisation energy increases across a period. But here first I.E. of O is less than the first I.E. of N. This is due to the half-filled  $2p$  orbital in N( $1s^2, 2s^2, 2p^3$ ) which is more stable than the  $2p$  orbital in O( $1s^2, 2s^2, 2p^4$ ).  
 (c) The correct order of electron affinity is I  $<$  Br  $<$  F  $<$  Cl
- NOTES**
- Halogens have high electron affinities which decreases on moving down the group. However, fluorine has lower value than chlorine which is due to its small size and repulsion between the electron added and electrons already present.
12. (b) In isoelectronic species the radius decrease with increase in nuclear charge hence increasing order of radius is  $\text{Ca}^{+2} < \text{K}^+ < \text{Ar}$
  13. (a) Incoming electrons occupies the smaller  $n = 2$  shell, also negative charge on oxygen ( $\text{O}^-$ ) is another factor due to which incoming electron feel repulsion.  
 Hence, electron repulsion outweigh the stability gained by achieving noble gas configuration.
  14. (N) All answers are incorrect.
- NOTES**
- $\text{H}^- > \text{H} > \text{H}^+$ ;  $\text{O}^{2-} > \text{F}^- < \text{Na}^+$   
 $\text{O}^{2-} > \text{F}^- > \text{Na}^+$ ;  $\text{N}^{3-} > \text{Mg}^{2+} > \text{Al}^{3+}$
- For isoelectronic species the size is determined by  $Z_{\text{eff}}$ . Higher the  $Z_{\text{eff}}$ , lower is the size of the ions/species.
15. (a) As the nuclear charge increases, the force of attraction between the nucleus and the incoming electron increases and hence the electron gain enthalpy becomes more negative, hence the correct order is  
 $\text{Ca} < \text{Al} < \text{C} < \text{O} < \text{F}$
  16. (a) As the positive charge increases on metal cation, radius decreases. This is due to the fact that nuclear charge in the case of a cation is acting on lesser number of electrons and pulls them closer.
- NOTES**
- Elements of gp.1 and 2 form basic oxides while gp. 13 and 14 elements form amphoteric oxides. Elements of gp. 16 and 17 form acidic oxides. Acidic character of oxides increases from left to right in the periodic table.

17. (a)  $\text{IE}_1$  of Na = – Electron gain enthalpy of  $\text{Na}^+ = -5.1 \text{ eV}$ .



In this question, temperature is to be defined as absolute zero. This is due to the fact that ionization energy and electron affinity are defined at absolute zero temperature.

$$\text{Ionization enthalpy} = \text{ionization energy} + \frac{5}{2} RT$$

$$\text{Electron gain enthalpy} = \text{electron affinity} - \frac{5}{2} RT$$

18. (c)  ${}_{12}\text{Mg}$      ${}_{15}\text{P}$      ${}_{17}\text{Cl}$      ${}_{20}\text{Ca}$   
             160        110        99        197(pm)

So, the order will be: Cl < P < Mg < Ca

19. (b) O < S < F < Cl

Electron gain enthalpy of given elements are  $-141, -200, -333$  and  $-349 \text{ kJ mol}^{-1}$  respectively.



Due to small size of atom, addition of an electron is not easy. This is the reason why the magnitude of electron gain enthalpy of oxygen and fluorine is less than that of sulphur and chlorine respectively.

20. (c) Among the isoelectronic species, size increases with the increase in negative charge. Thus  $\text{S}^{2-}$  has the highest negative charge and hence largest in size followed by  $\text{Cl}^-, \text{K}^+$  and  $\text{Ca}^{2+}$ .
21. (d) The smaller the atomic size, larger is the value of ionisation potential. Further the atoms having half filled or fully filled orbitals are comparatively more stable, hence more energy is required to remove the electron from such atoms.
22. (d) The stability of +1 oxidation state increases from aluminium to thallium i.e.  
 $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$

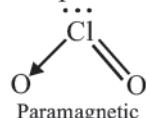


Inert pair effect is generally exhibited by some heavier nucleus p-block elements with common molecular formula  $\text{ns}^2\text{np}^{1-6}$ . These elements have less tendency to leave their outer most s-electrons at the time of chemical reaction i.e. electrons present in s-orbital does not participate in the bond formation. For example Tl, Po, Sn, Pb, Bi.

23. (a) Proton affinity decreases in moving across the period from left to right due to increase in charge, within a group the proton affinities decreases from top to bottom.  
 Nitrogen family > Oxygen family > Halogens
24. (b)  $1s^2, 2s^2, 2p^5, 3s^1$  is an unstable configuration with the outermost electron in 3<sup>rd</sup> orbit. Hence, it has lowest ionisation enthalpy.

25. (a) For isoelectronic species, size of anion increases as negative charge increases whereas size of cation decreases with increase in positive charge. Further ionic radii of anions is more than that of cations. Thus the correct order is  $\text{Ca}^{2+} < \text{K}^+ < \text{Ar} < \text{Cl}^- < \text{S}^{2-}$

26. (d) Due to odd number of electrons in  $\text{ClO}_2$ , it is expected to exhibit paramagnetic behaviour.



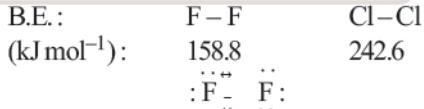
27. (a) Ionic radii are inversely proportional to effective nuclear charge.  
 Ionic radii in the  $n^{\text{th}}$  orbit is given as

$$r_n = \frac{n^2 a_0}{Z} \text{ or } r_n \propto \frac{1}{Z}$$

when  $n$  = principal quantum number  
 $Z$  = effective nuclear charge.

28. (a) Among the given options, only Fe shows variable oxidation states so it can form two chlorides, viz.  $\text{FeCl}_2$  and  $\text{FeCl}_3$ .

29. (b) This is because of inter-electronic repulsions between lone pairs.



30. (b) Along the period, I.P. generally increases but not regularly. Be and B are exceptions. First I.P. increases in moving from left to right in a period, but I.P. of B is lower than Be.

31. (a)  $\text{Be} - 1s^2 2s^2$ ;  $\text{B} - 1s^2 2s^2 2p^1$ ;  $\text{C} - 1s^2 2s^2 2p^2$ ;  $\text{N} - 1s^2 2s^2 2p^3$ ;  $\text{O} - 1s^2 2s^2 2p^4$ . IP increases along the period. But IP of Be > B. Further IP of O < N because atoms with fully or partly filled orbitals are most stable and hence have high ionisation energy.

32. (a)  $\text{Mg} = 1s^2 2s^2 2p^6 3s^2$

After the removal of 2 electrons, the magnesium ion will acquire noble gas configuration hence removal of 3rd electron will require large amount of energy.

33. (d) First ionisation potential of Be is greater than boron due to following configuration



Order of attraction of electrons towards nucleus  $2s > 2p$ , so more amount of energy is required to

- remove the electron in  $2s$ -orbital in comparison to  $2p$  orbital.
34. (a) In a period on moving from left to right ionic radii decreases.  
So order of cationic radii is  $\text{Cr}^{2+} > \text{Mn}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+}$
35. (b) Greater is the positive charge on atom, larger will be the effective nuclear charge. Hence smaller is the size.
36. (b)  $\text{N}_2\text{O}_5$  is strongly acidic,  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$  are amphoteric, therefore,  $\text{MgO}$  is most basic.
37. (a) Non metals form oxides with oxygen and thus reduce oxides of metals behaving as reducing agents.
38. (d) Abnormally high difference between 2nd and 3rd ionization energy means that the element has two valence electrons.
39. (d) Atomic volume is the volume occupied by one mole of an element. Within a period from left to right, atomic volume first decreases and then increases due to increase in nuclear charge and increase in molar mass.
40. (c) Amongst isoelectronic ions, the size of the cation decreases as the magnitude of the charge increases.
41. (c) Proton ( $\text{H}^+$ ) being very small in size would have very large hydration energy.
42. (c) N, O and F ( $p$ -block elements) are highly

electronegative non metals and will have the strongest tendency to form anions by gaining electrons from metal atoms.

43. (c) Elements of halogen group form anions most readily.

 NOTES

Electron affinity values are high in case of halogen because halogens have seven electrons ( $ns^2 np^5$ ) in the valence shell, they have a strong tendency to acquire the nearest inert gas configuration by gaining an electron from the metallic atom and form halide ions easily.

44. (a) Metallic character decreases in a period and increases in a group.
45. (c) Elements (a), (b) and (d) belong to the same group since each one of them has two electrons in the s-sub shell. In contrast, element (c) has seven electrons in the valence shell and hence does not lie in the same group.
46. (a) Paulings electronegativity values for elements are useful in predicting polarity of the molecule.

 NOTES

Pauling scale of electronegativity was helpful in predicting :

- (i) Nature of bond between two atoms
- (ii) Stability of bond

By calculating the difference in electro-negativities, polarity of bond can be calculated.

# 4

# Chemical Bonding and Molecular Structure



Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Dipole moment and bond polarity	dipole moment	1	A								
VSEPR theory and hybridisation	structure and hybridisation					2	A	2	A		
	VSEPR theory									2	E
Valence bond and molecular orbital theory	molecular orbital theory/bond order	1	A	1	A	1	A	1	A		
	valence bond theory			1	A						

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

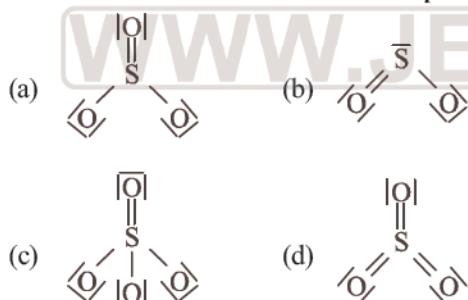
Qns - No. of Questions

## Topic 1: Electrovalent, Covalent and Co-ordinate Bonding

- Which of the following is electron - deficient?  
*[NEET 2013]*  
(a)  $(\text{SiH}_3)_2$       (b)  $(\text{BH}_3)_2$   
(c)  $\text{PH}_3$       (d)  $(\text{CH}_3)_2$
- The correct sequence of increasing covalent character is represented by  
*[2005]*  
(a)  $\text{LiCl} < \text{NaCl} < \text{BeCl}_2$   
(b)  $\text{BeCl}_2 < \text{LiCl} < \text{NaCl}$   
(c)  $\text{NaCl} < \text{LiCl} < \text{BeCl}_2$   
(d)  $\text{BeCl}_2 < \text{NaCl} < \text{LiCl}$
- Which of the following is the electron deficient molecule?  
*[2005]*  
(a)  $\text{C}_2\text{H}_6$       (b)  $\text{B}_2\text{H}_6$   
(c)  $\text{SiH}_4$       (d)  $\text{PH}_3$
- Cation and anion combines in a crystal to form following type of compound.  
*[2000]*  
(a) ionic      (b) metallic  
(c) covalent      (d) dipole-dipole
- Among the following electron deficient compound is :  
*[2000]*  
(a)  $\text{BCl}_3$       (b)  $\text{CCl}_4$   
(c)  $\text{PCl}_5$       (d)  $\text{PCl}_3$
- Which of the following compounds has a 3-centre bond?  
*[1996]*  
(a) Diborane      (b) Carbon dioxide  
(c) Boron trifluoroide      (d) Ammonia
- Linus Pauling received the Nobel Prize for his work on  
*[1994]*  
(a) atomic structure      (b) photosynthesis  
(c) chemical bonds      (d) thermodynamics
- Which of the following pairs will form the most stable ionic bond ?  
*[1994]*  
(a) Na and Cl      (b) Mg and F  
(c) Li and F      (d) Na and F
- The weakest among the following types of bonds is  
*[1994]*  
(a) ionic      (b) covalent  
(c) metallic      (d) H-bond.
- Strongest bond is in between  
*[1993]*  
(a)  $\text{CsF}$       (b)  $\text{NaCl}$   
(c) Both (a) and (b)      (d) None of above

## Topic 2: Octet rule, Resonance and Hydrogen Bonding

14. Which of the following structures is the most preferred and hence of lowest energy for  $\text{SO}_3$ ? [2011 M]



15. What is the dominant intermolecular force or bond that must be overcome in converting liquid  $\text{CH}_3\text{OH}$  to a gas? **[2009]**

  - (a) Dipole-dipole interaction
  - (b) Covalent bonds
  - (c) London dispersion force
  - (d) Hydrogen bonding

16. Which of the following is not a correct statement? **[2006]**

  - (a) The canonical structures have no real existence
  - (b) Every  $AB_5$  molecule does in fact have square pyramidal structure
  - (c) Multiple bonds are always shorter than corresponding single bonds
  - (d) The electron-deficient molecules can act as Lewis acids

17. In  $X-H-Y$ ,  $X$  and  $Y$  both are electronegative elements  
(a) Electron density on  $X$  will increase and on H will decrease [2001]  
(b) In both electron density will decrease  
(c) In both electron density will increase  
(d) Electron density will decrease on  $X$  and will increase on H

18. Which one of the following molecules will form a linear polymeric structure due to hydrogen bonding? [2000]  
(a)  $\text{NH}_3$  (b)  $\text{H}_2\text{O}$   
(c)  $\text{HCl}$  (d)  $\text{HF}$

19. In  $\text{PO}_4^{3-}$  ion, the formal charge on each oxygen atom and P—O bond order respectively are [1998]  
(a)  $-0.75, 0.6$  (b)  $-0.75, 1.0$   
(c)  $-0.75, 1.25$  (d)  $-3, 1.25$

20. The low density of ice compared to water is due to [1997]  
(a) hydrogen-bonding interactions  
(b) dipole-dipole interactions  
(c) dipole-induced dipole interactions  
(d) induced dipole-induced dipole interactions

21. The boiling point of *p*-nitrophenol is higher than that of *o*-nitrophenol because [1994]  
(a)  $\text{NO}_2$  group at *p*-position behave in a different way from that at *o*-position.  
(b) intramolecular hydrogen bonding exists in *p*-nitrophenol  
(c) there is intermolecular hydrogen bonding in *p*-nitrophenol  
(d) *p*-nitrophenol has a higher molecular weight than *o*-nitrophenol.

22. Which one of the following is the correct order of interactions ? [1993]  
(a) Covalent < hydrogen bonding < van der Waals < dipole-dipole  
(b) van der Waals < hydrogen bonding < dipole-dipole < covalent  
(c) van der Waals < dipole-dipole < hydrogen bonding < covalent  
(d) Dipole-dipole < van der Waals < hydrogen bonding < covalent.

23. Strongest hydrogen bond is shown by [1992]  
(a) Water  
(b) Ammonia  
(c) Hydrogen fluoride  
(d) Hydrogen sulphide.



36.  $\text{H}_2\text{O}$  has a non zero dipole moment while  $\text{BeF}_2$  has zero dipole moment because **[1989]**

  - $\text{H}_2\text{O}$  molecule is linear while  $\text{BeF}_2$  is bent
  - $\text{BeF}_2$  molecule is linear while  $\text{H}_2\text{O}$  is bent
  - Fluorine has more electronegativity than oxygen
  - Beryllium has more electronegativity than oxygen.

**Topic 4: VSEPR Theory and Hybridisation**

37. In the structure of  $\text{ClF}_3$ , the number of lone pair of electrons on central atom 'Cl' is **[2018]**

  - One
  - Two
  - Three
  - Four

38. Which of the following molecules represents the order of hybridisation  $sp^2, sp^2, sp, sp$  from left to right atoms? **[2018]**

  - $\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$
  - $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$
  - $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
  - $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

39. Which of the following pairs of compounds is isoelectronic and isostructural? **[2017]**

  - $\text{TeI}_2, \text{XeF}_2$
  - $\text{IBr}_2^-, \text{XeF}_2$
  - $\text{IF}_3, \text{XeF}_2$
  - $\text{BeCl}_2, \text{XeF}_2$

40. The species, having bond angles of  $120^\circ$  is :- **[2017]**

  - $\text{ClF}_3$
  - $\text{NCl}_3$
  - $\text{BCl}_3$
  - $\text{PH}_3$

41. Consider the molecules  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Which of the given statements is false? **[2016]**

  - The H–C–H bond angle in  $\text{CH}_4$ , the H–N–H bond angle in  $\text{NH}_3$ , and the H–O–H bond angle in  $\text{H}_2\text{O}$  are all greater than  $90^\circ$
  - The H–O–H bond angle in  $\text{H}_2\text{O}$  is larger than the H–C–H bond angle in  $\text{CH}_4$ .
  - The H–O–H bond angle in  $\text{H}_2\text{O}$  is smaller than the H–N–H bond angle in  $\text{NH}_3$ .
  - The H–C–H bond angle in  $\text{CH}_4$  is larger than the H–N–H bond angle in  $\text{NH}_3$ .

42. Predict the correct order of electron repulsion among the following : **[2016]**

  - lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

(b) lone pair - lone pair > bond pair - bond pair  
> lone pair - bond pair

(c) bond pair - bond pair > lone pair - bond pair > lone pair - lone pair

(d) lone pair - bond pair > bond pair - bond pair > lone pair - lone pair

43. Which of the following pairs of ions are isoelectronic and isostructural ? **[2015]**

  - $\text{ClO}_3^-, \text{CO}_3^{2-}$
  - $\text{SO}_3^{2-}, \text{NO}_3^-$
  - $\text{ClO}_3^-, \text{SO}_3^{2-}$
  - $\text{CO}_3^{2-}, \text{SO}_3^{2-}$

44. Maximum bond angle at nitrogen is present in which of the following ? **[2015]**

  - $\text{NO}_2^-$
  - $\text{NO}_2^+$
  - $\text{NO}_3^-$
  - $\text{NO}_2$

45. In which of the following pairs, both the species are not isostructural ? **[2015 RS]**

  - $\text{SiCl}_4, \text{PCl}_4^+$
  - diamond, silicon carbide
  - $\text{NH}_3, \text{PH}_3$
  - $\text{XeF}_4, \text{XeO}_4$

46.  $\text{Be}^{2+}$  is isoelectronic with which of the following ions? **[2014]**

  - $\text{H}^+$
  - $\text{Li}^+$
  - $\text{Na}^+$
  - $\text{Mg}^{2+}$

47. Which one of the following species has plane triangular shape ? **[2014]**

  - $\text{N}_3^-$
  - $\text{NO}_3^-$
  - $\text{NO}_2^-$
  - $\text{CO}_2$

48. In which of the following pair both the species have  $sp^3$  hybridization? **[NEET Kar. 2013]**

  - $\text{H}_2\text{S}, \text{BF}_3$
  - $\text{SiF}_4, \text{BeH}_2$
  - $\text{NF}_3, \text{H}_2\text{O}$
  - $\text{NF}_3, \text{BF}_3$

49.  $\text{XeF}_2$  is isostructural with **[NEET 2013]**

  - $\text{ICl}_2^-$
  - $\text{SbCl}_3$
  - $\text{BaCl}_2$
  - $\text{TeF}_2$

50. Which of the following species contains three bond pairs and one lone pair around the central atom ? **[2012]**

  - $\text{H}_2\text{O}$
  - $\text{BF}_3$
  - $\text{NH}_2^-$
  - $\text{PCl}_3$

51. Which one of the following pairs is isostructural (i.e., having the same shape and hybridization)?  
 (a)  $\left[ \text{BCl}_3 \text{ and } \text{BrCl}_3^- \right]$  [2012]  
 (b)  $\left[ \text{NH}_3 \text{ and } \text{NO}_3^- \right]$   
 (c)  $\left[ \text{NF}_3 \text{ and } \text{BF}_3 \right]$   
 (d)  $\left[ \text{BF}_4^- \text{ and } \text{NH}_4^+ \right]$
52. Which of the two ions from the list given below that have the geometry that is explained by the same hybridization of orbitals,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{SCN}^-$ ? [2011]  
 (a)  $\text{NO}_2^-$  and  $\text{NO}_3^-$  (b)  $\text{NH}_4^+$  and  $\text{NO}_3^-$   
 (c)  $\text{SCN}^-$  and  $\text{NH}_2^-$  (d)  $\text{NO}_2^-$  and  $\text{NH}_2^-$
53. Considering the state of hybridization of carbon atoms, find out the molecule among the following which is linear? [2011]  
 (a)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$   
 (b)  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$   
 (c)  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{C}\equiv\text{CH}$   
 (d)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$
54. In which of the following molecules the central atom does not have  $sp^3$  hybridization? [2010]  
 (a)  $\text{NH}_4^+$  (b)  $\text{CH}_4$   
 (c)  $\text{SF}_4$  (d)  $\text{BF}_4^-$
55. Some of the properties of the two species,  $\text{NO}_3^-$  and  $\text{H}_3\text{O}^+$  are described below. Which one of them is correct? [2010]  
 (a) Similar in hybridization for the central atom with different structures.  
 (b) Dissimilar in hybridization for the central atom with different structures.  
 (c) isostructural with same hybridization for the central atom.  
 (d) Isostructural with different hybridization for the central atom.
56. In which one of the following species the central atom has the type of hybridization which is not the same as that present in the other three?  
 (a)  $\text{SF}_4$  (b)  $\text{I}_3^-$  [2010]  
 (c)  $\text{SbCl}_5^{2-}$  (d)  $\text{PCl}_5$
57. In which of the following pairs of molecules/ions, the central atoms have  $sp^2$  hybridization? [2010]  
 (a)  $\text{NO}_2^-$  and  $\text{NH}_3$  (b)  $\text{BF}_3$  and  $\text{NO}_2^-$   
 (c)  $\text{NH}_2^-$  and  $\text{H}_2\text{O}$  (d)  $\text{BF}_3$  and  $\text{NH}_2^-$
58. In which of the following molecules / ions the central atom is  $sp^2$  hybridized? [2009]  
 (a)  $\text{NH}_2^-$  and  $\text{H}_2\text{O}$  (b)  $\text{NO}_2^-$  and  $\text{H}_2\text{O}$   
 (c)  $\text{BF}_3$  and  $\text{NO}_2^-$  (d)  $\text{NO}_2^-$  and  $\text{NH}_2^-$
59. The correct order of increasing bond angles in the following triatomic species is : [2008]  
 (a)  $\text{NO}_2^- < \text{NO}_2^+ < \text{NO}_2$   
 (b)  $\text{NO}_2^- < \text{NO}_2 < \text{NO}_2^+$   
 (c)  $\text{NO}_2^+ < \text{NO}_2 < \text{NO}_2^-$   
 (d)  $\text{NO}_2^+ < \text{NO}_2^- < \text{NO}$
60. In which of the following pairs, the two species are isostructural? [2007]  
 (a)  $\text{SO}_3^{2-}$  and  $\text{NO}_3^-$  (b)  $\text{BF}_3$  and  $\text{NF}_3$   
 (c)  $\text{BrO}_3^-$  and  $\text{XeO}_3$  (d)  $\text{SF}_4$  and  $\text{XeF}_4$
61. Which of the following is not isostructural with  $\text{SiCl}_4$ ? [2006]  
 (a)  $\text{SO}_4^{2-}$  (b)  $\text{PO}_4^{3-}$   
 (c)  $\text{NH}_4^+$  (d)  $\text{SCl}_4$
62. Which of the following species has a linear shape? [2006]  
 (a)  $\text{SO}_2$  (b)  $\text{NO}_2^+$   
 (c)  $\text{O}_3$  (d)  $\text{NO}_2^-$
63. In which of the following molecules all the bonds are not equal? [2006]  
 (a)  $\text{BF}_3$  (b)  $\text{AlF}_3$   
 (c)  $\text{NF}_3$  (d)  $\text{ClF}_3$
64. Which of the following molecules has trigonal planar geometry? [2005]  
 (a)  $\text{BF}_3$  (b)  $\text{NH}_3$   
 (c)  $\text{PCl}_3$  (d)  $\text{IF}_3$
65. In  $\text{BrF}_3$  molecule, the lone pairs occupy equatorial positions to minimize [2004]  
 (a) lone pair - bond pair repulsion only  
 (b) bond pair - bond pair repulsion only  
 (c) lone pair - lone pair repulsion and lone pair - bond pair repulsion  
 (d) lone pair - lone pair repulsion only
66. In an octahedral structure, the pair of  $d$  orbitals involved in  $d^2sp^3$  hybridization is [2004]  
 (a)  $d_{x^2-y^2}, d_{z^2}$  (b)  $d_{xz}, d_{x^2-y^2}$   
 (c)  $d_{z^2}, d_{xz}$  (d)  $d_{xy}, d_{yz}$



- |   |   |  |  |
|---|---|--|--|
| 86.   | In which one of the following molecules the central atom said to adopt $sp^2$ hybridization?  | (a) $\text{BeF}_2$ (b) $\text{BF}_3$ <b>[1989]</b><br>(c) $\text{C}_2\text{H}_2$ (d) $\text{NH}_3$   | (a) NO      (b) $\text{CN}^-$<br>(c) CN      (d) $\text{CN}^+$   |
| 87.   | Which of the following molecule does not have a linear arrangement of atoms ?   | <b>[1989]</b>  | 95. Which of the following pairs of species have the same bond order ? <b>[2017]</b>   |
|   | (a) $\text{H}_2\text{S}$ (b) $\text{C}_2\text{H}_2$<br>(c) $\text{BeH}_2$ (d) $\text{CO}_2$   | (a) $\text{O}_2, \text{NO}^+$ (b) $\text{CN}^-, \text{CO}$<br>(c) $\text{N}_2, \text{O}_2^-$ (d) $\text{CO}, \text{NO}$  |  |
| 88.   | Equilateral shape has   | <b>[1988]</b>  | 96. The correct bond order in the following species is: <b>[2015]</b>  |
|   | (a) $sp$ hybridisation      (b) $sp^2$ hybridisation<br>(c) $sp^3$ hybridisaiton      (d) $sp^3$ hybridisation  | (a) $\text{O}_2^{2+} < \text{O}_2^- < \text{O}_2^+$ (b) $\text{O}_2^+ < \text{O}_2^- < \text{O}_2^{2+}$<br>(c) $\text{O}_2^- < \text{O}_2^+ < \text{O}_2^{2+}$ (d) $\text{O}_2^{2+} < \text{O}_2^+ < \text{O}_2^-$   |  |
| 89.   | The angle between the overlapping of one $s$ -orbital and one $p$ -orbital is   | <b>[1988]</b>  | 97. Which of the following options represents the correct bond order ? <b>[2015]</b>   |
|   | (a) $180^\circ$ (b) $120^\circ$<br>(c) $109^\circ 28'$ (d) $120^\circ 60'$  | (a) $\text{O}_2^- < \text{O}_2 < \text{O}_2^+$ (b) $\text{O}_2^- > \text{O}_2 < \text{O}_2^+$<br>(c) $\text{O}_2^- < \text{O}_2 > \text{O}_2^+$ (d) $\text{O}_2^- > \text{O}_2 > \text{O}_2^+$   |  |
| <b>Topic 5: Valence Bond and Molecular Orbital Theory</b> |   |  |  |
| 90.   | Identify a molecule which does not exist.   | <b>[2020]</b>  | 98. Which of the following species contains equal number of $\sigma$ - and $\pi$ -bonds : <b>[2015]</b>  |
|   | (a) $\text{Li}_2$ (b) $\text{C}_2$<br>(c) $\text{O}_2$ (d) $\text{He}_2$  | (a) $\text{XeO}_4$ (b) $(\text{CN})_2$<br>(c) $\text{CH}_2(\text{CN})_2$ (d) $\text{HCO}_3^-$  |  |
| 91.   | Which of the following is paramagnetic?   | <b>[NEET Odisha 2019]</b>  | 99. Decreasing order of stability of $\text{O}_2$ , $\text{O}_2^-$ , $\text{O}_2^+$ and $\text{O}_2^{2-}$ is : <b>[2015 RS]</b>  |
|   | (a) $\text{O}_2$ (b) $\text{N}_2$<br>(c) $\text{H}_2$ (d) $\text{Li}_2$   | (a) $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$<br>(b) $\text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+$<br>(c) $\text{O}_2 > \text{O}_2^+ > \text{O}_2^{2-} > \text{O}_2^-$<br>(d) $\text{O}_2^- > \text{O}_2^{2-} > \text{O}_2^+ > \text{O}_2$ |  |
| 92.   | The manganate and permanganate ions are tetrahedral, due to:  | <b>[2019]</b>  | 100. The hybridization involved in complex $[\text{Ni}(\text{CN})_4]^{2-}$ . is (At. No. Ni = 28) <b>[2015 RS]</b>   |
|   | (a) The $\pi$ -bonding involves overlap of $p$ -orbitals of oxygen with $d$ -orbitals of manganese<br>(b) There is no $\pi$ -bonding<br>(c) The $\pi$ -bonding involves overlap of $p$ -orbital of oxygen with $p$ -orbitals of manganese<br>(d) The $\pi$ - bonding involves overlap of $d$ -orbital of oxygen with $d$ -orbitals of manganese | (a) $dsp^2$ (b) $sp^3$<br>(c) $d^2sp^2$ (d) $d^2sp^3$  |  |
| 93.   | Which of the following diatomic molecular species has only $\pi$ -bonds according to Molecular Orbital Theory ?   | <b>[2019]</b>  | 101. The outer orbitals of C in ethene molecule can be considered to be hybridized to give three equivalent $sp^2$ orbitals. The total number of sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds in ethene molecule is <b>[NEET Kar. 2013]</b> |
|   | (a) $\text{O}_2$ (b) $\text{N}_2$<br>(c) $\text{C}_2$ (d) $\text{Be}_2$   | (a) 1 sigma ( $\sigma$ ) and 2 pi ( $\pi$ ) bonds<br>(b) 3 sigma ( $\sigma$ ) and 2 pi ( $\pi$ ) bonds<br>(c) 4 sigma ( $\sigma$ ) and 1 pi ( $\pi$ ) bonds<br>(d) 5 sigma ( $\sigma$ ) and 1 pi ( $\pi$ ) bonds   |  |
| 94.   | Consider the following species : $\text{CN}^+, \text{CN}^-, \text{NO}$ and $\text{CN}$  |  |  |
|   | Which one of these will have the highest bond order? <b>[2018]</b>  |  |  |

102. In which of the following ionisation processes the bond energy increases and the magnetic behaviour changes from paramagnetic to diamagnetic? *[NEET Kar. 2013]*
- (a)  $\text{N}_2 \rightarrow \text{N}_2^+$       (b)  $\text{O}_2 \rightarrow \text{O}_2^+$   
 (c)  $\text{C}_2 \rightarrow \text{C}_2^+$       (d)  $\text{NO} \rightarrow \text{NO}^+$
103. The pair of species that has the same bond order in the following is: *[NEET Kar. 2013]*
- (a)  $\text{O}_2, \text{B}_2$       (b)  $\text{CO}, \text{NO}^+$   
 (c)  $\text{NO}^-, \text{CN}^-$       (d)  $\text{O}_2, \text{N}_2$
104. Which of the following is paramagnetic? *[NEET 2013]*
- (a)  $\text{O}_2^-$       (b)  $\text{CN}^-$   
 (c)  $\text{NO}^+$       (d)  $\text{CO}$
105. Which one of the following molecules contains no  $\pi$  bond? *[NEET 2013]*
- (a)  $\text{H}_2\text{O}$       (b)  $\text{SO}_2$   
 (c)  $\text{NO}_2$       (d)  $\text{CO}_2$
106. Four diatomic species are listed below. Identify the correct order in which the bond order is increasing in them: *[2008, 2012 MJ]*
- (a)  $\text{NO} < \text{O}_2^- < \text{C}_2^{2-} < \text{He}_2^+$   
 (b)  $\text{O}_2^- < \text{NO} < \text{C}_2^{2-} < \text{He}_2^+$   
 (c)  $\text{C}_2^{2-} < \text{He}_2^+ < \text{O}_2^- < \text{NO}$   
 (d)  $\text{He}_2^+ < \text{O}_2^- < \text{NO} < \text{C}_2^{2-}$
107. During change of  $\text{O}_2$  to  $\text{O}_2^-$  ion, the electron adds on which one of the following orbitals? *[2012 MJ]*
- (a)  $\pi^*$  orbital      (b)  $\pi$  orbital  
 (c)  $\sigma^*$  orbital      (d)  $\sigma$  orbital
108. The pair of species with the same bond order is:
- (a)  $\text{O}_2^-, \text{B}_2$       (b)  $\text{O}_2^+, \text{NO}^+$  *[2012]*  
 (c)  $\text{NO}, \text{CO}$       (d)  $\text{N}_2, \text{O}_2$
109. Bond order of 1.5 is shown by: *[2012]*
- (a)  $\text{O}_2^+$       (b)  $\text{O}_2^-$   
 (c)  $\text{O}_2^{2-}$       (d)  $\text{O}_2$
110. The pairs of species of oxygen and their magnetic behaviours are noted below. Which of the following presents the correct description?
- (a)  $\text{O}_2^-, \text{O}_2^{2-}$  – Both diamagnetic *[2011 MJ]*  
 (b)  $\text{O}^+, \text{O}_2^{2-}$  – Both paramagnetic  
 (c)  $\text{O}_2^+, \text{O}_2$  – Both paramagnetic  
 (d)  $\text{O}, \text{O}_2^{2-}$  – Both paramagnetic
111. Which of the following has the minimum bond length? *[2011]*
- (a)  $\text{O}_2^+$       (b)  $\text{O}_2^-$   
 (c)  $\text{O}_2^{2-}$       (d)  $\text{O}_2$
112. Which one of the following species does not exist under normal conditions? *[2010]*
- (a)  $\text{Be}_2^+$       (b)  $\text{Be}_2$   
 (c)  $\text{B}_2$       (d)  $\text{Li}_2$
113. According to MO theory which of the following lists ranks the nitrogen species in terms of increasing bond order? *[2009]*
- (a)  $\text{N}_2^{2-} < \text{N}_2^- < \text{N}_2$       (b)  $\text{N}_2 < \text{N}_2^- < \text{N}_2^-$   
 (c)  $\text{N}_2^- < \text{N}_2^{2-} < \text{N}_2$       (d)  $\text{N}_2^- < \text{N}_2 < \text{N}_2^{2-}$
114. The angular shape of ozone molecule ( $\text{O}_3$ ) consists of: *[2008]*
- (a) 1 sigma and 2 pi bonds  
 (b) 2 sigma and 2 pi bonds  
 (c) 1 sigma and 1 pi bonds  
 (d) 2 sigma and 1 pi bonds
115. The correct order of C–O bond length among  $\text{CO}, \text{CO}_3^{2-}, \text{CO}_2$  is *[2007]*
- (a)  $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$       (b)  $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$   
 (c)  $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$       (d)  $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
116. The number of unpaired electrons in a paramagnetic diatomic molecule of an element with atomic number 16 is *[2006]*
- (a) 3      (b) 4  
 (c) 1      (d) 2
117. Among the following the pair in which the two species are **not** isostructural is *[2004]*
- (a)  $\text{SiF}_4$  and  $\text{SF}_4$       (b)  $\text{IO}_3^-$  and  $\text{XeO}_3$   
 (c)  $\text{BH}_4^-$  and  $\text{NH}_4^+$       (d)  $\text{PF}_6^-$  and  $\text{SF}_6$
118. Which of the following statements is not correct for sigma and pi-bonds formed between two carbon atoms? *[2003]*
- (a) Sigma-bond determines the direction between carbon atoms but a pi-bond has no primary effect in this regard  
 (b) Sigma-bond is stronger than a pi-bond  
 (c) Bond energies of sigma- and pi-bonds are of the order of 264 kJ/mol and 347 kJ/mol, respectively  
 (d) Free rotation of atoms about a sigma-bond is allowed but not in case of a pi-bond
119. In  $\text{NO}_3^-$  ion, number of bond pair and lone pair of electrons on nitrogen atom respectively are
- (a) 2, 2      (b) 3, 1      (c) 1, 3      (d) 4, 0 *[2002]*

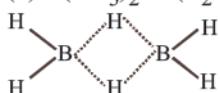
120. The relationship between the dissociation energy of  $N_2$  and  $N_2^+$  is : **[2000]**
- Dissociation energy of  $N_2^+ >$  dissociation energy of  $N_2$
  - Dissociation energy of  $N_2 =$  dissociation energy of  $N_2^+$
  - Dissociation energy of  $N_2 >$  dissociation energy of  $N_2^+$
  - Dissociation energy of  $N_2$  can either be lower or higher than the dissociation energy of  $N_2^+$
121. Which one of the following arrangements represents the increasing bond orders of the given species? **[1999]**
- $NO^+ < NO < NO^- < O_2^-$
  - $O_2^- < NO^- < NO < NO^+$
  - $NO^- < O_2^- < NO < NO^+$
  - $NO < NO^+ < O_2^- < NO^-$
122. Among the following which one is not paramagnetic? [Atomic numbers : Be = 4, Ne = 10, As = 33, Cl = 17] **[1998]**
- $Cl^-$
  - $Be^+$
  - $Ne^{+2}$
  - $As^+$
123. The number of anti-bonding electron pairs in  $O_2^{-2}$  molecular ion on the basis of molecular orbital theory is, (Atomic number of O is 8) **[1998]**
- 5
  - 2
  - 3
  - 4
124.  $N_2$  and  $O_2$  are converted into monoanions,  $N_2^-$  and  $O_2^-$  respectively. Which of the following statements is wrong ? **[1997]**
- In  $N_2$ , the N—N bond weakens
  - In  $O_2$ , the O—O bond order increases
  - In  $O_2$ , bond length decreases
  - $N_2^-$  becomes diamagnetic
125. The correct order of N—O bond lengths in  $NO$ ,  $NO_2^-$ ,  $NO_3^-$  and  $N_2O_4$  is **[1996]**
- $N_2O_4 > NO_2^- > NO_3^- > NO$
  - $NO > NO_3^- > N_2O_4 > NO_2^-$
  - $NO_3^- > NO_2^- > N_2O_4 > NO$
  - $NO > N_2O_4 > NO_2^- > NO_3^-$
126. The ground state electronic configuration of valence shell electrons in nitrogen molecule ( $N_2$ ) is written as KK  $\sigma 2s^2$ ,  $\sigma^* 2s^2$ ,  $\pi 2p_x^2$ ,  $\pi 2p_y^2 \sigma 2p_z^2$  Bond order in nitrogen molecule is **[1995]**
- 0
  - 1
  - 2
  - 3
127. Which of the following species is paramagnetic? **[1995]**
- $O_2^{2-}$
  - $NO$
  - CO
  - $CN^-$
128. Mark the incorrect statement in the following **[1994]**
- The bond order in the species  $O_2$ ,  $O_2^+$  and  $O_2^-$  decreases as  $O_2^+ > O_2 > O_2^-$
  - The bond energy in a diatomic molecule always increases when an electron is lost
  - Electrons in antibonding M.O. contribute to repulsion between two atoms.
  - With increase in bond order, bond length decreases and bond strength increases.
129. Linear combination of two hybridized orbitals belonging to two atoms and each having one electron leads to a **[1990]**
- Sigma bond
  - Double bond
  - Co-ordinate covalent bond
  - Pi bond.

## ANSWER KEY

1	(b)	14	(d)	27	(c)	40	(c)	53	(b)	66	(a)	79	(b)	92	(a)	105	(a)	118	(c)
2	(c)	15	(d)	28	(c)	41	(b)	54	(c)	67	(a)	80	(b)	93	(c)	106	(d)	119	(d)
3	(b)	16	(b)	29	(a)	42	(a)	55	(b)	68	(b)	81	(b)	94	(b)	107	(a)	120	(c)
4	(a)	17	(a)	30	(a)	43	(c)	56	(c)	69	(a)	82	(b)	95	(b)	108	(a)	121	(b)
5	(a)	18	(d)	31	(b)	44	(b)	57	(b)	70	(c)	83	(c)	96	(c)	109	(b)	122	(a)
6	(a)	19	(c)	32	(d)	45	(d)	58	(c)	71	(c)	84	(b)	97	(a)	110	(c)	123	(d)
7	(c)	20	(a)	33	(d)	46	(b)	59	(b)	72	(c)	85	(a)	98	(a)	111	(a)	124	(b)
8	(b)	21	(c)	34	(c)	47	(b)	60	(c)	73	(d)	86	(b)	99	(a)	112	(b)	125	(c)
9	(d)	22	(b)	35	(c)	48	(c)	61	(d)	74	(b)	87	(a)	100	(a)	113	(a)	126	(d)
10	(a)	23	(c)	36	(b)	49	(a)	62	(b)	75	(c)	88	(b)	101	(d)	114	(d)	127	(b)
11	(b)	24	(d)	37	(b)	50	(d)	63	(d)	76	(d)	89	(a)	102	(d)	115	(c)	128	(b)
12	(c)	25	(d)	38	(b)	51	(d)	64	(a)	77	(d)	90	(d)	103	(b)	116	(d)	129	(a)
13	(d)	26	(c)	39	(b)	52	(a)	65	(c)	78	(c)	91	(a)	104	(a)	117	(a)		

# Hints & Solutions

1. (b)  $(BH_3)_2$  or  $(B_2H_6)$



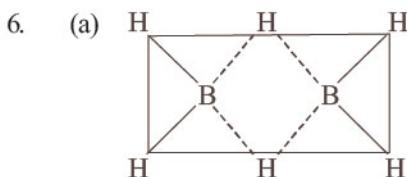
It contains two, 3 centre - 2 electron bonds that are present above and below the plane of molecules. Compounds which do not have sufficient number of electrons to form normal covalent bonds are called electron deficient molecules.

2. (c) As difference of electronegativity increases % ionic character increases and covalent character decreases i.e., as electronegativity difference decreases covalent character increases. Further greater the charge on the cation more will be its covalent character. Be has maximum (+2) charge.
3. (b) The compound, of which central atom is octetless known as electron deficient compound. Hence  $B_2H_6$  is electron deficient compound.
4. (a) Cation and anion form ionic bond in crystal.



The electrostatic force that binds the oppositely charged ions which are formed by transfer of electron from one atom to another is called ionic bond.

5. (a) Boron in  $BCl_3$  has 6 electrons in outer most shell. Hence  $BCl_3$  is an electron pair deficient compound.



The bond represented by dots form the 3-centred electron pair bond.



The idea of three centred electron pair bond B-H-B bridges is necessary because diborane does not have sufficient electrons to form normal covalent bonds. It has only 12 electrons instead of 14 that are required to give simple ethane like structure.

7. (c) Chemical bonds.  
8. (b) The stability of the ionic bond depends upon the lattice energy which is expected to be more between Mg and F due to +2 charge on Mg atom.

9. (d) H-bond is the weakest.

10. (a) According to Fajan's rule, ionic character increases with increase in size of the cation and decrease in size of the anion. Thus, CsF has higher ionic character than NaCl and hence bond strength of CsF is stronger than NaCl.

11. (b) For compounds containing ions of same charge, lattice energy increases as the size the ions decrease. Thus, NaF has highest lattice energy. The size of cation is in the order  $Na^+ < K^+ < Rb^+ < Cs^+$ .

12. (c) As we move in period from Li  $\rightarrow$  Be  $\rightarrow$  B  $\rightarrow$  C, the electronegativity (EN) increases and hence the EN difference between the element and Cl decreases and accordingly the covalent character increases. Thus  $LiCl < BeCl_2 < BCl_3 < CCl_4$  is correct.

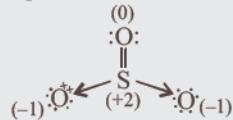
13. (d) In metallic bonds each ion is surrounded by equal no. of oppositely charged ions hence have electrostatic attraction on all sides and hence do not have directional characteristics.

14. (d) The lowest energy structure is the one with the smallest formal charges on the atoms.

Option (b) and (c) are not possible structures of  $SO_3$ .



Option (a) :

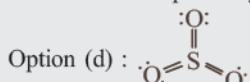


Formal charge = total no. of valence  $e^-$  in the free atom – total no. of non-bonding (lone pair)

$$e^- - \frac{1}{2}(\text{total no. of bonding } e^-).$$

$$\text{Formal charge on S atom} = 6 - 0 - \frac{1}{2}(8) = +2$$

Similarly, formal charges on coordinated bonded oxygen atom and covalently bonded oxygen atom are -1 and 0 respectively.



Formal charge on S atom

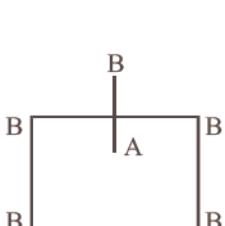
$$= 6 - 0 - \frac{1}{2}(12) = 0$$

Formal charge on O atom

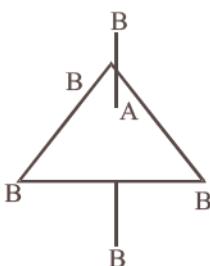
$$= 6 - 4 - \frac{1}{2}(4) = 0$$

15. (d) Due to intermolecular hydrogen bonding in methanol, it exist as assosiated molecule.  
 16. (b) Statement (a), (c), (d) are correct. Statement (b) is incorrect statement.

$AB_5$  may have two structures as follows :



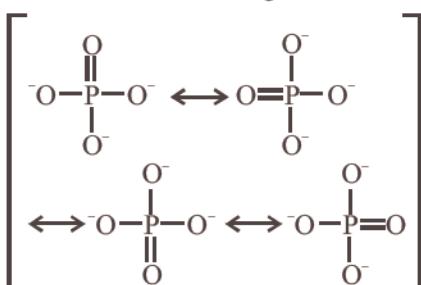
Square Pyramidal



Trigonal Bipyramidal

- NOTES** Individual canonical structures do not exist. The molecule as such has a single structure, which is the resonance hybrid of the canonical forms.
17. (a) In  $X - H - \cdots - Y$ ,  $X$  and  $Y$  both are electronegative elements (i.e attracts the electron pair) then electron density on  $X$  will increase and on  $H$  will decrease.  
 18. (d)  $F-H\cdots F-H\cdots F-H\cdots F$   
 HF form linear polymer structure due to hydrogen bonding.  
 19. (c) Bond order between P—O

$$= \frac{\text{no. of bonds in all possible direction}}{\text{total no. of resonating structures}} = \frac{5}{4} = 1.25$$



$$\text{or Formal charge on oxygen} = -\frac{3}{4} = -0.75$$

20. (a) We know that due to polar nature, water molecules are held together by intermolecular hydrogen bonds. The structure of ice is open with large number of vacant spaces, therefore the density of ice is less than water.  
 21. (c) The b.p. of *p*-nitrophenol is higher than that of *o*-nitrophenol because in *p*-nitrophenol there is intermolecular H-bonding but in *o*-nitrophenol it is intramolecular H-bonding.



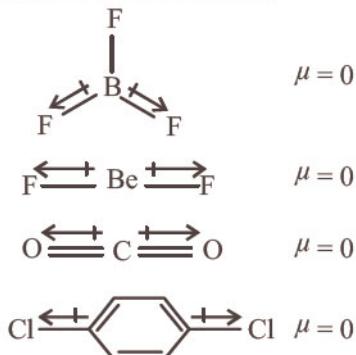
Intramolecular Hydrogen bonding in *o*-nitrophenol is a interaction with in the molecule whereas the intermolecular H-bonding in *p*-nitrophenol is a interaction between the molecules which results into higher boiling point. Intermolecular hydrogen bonding also results in a stronger driving force for crystal formation in other molecules generating higher melting temperature e.g. *p*-hydroxy benzoic acid.

22. (b) The strength of the interactions follows the order: van der Waal's < hydrogen – bonding < dipole-dipole < covalent.  
 23. (c) Hydrogen fluoride shows strongest hydrogen bonding due to high electronegativity of fluorine.

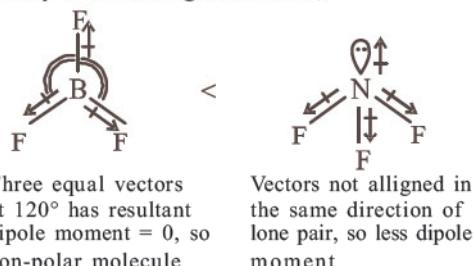
- NOTES**
24. (d)  $H-C=C^*-O-H$   
 The star marked carbon has a valency of 5 and hence this formula is not correct.  
 25. (d) As F is most electronegative thus HF shows maximum strength of hydrogen bond.

**NOTES** With the increase of electronegativity and decrease in size of the atom to which hydrogen is covalently linked, the strength of hydrogen bond increases.

26. (c)  $BF_3$ ,  $BeF_2$ ,  $CO_2$  and 1, 4-dichlorobenzene all are symmetrical molecules.

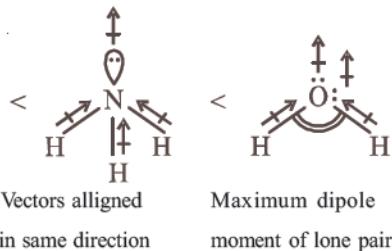


27. (c) Dipole moment of a molecule is the vector sum of dipoles of bonds. So based on molecular geometry of following molecules,

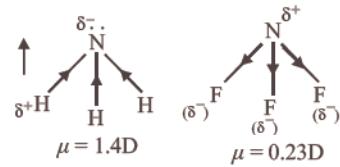


Three equal vectors at  $120^\circ$  has resultant dipole moment = 0, so non-polar molecule

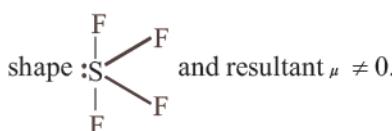
Vectors not aligned in the same direction of lone pair, so less dipole moment



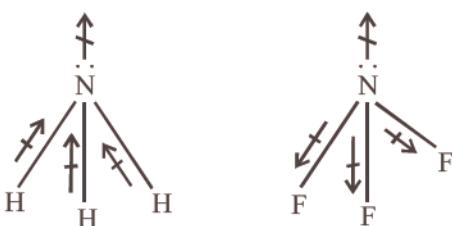
28. (c) Dipole moment of  $\text{NH}_3 > \text{NF}_3$



29. (a)  $\text{SF}_4$  has 4 bond pairs and 1 lone pair of electrons,  $sp^3d$  hybridisation leads to irregular



30. (a) In  $\text{NH}_3$  the atomic dipole and bond dipole are in the same direction whereas in  $\text{NF}_3$  these are in opposite direction so in the former case they are added up whereas in the latter case net result is reduction of dipole moment. It has been shown in the following figure :



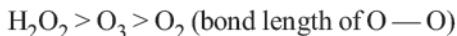
31. (b)  $\text{SF}_4$  has permanent dipole moment.  $\text{SF}_4$  has  $sp^3d$  hybridization and see saw shape (irregular geometry).

$$\mu \neq 0$$

Whereas  $\text{XeF}_4$  shows square planar geometry,  $\text{SiF}_4$  has tetrahedral shape and  $\text{BF}_3$  has Trigonal planar shape. All these are symmetric molecules. Hence  $\mu = 0$ .

32. (d) In  $\text{H}-\text{O}-\text{O}-\text{H}$ , the  $\text{O}-\text{O}$  bond is purely single.  $\text{O}_3$  molecule is a resonance hybrid of two structures :  $\text{O}=\text{O} \rightarrow \text{O}$  and  $\text{O} \leftarrow \text{O}=\text{O}$ . Thus, its bond length will be longer than

$\text{O}_2$  molecule which has purely double bond ( $\text{O}=\text{O}$ ). Hence, the correct order is:



33. (d) In a linear symmetrical molecule like  $\text{BeF}_2$ , the bond angle between three atoms is  $180^\circ$ , hence the polarity due to one bond is cancelled by the equal polarity due to other bond.  $\text{H}_2\text{O}$  is angular.

34. (c) As dipole moment = electric charge  $\times$  bond length

D. M. of  $AB$  molecules

$$= 4.8 \times 10^{-10} \times 2.82 \times 10^{-8} = 13.53\text{D}$$

D. M. of  $CD$  molecules

$$= 4.8 \times 10^{-10} \times 2.67 \times 10^{-10} = 12.81\text{D}$$

now % ionic character

$$= \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of pure ionic compound}}$$

% ionic character in

$$AB = \frac{10.41}{13.53} \times 100 = 76.94\%$$

% ionic character in

$$CD = \frac{10.27}{12.81} \times 100 = 80.23\%$$

35. (c) As the electronegativity difference between N and F is maximum hence, this bond is most polar.

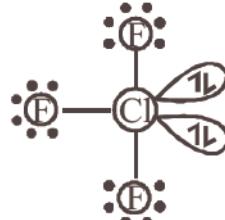


Polarity of the bond depends upon the electronegativity difference of the two atoms forming the bond. Greater the electronegativity difference, more is the polarity of the bond.

$\text{N}-\text{Cl}$	$\text{O}-\text{F}$	$\text{N}-\text{F}$	$\text{N}-\text{N}$
3.0–3.0	3.5–4.0	3.0–4.0	3.0–3.0

36. (b)  $\text{BeF}_2$  is linear and hence has zero dipole moment while  $\text{H}_2\text{O}$ , being a bent molecule, has a finite or non-zero dipole moment.

37. (b) The structure of  $\text{ClF}_3$  is



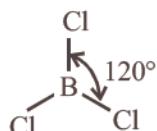
The number of lone pair of electrons on central Cl is 2.

38. (b)  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$

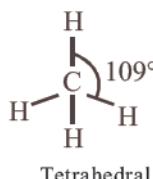
39. (b)  $\text{IBr}_2^-$ ,  $\text{XeF}_2$

Total number of valence electrons are equal in both the species and both the species exhibit linear shape.

40. (c)  $\text{BCl}_3$  is trigonal planar and hence the bond angle is  $120^\circ$ .

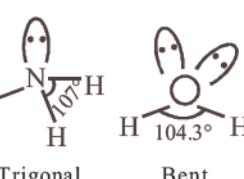


41. (b)  $\text{CH}_4$



Tetrahedral;

- $\text{NH}_3$



Trigonal  
pyramidal

- $\text{H}_2\text{O}$



Bent



The geometry of  $\text{H}_2\text{O}$  should have been tetrahedral if there are all bond pairs. But due to presence of two lone pairs the shape is distorted tetrahedral. Hence bond angle reduced to  $104.5^\circ$  from  $109.5^\circ$ .

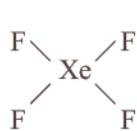
42. (a) According to VSEPR theory order of repulsion in between lp – lp, lp – bp and bp – bp is as under

$$\text{lp} - \text{lp} > \text{lp} - \text{bp} > \text{bp} - \text{bp}$$

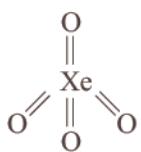
43. (c)  $\text{ClO}_3^-$  and  $\text{SO}_3^{2-}$  both have same number of electrons (42) and central atom in each being  $sp^3$  hybridised. Both are having one lone pair on central atom hence they are pyramidal.

44. (b)  $\text{NO}_2^+$  has  $sp$  hybridisation so it is linear with bond angle =  $180^\circ$ .

45. (d)  $\text{XeF}_4$ ,  $\text{XeO}_4$



(Square planar)



[Tetrahedral]

46. (b)  $\text{Be}^{2+} = (4 - 2) = 2$

is isoelectronic with  $\text{Li}^+$  ( $3 - 1 = 2$ )

Since both have same number of electrons in their outermost shell.

47. (b) Hybridization of  $\text{NO}_3^- = \frac{1}{2}(5 + 0 + 1 - 0)$

$$= \frac{6}{2} = 3 = sp^2 \text{ hence geometry is trigonal planar.}$$



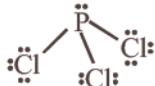
$\text{NO}_2^-$  (nitrite ion) also has  $sp^2$  hybridization and gives a trigonal planar geometry but because there are only two outer atoms, the molecular geometry is bent with  $120^\circ$  bond angles.

48. (c) Applying VSEPR theory, both  $\text{NF}_3$  and  $\text{H}_2\text{O}$  are  $sp^3$  hybridized.

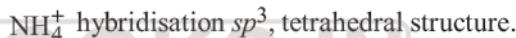
49. (a)  $\text{F}-\ddot{\text{Xe}}-\text{F}$   $sp^3d$  and Linear



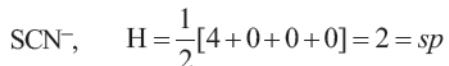
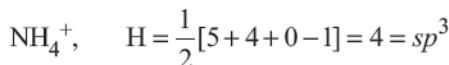
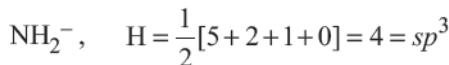
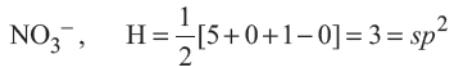
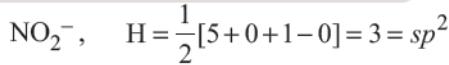
50. (d)  $\text{PCl}_3$



51. (d)  $\text{BF}_4^-$  hybridisation  $sp^3$ , tetrahedral structure.



52. (a)



$\therefore \text{NO}_2^-$  and  $\text{NO}_3^-$  have same hybridisation.

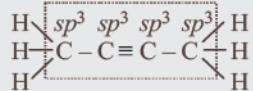


Hybridisation =  $\frac{1}{2}$  [No. of valence electrons of central atom + no. of monovalent atoms attached to it + Negative charge if any – Positive charge if any]

53. (b)  $\text{H}_3\overset{sp^3}{\text{C}}-\overset{sp}{\text{C}}\equiv\overset{sp}{\text{C}}-\overset{sp^3}{\text{C}}\text{H}_3$   
linear

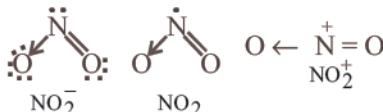


It is important to note that in but-2-yne, the hydrogen atoms are not linear.



Linear part of molecule

54. (c) (a)  $\text{NH}_4^+$ :  $sp^3$  hybridisation  
 (b)  $\text{CH}_4$ :  $sp^3$  hybridisation  
 (c)  $\text{SF}_4$ :  $sp^3d$  hybridisation  
 (d)  $\text{BF}_4^-$ :  $sp^3$  hybridisation
55. (b) In  $\text{NO}_3^-$ , nitrogen is in  $sp^2$  hybridisation, thus planar in shape. In  $\text{H}_3\text{O}^+$ , oxygen is in  $sp^3$  hybridisation, thus trigonal pyramidal in shape.
56. (c)  $\text{SbCl}_5^{2-}$ :  $\frac{5+5+2}{2} = 6$  means  $sp^3d^2$  hybridisation  
 $\text{I}_3^-$ ,  $\text{SF}_4$ , and  $\text{PCl}_5$ ; all have  $sp^3d$  hybridization.
57. (b)  $\text{BF}_3$ :  $\frac{3+3}{2} = 3$  means  $sp^2$  hybridisation  
 $\text{NO}_2^-$ :  $\frac{5+1}{2} = 3$  means  $sp^2$  hybridisation
58. (c) We find that in the given molecules hybridisation is  
 $\text{BF}_3 \rightarrow sp^2$   
 $\text{NO}_2^- \rightarrow sp^2$   
 $\text{NH}_2^- \rightarrow sp^3$   
 $\text{H}_2\text{O} \rightarrow sp^3$
59. (b) From the structure of three species we can determine the number of lone pair electrons on central atom (i.e. N atom) and thus the bond angle.

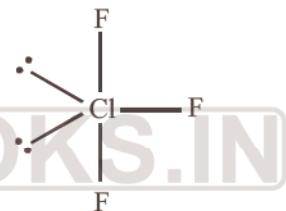


We know that higher the number of lone pair of electron on central atom, greater is the lp – lp repulsion between Nitrogen and oxygen atoms. Thus smaller is bond angle.

The correct order of bond angle is

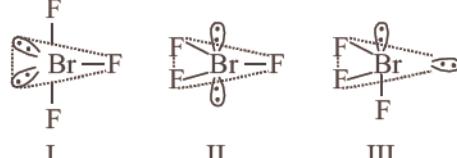


60. (c) Hybridization of Br in  $\text{BrO}_3^-$   
 $H = \frac{1}{2}(7+0-0+1) = 4$   
 hybridization =  $sp^3$   
 Hybridization of Xe in  $\text{XeO}_3$ .  
 $H = \frac{1}{2}(8+0-0+0) = 4$   
 Hybridization =  $sp^3$
- In both cases, the structure is trigonal pyramidal.
61. (d) In  $\text{SiCl}_4$  there is  $sp^3$  hybridisation, so the structure is tetrahedral. In  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$  the structure is tetrahedral with  $sp^3$  hybridisation. But in  $\text{SCl}_4$ ,  $sp^3d$  hybridisation is present, so its shape is different i.e., see saw.
62. (b)  $\text{NO}_2^+$  will have linear shape as it will have  $sp$  hybridisation.
63. (d) In  $\text{BF}_3$ ,  $\text{AlF}_3$  &  $\text{NF}_3$  all fluoride atoms are symmetrically oriented with respect to central metal atom but in  $\text{ClF}_3$  three fluorine atoms are arranged as follows :



Here two bonds are in equatorial plane & one bond is in axial plane.

64. (a)  $\text{BF}_3$  is  $sp^2$  hybridised. So, it is trigonal planar.  $\text{NH}_3$ ,  $\text{PCl}_3$  has  $sp^3$  hybridisation hence has trigonal pyramidal shape,  $\text{IF}_3$ , has  $sp^3d$  hybridization and is T-shaped.
65. (c) The possible structures are:



$90^\circ lp-lp$		
repulsion 0	0	1
$90^\circ lp-bp$		
repulsion 4	6	3
$90^\circ bp-bp$		
repulsion 2	0	2

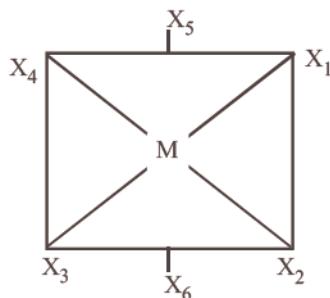
The first structure is minimizing the  $lp-lp$  repulsion if we compare it with III. The same is minimizing the  $lp-bp$  repulsions if we compare it with II. Also it can be noted that, I structure is not minimizing the  $bp-bp$  repulsions.

66. (a)  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals are involved in  $d^2sp^3$  hybridisation.



Only those  $d$  orbitals whose lobes are directed along X, Y and Z directions hybridise with  $s$  and  $p$  orbitals. In other three  $d$  orbitals namely  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$ , the lobes are at an angle of  $45^\circ$  from both axis, hence the extent of their overlap with  $s$  and  $p$  orbitals is much lesser than  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.

67. (a)



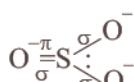
Thus here bond angles between

$$X_4 - M - X_2 = 180^\circ$$

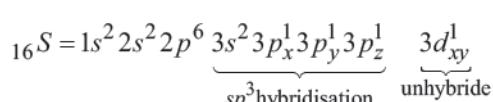
$$X_1 - M - X_3 = 180^\circ$$

$$X_5 - M - X_6 = 180^\circ$$

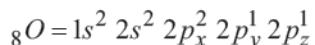
68. (b) In  $\text{SO}_3^{2-}$



S is  $sp^3$  hybridised, so



In 'S' unhybridized  $d$ -orbital is present, which will be involved in  $\pi$  bond formation with oxygen atom.



In oxygen two unpaired  $p$ -orbital is present in these one is involved in  $\sigma$  bond formation while other is used in  $\pi$  bond formation.

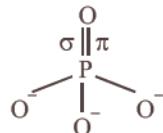
Thus in  $\text{SO}_3^{2-}$ ,  $p\pi$  and  $d\pi$  orbitals are involved for  $p\pi-d\pi$  bonding.

69. (a) For  $\pi$ -overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei.

70. (c) In  $\text{XeF}_2$  and  $\text{IF}_2^-$ . Both  $\text{XeF}_2$  and  $\text{IF}_2^-$  are  $sp^3d$  hybridized and have linear shape.

71. (c) In all the species, the center atom is  $sp^3$  hybridized. But only in  $\text{NH}_4^+$ , no lone pair of electrons are present. Thus, it has maximum bond angle.

72. (c) In P-O bond,  $\pi$  bond is formed by the sidewise overlapping of  $d$ -orbital of P and  $p$ -orbital of oxygen. Hence it is formed by  $p\pi$  and  $d\pi$  overlapping.



73. (d)  $\text{PF}_3$  has pyramidal shape

Phosphorus exist in  $sp^3$  hybridization state hence it exist in tetrahedral geometry. But due to presence of lone pair its shape is pyramidal.

74. (b)  $\text{XeF}_4$  hybridisation is  $= \frac{1}{2}(V + X - C + A)$

hence  $V = 8$  (no. of valence  $e^-$ )

$X = 4$  (no of monovalent atom)

$$\frac{1}{2}(8+4+0-0) = 6, \text{ } sp^3d^2$$

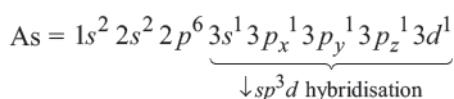
$C = 0$  charge on cation

$A = 0$  (charge on anion).



The shape is Square planar shape.

75. (c) The electronic configuration of As is

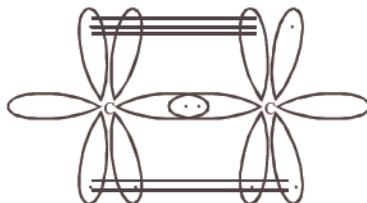


So, the hybrid orbitals used by As atom in  $\text{AsF}_5$  molecule are  $s, p_x, p_y, p_z, d_z^2$ .



In the formation of a stable trigonal pyramid, the two axial bonds above and below the equatorial xy-plane have to be equally strong. Thus, the  $d_z^2$  orbital is used.

76. (d) In alkynes the hybridisation is  $sp$  i.e each carbon atom undergoes  $sp$  hybridisation to form two  $sp$ -hybrid orbitals. The two  $2p$ -orbitals remain unhybridised. Hybrid orbitals form one sigma and two unhybridised orbitals form  $\pi$ -bonds.



Hence two  $\pi$  bond and one sigma bond between C—C lead to cylindrical shape.

77. (d) As there is no lone pair on boron in  $BCl_3$ , therefore no repulsion takes place. But there is a lone pair on nitrogen in  $NCl_3$ . Therefore repulsion takes place. Thus,  $BCl_3$  is planar molecule but  $NCl_3$  is a pyramidal molecule.
78. (c) The C—C bond distance decreases as the multiplicity of the bond increases. Thus, bond distance decreases in the order: butane ( $1.54\text{ \AA}$ ) > benzene ( $1.39\text{ \AA}$ ) > ethene ( $1.34\text{ \AA}$ ) > ethyne ( $1.20\text{ \AA}$ ). Thus in butane, C—C bond distance is the largest.
79. (b) The angle between the bonds formed by  $p_x$  and  $p_y$  orbitals is the minimum i.e.  $90^\circ$ .
80. (b)  $BH_3$  has  $sp^2$  hybridization and hence does not have tetrahedral structure while all others have tetrahedral structures.
81. (b) Sigma bond is stronger than  $\pi$ -bond. The electrons in the  $\pi$  bond are loosely held. The bond is easily broken and is more reactive than  $\sigma$ -bond. Energy released during sigma bond formation is always more than  $\pi$  bond because of greater extent of overlapping.
82. (b)  $CO_2$  has  $sp$ -hybridization and is linear.  $SO_2$  and  $CO_3^{2-}$  are planar ( $sp^2$ ) while  $SO_4^{2-}$  is tetrahedral ( $sp^3$ ).
83. (c) The bond length decreases in the order  $sp^3 > sp^2 > sp$ .  
Because of the triple bond, the carbon-carbon bond distance in ethyne is shortest.
84. (b) All compounds have  $sp^3$  hybridisation, but in  $CCl_4$ , all bonded atoms are same. Hence, the bond angle will be exactly  $109^\circ 28'$ .

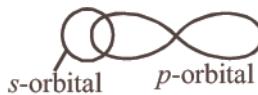
85. (a) A  $\sigma$ -bond is stronger than a  $\pi$ -bond hence option (a) is not correct.



Sigma (s) bonds are formed by head on overlap of unhybridised  $s-s$ ,  $p-p$  or  $s-p$  orbitals and hybridised orbitals ( $sp$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$  and  $sp^3d^2$ ) hence s bonds are strong bonds whereas  $\pi$  (p)-bonds are formed by side ways overlap of unhybridised  $p$ - and  $d$ -orbitals hence p bonds are weak bonds.

86. (b)  $BF_3$  involves  $sp^2$ -hybridization.
87. (a) For linear arrangement of atoms the hybridisation should be  $sp$ (linear shape,  $180^\circ$  angle). Only  $H_2S$  has  $sp^3$ -hybridization and hence has angular shape while  $C_2H_2$ ,  $BeH_2$  and  $CO_2$  all involve  $sp$ -hybridization and hence have linear arrangement of atoms.
88. (b) Equilateral or triangular planar shape involves  $sp^2$  hybridization.

89. (a)



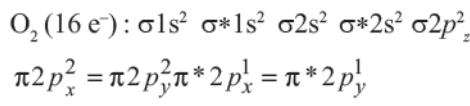
The overlap between  $s$ - and  $p$ -orbitals occurs along internuclear axis and hence the angle is  $180^\circ$ .

90. (d) For  $He_2$  molecule, Electronic configuration is  $\sigma 1s^2$ ,  $\sigma^* 1s^2$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 2) = 0$$

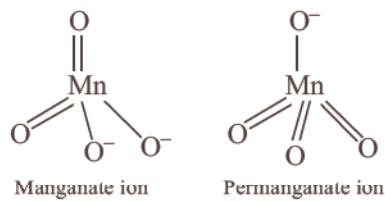
Since, bond order of  $He_2$  is zero, so it does not exist.

91. (a) Molecular orbital configuration of  $O_2$  is given as :



So, in  $O_2$  molecule, there are two (2) unpaired electrons, so, it is a "paramagnetic" substance in nature.

92. (a)



93. (c) Only  $\pi$  bond is present in  $C_2$  molecule.

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2$$

94. (b) NO :  $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x)^1 = (\pi^* 2p_y)^0$   
 $B.O. = \frac{10-5}{2} = 2.5$
- CN<sup>-</sup> :  $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^0$   
 $B.O. = \frac{10-4}{2} = 3$
- CN :  $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\sigma 2p_z)^1$   
 $B.O. = \frac{9-4}{2} = 2.5$
- CN<sup>+</sup> :  $(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2$   
 $B.O. = \frac{8-4}{2} = 2$

Hence, option (2) should be the right answer.

95. (b) CN<sup>-</sup> and CO have same no. of electrons and have same bond order equal to 3.



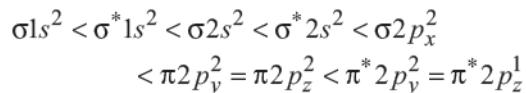
Short cut trick to calculate the bond order:  
N<sub>2</sub> has 14 electrons and its bond order is 3. We have to remember this concept that every electron added or subtracted to 14, reduces the bond order by 0.5. For example  
CN<sup>-</sup>  $\Rightarrow$  no. of electrons = 6 + 7 + 1 = 14  
 $\therefore$  bond order = 3  
CO  $\Rightarrow$  no. of electrons = 6 + 8 = 14  
 $\therefore$  bond order = 3  
NO  $\Rightarrow$  no. of electrons = 7 + 8 = 15  
 $\therefore$  bond order = 3 - 0.5 = 2.5  
NO<sup>+</sup>  $\Rightarrow$  no. of electrons = 7 + 8 - 1 = 14  
 $\therefore$  bond order = 3  
O<sub>2</sub><sup>-</sup>  $\Rightarrow$  no. of electrons = 8 + 8 + 1 = 17  
 $\therefore$  bond order = 3 - 1.5  
Please note that this method will work for any species that have electrons between 10 and 18.

96. (c) O<sub>2</sub><sup>+</sup> ion - Total number of electrons  
 $(16-1) = 15$ .  
Electronic configuration  
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2$   
 $< \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y^1$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$$

O<sub>2</sub><sup>-</sup> (Super oxide ion): Total number of electrons  
 $(16+1) = 17$ .

Electronic configuration



$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2}$$

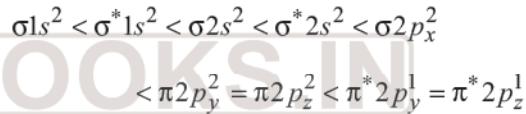
O<sub>2</sub><sup>2+</sup> ion: Total number of electrons

$$= (16-2) = 14 \text{ Electronic configuration} \\ \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 \\ = \pi 2p_z^2$$

$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10-4}{2} = \frac{6}{2} = 3$$

So bond order: O<sub>2</sub><sup>-</sup> < O<sub>2</sub><sup>+</sup> < O<sub>2</sub><sup>2+</sup>

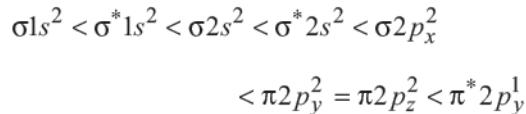
97. (a) Oxygen molecule (O<sub>2</sub>) – Total number of electrons = 16 and electronic configuration is



$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$$

O<sub>2</sub><sup>+</sup> ion - Total number of electrons  $(16-1) = 15$ .

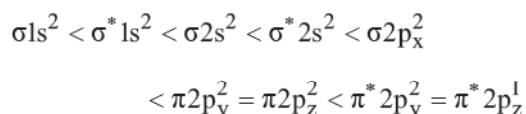
Electronic configuration



$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$$

O<sub>2</sub><sup>-</sup> (Super oxide ion) Total number of electrons

$(16+1) = 17$ . Electronic configuration



$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2}$$

98. (a) 

Number of  $\sigma$  bonds = 4  
Number of  $\pi$  bonds = 4

99. (a) According to molecular orbital theory as bond order decreases stability of the molecule decreases

Bond order =  $\frac{1}{2}(N_b - N_a)$

Bond order for  $O_2^+$  =  $\frac{1}{2}(10 - 5) = 2.5$

Bond order for  $O_2$  =  $\frac{1}{2}(10 - 6) = 2$

Bond order for  $O_2^-$  =  $\frac{1}{2}(10 - 7) = 1.5$

Bond order for  $O_2^{2-}$  =  $\frac{1}{2}(10 - 8) = 1.0$

hence the correct order is

$O_2^+ > O_2 > O_2^- > O_2^{2-}$

100. (a)  $Ni^{2+} = [Ar] 3d^8, 4s^0$   
In the presence of strong ligand  $CN^-$ , pairing of electrons will occur:

$Ni^{2+} = \boxed{\begin{array}{|c|c|c|c|c|} \hline & \backslash & / & \backslash & / \\ \hline & 1 & 1 & 1 & 1 \\ \hline & / & \backslash & / & \backslash \\ \hline & 1 & 1 & 1 & 1 \\ \hline \end{array}} \quad \boxed{\phantom{\boxed{\begin{array}{|c|c|c|c|c|}}}} \quad \boxed{\begin{array}{|c|c|c|} \hline & \backslash & / \\ \hline & 1 & 1 \\ \hline & / & \backslash \\ \hline & 1 & 1 \\ \hline \end{array}} \quad G.S.$

$[Ni(CN)_4]^{2-} = \boxed{\begin{array}{|c|c|c|c|c|} \hline & \backslash & / & \backslash & / \\ \hline & 1 & 1 & 1 & 1 \\ \hline & / & \backslash & / & \backslash \\ \hline & 1 & 1 & 1 & 1 \\ \hline \end{array}} \quad \underbrace{\boxed{\vdots} \quad \boxed{\vdots} \quad \boxed{\vdots} \quad \boxed{\vdots}}_{dsp^2} \quad E.S.$

101. (d)  $H-\overset{\sigma}{C}=\overset{\sigma}{C}-\overset{\pi}{C}-\overset{\sigma}{H}$

102. (d) (a)  $N_2 \longrightarrow N_2^+$   
B.O. 3      2.5  
Bond energy decreases  
Magnetic behaviour changes from diamagnetic to paramagnetic

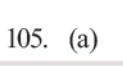
(b)  $O_2 \longrightarrow O_2^+$   
B.O. 2      2.5  
Bond energy increases  
Magnetic behaviour does not change.

(c)  $C_2 \longrightarrow C_2^+$   
B.O. 2      2.5  
Bond energy decreases  
Magnetic behaviour changes from diamagnetic to paramagnetic

(d)  $NO \longrightarrow NO^+$   
B.O. 2      2.5  
bond energy increases  
Magnetic behaviour changes from paramagnetic to diamagnetic

103. (b) No. of electrons in  $CO = 6 + 8 = 14$   
No. of electrons in  $NO^+ = 7 + 8 - 1 = 14$   
 $\therefore CO$  and  $NO^+$  are isoelectronic species.  
Isoelectronic species have identical bond order.

104. (a) Molecular orbital configuration of  $O_2^-$   
 $O_2^- (17) = \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2,$   
 $\sigma 2p_z^2, \pi 2p_x^2 = \pi 2p_y^2, \pi^* 2p_x^2 = \pi^* 2p_y^1$

105. (a) 

106. (d) Calculating the bond order of various species.

$O_2^- : KK \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2$   
 $\pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^2 \pi^* 2p_y^1$

Number of electrons in bonding – Number of electrons in non-bonding  
 $B.O. = \frac{N_b - N_a}{2}$

$= \frac{8 - 5}{2}$  or 1.5

$NO : KK \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \approx \pi 2p_y^2 \sigma 2p_z^2 \pi^* 2p_x^1$

$B.O. = \frac{N_b - N_a}{2} = \frac{8 - 2}{2}$  or 2.5

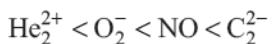
$C_2^{2-} : kk \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$

$B.O. = \frac{N_b - N_a}{2} = \frac{8 - 2}{2}$  or 3

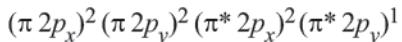
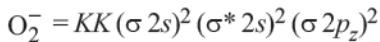
$He_2^+ = \sigma 1s^2 \sigma^* 1s^1$

$$\text{B.O.} = \frac{N_b - N_a}{2} = \frac{2-1}{2} \text{ or } 0.5$$

From these values we find the correct order of increasing bond order is



107. (a)  $\text{O}_2 = \text{KK}(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2$   
 $(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^1(\pi^* 2p_y)^1$



108. (a) Both  $\text{O}_2^{2-}$  and  $\text{B}_2$  has bond order equal to 1.

$$\text{B}_2(10) = [\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 \pi 2p_z^1]$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{6-4}{2} = \frac{2}{2} = 1$$

$\text{B}_2$  is known to be in the gas phase.

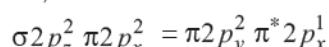
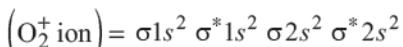
$$\text{O}_2^{2-} = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2$$

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

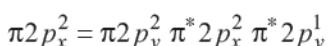
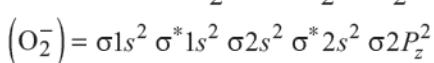
$$\text{Bond order} = \frac{1}{2}(10-8) = 1$$

109. (b)  $(\text{O}_2) = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2$   
 $= \pi 2p_y^2 \pi^* 2p_x^1 = \pi^* 2p_y^1$

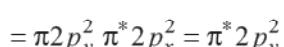
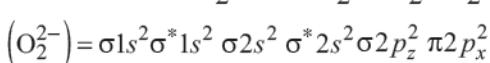
$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-6}{2} = \frac{4}{2} = 2$$



$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{10-5}{2} = \frac{5}{2} = 2\frac{1}{2}$$



$$\text{Bond order} = \frac{(N_b - N_a)}{2} = \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2}$$



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

110. (c) MOT configurations of  $\text{O}_2$  and  $\text{O}_2^+$ :  
 $\text{O}_2^+ : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$   
 $(\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^1)$   
Number of unpaired electrons = 2, so paramagnetic.  
 $\text{O}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2$   
 $(\pi 2p_x^2 = \pi 2p_y^2) (\pi^* 2p_x^1 = \pi^* 2p_y^0)$   
Number of unpaired electrons = 2, so paramagnetic.

111. (a)  $\text{O}_2(16) : \text{KK}(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2$   
 $(\pi 2p_y)^2, (\pi^* 2p_y)^1 = (\pi^* 2p_x)^1$ , B.O.: 2

$\text{O}_2^+(15) : \text{Remove one electron from } \pi^* 2p_y \text{ from } \text{O}_2$ , B.O.: 2.5

$$\text{O}_2^-(17) : \text{KK}(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2$$
 $(\pi 2p_y)^2, (\pi^* 2p_x)^2(\pi^* 2p_y)^1$ , B.O.: 1.5

$$\text{O}_2^{2-}(18) : \text{KK}(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2$$
 $(\pi 2p_y)^2, (\pi^* 2p_x)^2(\pi^* 2p_y)^2$

Since, the bond length decreases as the bond order increases, hence,  $\text{O}_2^+$  have least bond length.

112. (b) Bond order of  $\text{Be}_2 = 0$ , hence  $\text{Be}_2$  cannot exist.

113. (a) Molecular orbital configuration of

$$\text{N}_2^{2-} = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 -$$

$$\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases} \quad \begin{cases} \sigma 2p_x^2 \\ \pi^* 2p_z^1 \end{cases}$$

$$\text{Bond order} = \frac{10-6}{2} = 2$$

$$\text{N}_2^- = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$$

$$\begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases} \quad \begin{cases} \sigma 2p_x^2 \\ \pi^* 2p_z^0 \end{cases}$$

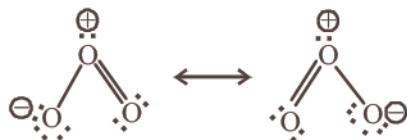
$$\text{Bond order} = \frac{10-5}{2} = 2.5$$

$$\text{N}_2 = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \begin{cases} \pi 2p_y^2, \\ \pi 2p_z^2 \end{cases} \quad \begin{cases} \sigma 2p_x^2 \\ \pi^* 2p_z^1 \end{cases}$$

$$\text{Bond order} = \frac{10-4}{2} = 3$$

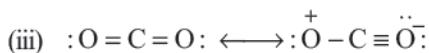
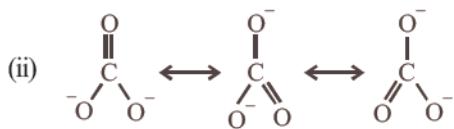
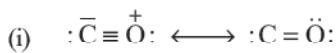
∴ The correct order is =  $\text{N}_2^{2-} < \text{N}_2^- < \text{N}_2$

114. (d) The shape of ozone molecule is

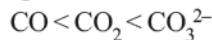


In it we find 2  $\sigma$  and 1  $\pi$  bond, i.e., option (d) is correct.

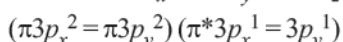
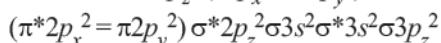
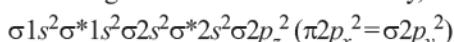
115. (c) All these structures exhibits resonance and can be represented by the following resonating structures.



More is the single bond character. More will be the bond length. Hence, the correct order is :



116. (d) Electronic configuration of the molecule according to molecular orbital theory, is



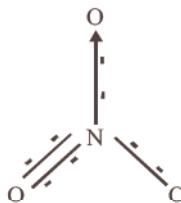
Last two electrons are unpaired. So no. of unpaired electron is 2.

117. (a)  $SiF_4$  has symmetrical tetrahedral shape which is due to  $sp^3$  hybridisation of silicon atom in its excited state while  $SF_4$  has distorted tetrahedral or sea-saw geometry which arises due to  $sp^3d$  hybridisation of sulphur atom and one lone pair of  $e^-s$  in one of the equatorial hybrid orbital.

118. (c) As sigma bond is stronger than the  $\pi$  (pi) bond, so it must be having higher bond energy than  $\pi$  (pi) bond.

119. (d) N:

To form  $NO_3^-$ , nitrogen uses one  $p$ -electron for  $\pi$ -bond formation and two  $p$ -electrons for  $\sigma$ -bond formation.  $2s$  electrons are used for coordinate bond formation. Thus there is no lone pair on nitrogen and four bond pairs are present.



120. (c) Dissociation energy of any molecules depends upon bond order. Bond order in  $N_2$  molecule is 3 while bond order in  $N_2^+$  is 2.5. Further we know that more the Bond order, more is the stability and more is the BDE.

$$NO^+ = \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2$$

$$\pi 2p_y^2 = \pi 2p_z^2$$

$$\text{Bond order of } NO^+ = \frac{1}{2}(N_b - N_a)$$

$$= \frac{1}{2}(10 - 4) = \frac{1}{2} \times 6 = 3$$

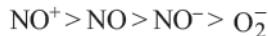
$$\text{Similarly, Bond order of } NO = \frac{1}{2}(10 - 5)$$

$$= \frac{1}{2}(5) = 2.5$$

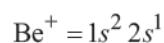
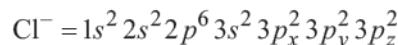
$$\text{Bond order of } NO^- = \frac{1}{2}(10 - 6) = \frac{1}{2}(4) = 2$$

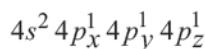
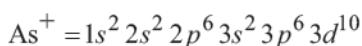
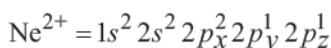
$$\text{Bond order of } O_2^- = \frac{1}{2}(10 - 7) = \frac{1}{2}(3) = 1.5$$

By above calculation, we get  
Decreasing bond order



122. (a) Paramagnetic character is based upon presence of unpaired electron

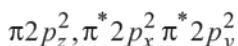
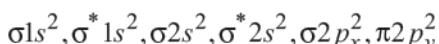




Hence only  $\text{Cl}^-$  do not have unpaired electrons.

123. (d) Total no. of electrons in  $\text{O}_2^{2-} = 16 + 2 = 18$

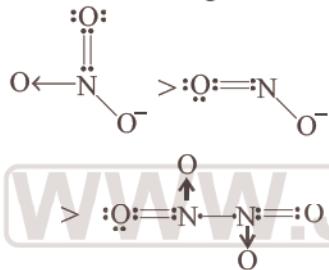
Distribution of electrons in molecular orbital



Anti bonding electron = 8 (4 pairs)

124. (b) We know that in  $\text{O}_2$  bond, the order is 2 and in  $\text{O}_2^-$  bond, the order is 1.5. Therefore, the wrong statements is (b).

125. (c) The N–O bond length decreases in the order



126. (d) In this configuration, there are four completely filled bonding molecular orbitals and one completely filled antibonding molecular orbital. So that  $N_b = 8$  and  $N_a = 2$ .

$$\therefore \text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) = 3.$$

127. (b) The structure of NO:



In NO, the presence of unpaired electron is clear. Therefore, it is paramagnetic.

128. (b) The removal of an electron from a diatomic molecule may increase or decrease the bond order.



Removal of an electron from bonding orbital results in decrease of bond order, hence reduces bond strength while removal of an electron from antibonding orbital results into increase in bond order hence increases the bond strength.

129. (a) Linear combination of two hybridized orbitals leads to the formation of sigma bond.

# 5

# States of Matter



## Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Gas law and ideal gas equation	Graham's law of diffusion									1	A
	Dalton's law of partial pressure	1	A								
van der Waal's equation and liquefaction of gases	van der Waal's equation			1	A	1	A				
	liquefaction of gases					1	A				

LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

### Topic 1: Gas laws and Ideal gas Equation

- A mixture of  $N_2$  and Ar gases in a cylinder contains 7 g of  $N_2$  and 8 g of Ar. If the total pressure of the mixture of the gases in the cylinder is 27 bar, the partial pressure of  $N_2$  is: [Use atomic masses (in g mol<sup>-1</sup>): N = 14, Ar = 40]
 

(a) 12 bar	(b) 15 bar	[2020]
(c) 18 bar	(d) 9 bar	
- The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be [Use R = 0.083 bar L K<sup>-1</sup> mol<sup>-1</sup>]
 

[NEET Odisha 2019]	
(a) 5.37 L	(b) 96.66 L
(c) 55.87 L	(d) 3.10 L
- Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape? [2016]
 

(a) 1/8	(b) 1/4
(c) 3/8	(d) 1/2
- Equal masses of  $H_2$ ,  $O_2$  and methane have been taken in a container of volume V at temperature

27°C in identical conditions. The ratio of the volumes of gases  $H_2$  :  $O_2$  : methane would be :

- |                |                |        |
|----------------|----------------|--------|
| (a) 8 : 16 : 1 | (b) 16 : 8 : 1 | [2014] |
| (c) 16 : 1 : 2 | (d) 8 : 1 : 2  |        |

5. Dipole-induced dipole interactions are present in which of the following pairs : [NEET 2013]

- |                          |                        |
|--------------------------|------------------------|
| (a) $Cl_2$ and $CCl_4$   | (b) HCl and He atoms   |
| (c) $SiF_4$ and He atoms | (d) $H_2O$ and alcohol |

6. 50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar condition. If molecular mass of gas B is 36, the molecular mass of gas A will be : [2012]

- |        |         |
|--------|---------|
| (a) 96 | (b) 128 |
| (c) 32 | (d) 64  |

7. A certain gas takes three times as long to effuse out as helium. Its molecular mass will be :

- |          |          |           |
|----------|----------|-----------|
| (a) 27 u | (b) 36 u | [2012 MJ] |
| (c) 64 u | (d) 9 u  |           |

8. Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49 u. Molecular mass of B will be : [2011]

9. A bubble of air is underwater at temperature  $15^{\circ}\text{C}$  and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is  $25^{\circ}\text{C}$  and the pressure is 1.0 bar, what will happen to the volume of the bubble ? **[2011]**

(a) Volume will become greater by a factor of 1.6.  
 (b) Volume will become greater by a factor of 1.1.  
 (c) Volume will become smaller by a factor of 0.70.  
 (d) Volume will become greater by a factor of 2.5.

10. From a heated mixture of nitrogen, oxygen and carbon, two compounds (out of the many obtained) are isolated. The rates of diffusion of the two isolated compounds are almost identical. The two compounds are **[1999]**

(a)  $\text{N}_2\text{O}$  and  $\text{CO}_2$       (b)  $\text{CO}$  and  $\text{NO}$   
 (c)  $\text{CO}_2$  and  $\text{NO}_2$       (d)  $\text{N}_2\text{O}$  and  $\text{CO}$

11. If 500 mL of gas A at 400 torr and 666.6 mL of B at 600 torr are placed in a 3 litre flask, the pressure of the system will be **[1999]**

(a) 200 torr      (b) 100 torr  
 (c) 550 torr      (d) 366 torr

12. A gaseous mixture contains  $\text{H}_2$  and  $\text{O}_2$  in the molar ratio 8 : 1. The ratio of  $\text{H}_2$  :  $\text{O}_2$  by weight in this mixture would be **[1999]**

(a) 4 : 1      (b) 1 : 8  
 (c) 8 : 1      (d) 1 : 2

13. 500 mL of nitrogen at  $27^{\circ}\text{C}$  is cooled to  $-5^{\circ}\text{C}$  at the same pressure. The new volume becomes **[1995]**

(a) 326.32 mL      (b) 446.66 mL  
 (c) 546.32 mL      (d) 771.56 mL

14. 600 c.c. of a gas at a pressure of 750 mm is compressed to 500 c.c. Taking the temperature to remain constant, the increase in pressure, is **[1995]**

(a) 150 mm      (b) 250 mm  
 (c) 350 mm      (d) 450 mm

15. The correct value of the gas constant 'R' is close to : **[1992]**

(a) 0.082 litre-atmosphere K  
 (b) 0.082 litre-atmosphere  $\text{K}^{-1} \text{mol}^{-1}$   
 (c) 0.082 litre-atmosphere $^{-1}$  K mol $^{-1}$   
 (d) 0.082 litre $^{-1}$  atmosphere $^{-1}$  K mol

16. At constant temperature, for a given mass of an ideal gas **[1991]**

(a) The ratio of pressure and volume always remains constant.

(b) Volume always remains constant.  
 (c) Pressure always remains constant.  
 (d) The product of pressure and volume always remains constant.

17. Pressure remaining the same, the volume of a given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at **[1989]**

(a)  $0^{\circ}\text{C}$   
 (b) its critical temperature  
 (c) absolute zero  
 (d) its Boyle temperature

### Topic 2: Kinetic Theory of Gases and Molecular Speeds

18. By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled ? **[2011]**

(a) 2.0      (b) 2.8  
 (c) 4.0      (d) 1.4

19. If a gas expands at constant temperature, it indicates that : **[2008]**

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

20. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, KE, of CO and  $\text{N}_2$  molecules at the same temperature ? **[2000]**

(a)  $\text{KE}_{\text{CO}} < \text{KE}_{\text{N}_2}$   
 (b)  $\text{KE}_{\text{CO}} > \text{KE}_{\text{N}_2}$   
 (c)  $\text{KE}_{\text{CO}} = \text{KE}_{\text{N}_2}$   
 (d) cannot be predicted unless volumes of the gases are given

21. The temperature of the gas is raised from  $27^{\circ}\text{C}$  to  $927^{\circ}\text{C}$ , the root mean square velocity is **[1994]**

(a)  $\sqrt{927/27}$  time the earlier value  
 (b) same as before  
 (c) halved  
 (d) doubled

22. At STP, 0.50 mol  $\text{H}_2$  gas and 1.0 mol He gas

(a) have equal average kinetic energies **[1993]**  
 (b) have equal molecular speeds  
 (c) occupy equal volumes  
 (d) have equal effusion rates

## **Topic 2: Kinetic Theory of Gases and Molecular Speeds**

23. Internal energy and pressure of a gas per unit volume are related as : **[1993]**
- (a)  $P = \frac{2}{3}E$       (b)  $P = \frac{3}{2}E$   
 (c)  $P = \frac{1}{2}E$       (d)  $P = 2E$
24. The ratio among most probable velocity, mean velocity and root mean square velocity is given by **[1993]**
- (a)  $1:2:3$       (b)  $1:\sqrt{2}.\sqrt{3}$   
 (c)  $\sqrt{2}:\sqrt{3}:\sqrt{8/\pi}$       (d)  $\sqrt{2}:\sqrt{8/\pi}:\sqrt{3}$
25. A closed flask contains water in all its three states solid, liquid and vapour at  $0^\circ\text{C}$ . In this situation, the average kinetic energy of water molecules will be **[1992]**
- (a) the greatest in all the three states  
 (b) the greatest in vapour state  
 (c) the greatest in the liquid state  
 (d) the greatest in the solid state
26. In a closed flask of 5 litres, 1.0 g of  $\text{H}_2$  is heated from 300 to 600 K. Which statement is not correct?
- (a) Pressure of the gas increases **[1991]**  
 (b) The rate of collision increases  
 (c) The number of moles of gas increases  
 (d) The energy of gaseous molecules increases
27. The root mean square speeds at STP for the gases  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{HBr}$  are in the order : **[1991]**
- (a)  $\text{H}_2 < \text{N}_2 < \text{O}_2 < \text{HBr}$  (b)  $\text{HBr} < \text{O}_2 < \text{N}_2 < \text{H}_2$   
 (c)  $\text{H}_2 < \text{N}_2 = \text{O}_2 < \text{HBr}$  (d)  $\text{HBr} < \text{O}_2 < \text{H}_2 < \text{N}_2$ .
28. Root mean square velocity of a gas molecule is proportional to **[1990]**
- (a)  $m^{1/2}$       (b)  $m^0$   
 (c)  $m^{-1/2}$       (d)  $m$
29. Absolute zero is defined as the temperature
- (a) at which all molecular motion ceases  
 (b) at which liquid helium boils **[1990]**  
 (c) at which ether boils  
 (d) all of the above
- Topic 3 : van der Waal's Equation and liquefaction of Gases**
30. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The **correct** option about the gas and its compressibility factor ( $Z$ ) is: **[2019]**
- (a)  $Z > 1$  and attractive forces are dominant  
 (b)  $Z > 1$  and repulsive forces are dominant
31. (c)  $Z < 1$  and attractive forces are dominant  
 (d)  $Z < 1$  and repulsive forces are dominant
32. The correction factor 'a' to the ideal gas equation corresponds to **[2018]**
- (a) Density of the gas molecules  
 (b) Volume of the gas molecules  
 (c) Forces of attraction between the gas molecules  
 (d) Electric field present between the gas molecules
33. Given van der Waals constants for  $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  are respectively 4.17, 0.244, 1.36 and 3.59, which one of the following gases is most easily liquefied? **[2018]**
- (a)  $\text{NH}_3$       (b)  $\text{H}_2$   
 (c)  $\text{CO}_2$       (d)  $\text{O}_2$
34. A gas such as carbon monoxide would be most likely to obey the ideal gas law at : **[2015 RS]**
- (a) high temperatures and low pressures.  
 (b) low temperatures and high pressures.  
 (c) high temperatures and low pressures.  
 (d) low temperatures and low pressures.
35. Maximum deviation from ideal gas is expected from : **[NEET 2013]**
- (a)  $\text{N}_2(\text{g})$       (b)  $\text{CH}_4(\text{g})$   
 (c)  $\text{NH}_3(\text{g})$       (d)  $\text{H}_2(\text{g})$
36. What is the density of  $\text{N}_2$  gas at  $227^\circ\text{C}$  and 5.00 atm pressure? ( $R = 0.0821 \text{ atm K}^{-1} \text{ mol}^{-1}$ ) **[NEET Kar. 2013]**
- (a) 0.29 g/ml      (b) 1.40 g/ml  
 (c) 2.81 g/ml      (d) 3.41 g/ml
37. For real gases, van der Waals equation is written as
- $$\left( p + \frac{an^2}{V^2} \right) (V - nb) = nRT$$
- where 'a' and 'b' are van der Waals constants. Two sets of gases are :
- (I)  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{He}$  (II)  $\text{CH}_4$ ,  $\text{O}_2$  and  $\text{H}_2$
- The gases given in set-I in increasing order of 'b' and gases given in set-II in decreasing order of 'a', are arranged below. Select the correct order from the following : **[2012 MJ]**
- (a) (I)  $\text{He} < \text{H}_2 < \text{CO}_2 < \text{O}_2$  (II)  $\text{CH}_4 > \text{H}_2 > \text{O}_2$   
 (b) (I)  $\text{O}_2 < \text{He} < \text{H}_2 < \text{CO}_2$  (II)  $\text{H}_2 > \text{O}_2 > \text{CH}_4$   
 (c) (I)  $\text{H}_2 < \text{He} < \text{O}_2 < \text{CO}_2$  (II)  $\text{CH}_4 > \text{O}_2 > \text{H}_2$   
 (d) (I)  $\text{H}_2 < \text{O}_2 < \text{He} < \text{CO}_2$  (II)  $\text{O}_2 > \text{CH}_4 > \text{H}_2$
37. A gaseous mixture was prepared by taking equal mole of  $\text{CO}$  and  $\text{N}_2$ . If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen ( $\text{N}_2$ ) in the mixture is :

- |   |   |
|---|---|
| <p>38. The pressure exerted by 6.0 g of methane gas in a <math>0.03 \text{ m}^3</math> vessel at <math>129^\circ\text{C}</math> is (Atomic masses : C = 12.01, H = 1.01 and R = <math>8.314 \text{ JK}^{-1} \text{ mol}^{-1}</math>)</p> <p>(a) 31684 Pa      (b) 215216 Pa [2010]<br/>     (c) 13409 Pa      (d) 41648 Pa</p> <p>39. van der Waal's real gas, act as an ideal gas, at which conditions? [2002]</p> <p>(a) High temperature, low pressure<br/>     (b) Low temperature, high pressure<br/>     (c) High temperature, high pressure<br/>     (d) Low temperature, low pressure</p> <p>40. 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 (<math>n\text{C}_3\text{H}_6/n\text{O}_2</math>)? [1996]</p> <p>(a) <math>\frac{170 \times 42}{570 \times 32} = 0.39</math><br/>     (b) <math>\frac{170}{42} / \left( \frac{170}{42} + \frac{570}{32} \right) \approx 0.19</math><br/>     (c) <math>\frac{170}{740} = 0.23</math><br/>     (d) <math>\frac{170}{570} = 0.30</math></p> <p>41. At which one of the following temperature - pressure conditions the deviation of a gas from ideal behaviour is expected to be minimum? [1996]</p> <p>(a) 350 K and 3 atm.    (b) 550 K and 1 atm.<br/>     (c) 250 K and 4 atm.    (d) 450 K and 2 atm.</p> <p>42. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mole litre<math>^{-1}</math>?<br/> <math>(R = 0.082 \text{ litre atm mol}^{-1} \text{ deg}^{-1})</math> [1993]</p> <p>(a) At STP<br/>     (b) When V = 22.4 litres<br/>     (c) When T = 12 K<br/>     (d) Impossible under any conditions</p> <p>43. When is deviation more in the behaviour of a gas from the ideal gas equation <math>PV = nRT</math>? [1993]</p> <p>(a) At high temperature and low pressure<br/>     (b) At low temperature and high pressure<br/>     (c) At high temperature and high pressure<br/>     (d) At low temperature and low high pressure</p> <p>44. Which is not true in case of an ideal gas? [1992]</p> <p>(a) It cannot be converted into a liquid</p> | <p>(b) 0.8 atm [2011]<br/>     (c) 0.9 atm<br/>     (d) 1 atm</p> <p>45. An ideal gas can't be liquefied because [1992]</p> <p>(a) its critical temperature is always above <math>0^\circ\text{C}</math><br/>     (b) its molecules are relatively smaller in size<br/>     (c) it solidifies before becoming a liquid<br/>     (d) forces operated between its molecules are negligible</p> <p>46. Select one correct statement. In the gas equation, <math>PV = nRT</math> [1992]</p> <p>(a) <math>n</math> is the number of molecules of a gas<br/>     (b) <math>V</math> denotes volume of one mole of the gas<br/>     (c) <math>n</math> moles of the gas have a volume <math>V</math><br/>     (d) <math>P</math> is the pressure of the gas when only one mole of gas is present.</p> <p>47. A gas is said to behave like an ideal gas when the relation <math>PV/T = \text{constant}</math>. When do you expect a real gas to behave like an ideal gas?</p> <p>(a) When the temperature is low [1991]<br/>     (b) When both the temperature and pressure are low<br/>     (c) When both the temperature and pressure are high<br/>     (d) When the temperature is high and pressure is low</p> <p>48. In van der Waal's equation of state for a non-ideal gas, the term that accounts for intermolecular forces is: [1990]</p> <p>(a) <math>(V - b)</math>      (b) <math>(RT)^{-1}</math><br/>     (c) <math>\left( P + \frac{a}{V^2} \right)</math>      (d) <math>RT</math></p> <p>49. If <math>P</math>, <math>V</math>, <math>M</math>, <math>T</math> and <math>R</math> are pressure, Volume, molar mass, temperature and gas constant respectively, then for an ideal gas, the density is given by [1989]</p> <p>(a) <math>\frac{RT}{PM}</math>      (b) <math>\frac{P}{RT}</math><br/>     (c) <math>\frac{M}{V}</math>      (d) <math>\frac{PM}{RT}</math></p> <p>50. Correct gas equation is: [1989]</p> <p>(a) <math>\frac{V_1 T_2}{P_1} = \frac{V_2 T_1}{P_2}</math>      (b) <math>\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}</math><br/>     (c) <math>\frac{P_1 T_2}{V_1} = \frac{P_2 V_2}{T_2}</math>      (d) <math>\frac{V_1 V_2}{T_1 T_2} = P_1 P_2</math></p> |
|---|---|

### Topic 4: Liquid State

51. The surface tension of which of the following liquid is maximum? **[2005]**

(a)  $C_2H_5OH$       (b)  $CH_3OH$   
 (c)  $H_2O$       (d)  $C_6H_6$

52. In a pair of immiscible liquids, a common solute dissolves in both and the equilibrium is reached. Then the concentration of the solute in upper layer is **[1994]**

- (a) In fixed ratio with that in the lower layer  
 (b) Same as the lower layer  
 (c) Lower than the lower layer  
 (d) Higher than the lower layer.

53. A liquid can exist only : **[1994]**
- (a) between triple point and critical temperature  
 (b) at any temperature above the melting point  
 (c) between melting point and critical temperature  
 (d) between boiling and melting temperature.

### ANSWER KEY

<b>1</b>	(b)	<b>7</b>	(b)	<b>13</b>	(b)	<b>19</b>	(c)	<b>25</b>	(b)	<b>31</b>	(c)	<b>37</b>	(a)	<b>43</b>	(b)	<b>49</b>	(d)		
<b>2</b>	(a)	<b>8</b>	(b)	<b>14</b>	(a)	<b>20</b>	(c)	<b>26</b>	(c)	<b>32</b>	(a)	<b>38</b>	(d)	<b>44</b>	(c)	<b>50</b>	(b)		
<b>3</b>	(a)	<b>9</b>	(a)	<b>15</b>	(b)	<b>21</b>	(d)	<b>27</b>	(b)	<b>33</b>	(a)	<b>39</b>	(a)	<b>45</b>	(d)	<b>51</b>	(c)		
<b>4</b>	(c)	<b>10</b>	(a)	<b>16</b>	(d)	<b>22</b>	(a)	<b>28</b>	(c)	<b>34</b>	(c)	<b>40</b>	(d)	<b>46</b>	(c)	<b>52</b>	(a)		
<b>5</b>	(b)	<b>11</b>	(a)	<b>17</b>	(a)	<b>23</b>	(a)	<b>29</b>	(a)	<b>35</b>	(d)	<b>41</b>	(b)	<b>47</b>	(d)	<b>53</b>	(d)		
<b>6</b>	(N)	<b>12</b>	(d)	<b>18</b>	(d)	<b>24</b>	(d)	<b>30</b>	(c)	<b>36</b>	(c)	<b>42</b>	(c)	<b>48</b>	(c)				

## Hints & Solutions

1. (b)  $n_{N_2} = \frac{7}{28} = \frac{1}{4} = 0.25$

$$n_{Ar} = \frac{8}{40} = \frac{1}{5} = 0.20$$

Now, applying Dalton's law of partial pressure,

$$p_{N_2} = \text{mole fraction of } N_2 \cdot P_{\text{Total}}$$

$$\frac{0.25}{0.45} \times 27 = \frac{5}{9} \times 27 = 15 \text{ bar}$$

2. (a) According to ideal gas equation.  
 $PV = nRT$

$$V = \frac{W}{M} \left( \frac{RT}{P} \right)$$

$$V = \frac{1.8}{18} \times \frac{0.083 \times 647}{1} = 5.37 \text{ L}$$

3. (a) Given,  $n_{H_2} = n_{O_2}$  and  $t_{H_2} = t_{O_2}$   
 According to Graham's law of diffusion for two different gases.

$$\frac{r_{H_2}}{r_{O_2}} = \frac{v_1 / t_1}{v_2 / t_2} \Rightarrow \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}}$$

$$\frac{1/2}{1/x} = \sqrt{16} = 4$$

$$\frac{x}{2} = 4$$

$$\therefore x = 8$$

$\therefore$  Fraction of  $O_2 = 1/8$

4. (c) According to Avogadro's law "At same temperature and pressure. Volume  $\propto$  no. of moles"

$$n_{H_2} = \frac{w}{2}; \quad n_{O_2} = \frac{w}{32}; \quad n_{CH_4} = \frac{w}{16}$$

$$\therefore V_{H_2} : V_{O_2} : V_{CH_4} = n_{H_2} : n_{O_2} : n_{CH_4}$$

$$= \frac{w}{2} : \frac{w}{32} : \frac{w}{16} = 16 : 1 : 2$$

5. (b) HCl is polar ( $\mu \neq 0$ ) and He is non-polar ( $\mu = 0$ ), thus gives dipole-induced dipole interaction.



**NOTES**

Induced dipole forces result when an ion or a dipole induces a dipole in an atom or a molecule with no dipole. These are weak forces. These are of two types namely. Ion-induced dipole force and dipole-induced force. Ion-induced dipole force: when the approach of an ion induces a dipole in an atom by disturbing the arrangement of electrons. Dipole induced dipole force: when a polar molecule induces a dipole in an atom or in a non-polar molecule.

$$6. \text{ (N)} \frac{V_A}{t_A} \left/ \frac{V_B}{t_B} \right. = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{t_B}{t_A} \Rightarrow \frac{200}{150} = \sqrt{\frac{36}{M_A}} \Rightarrow \frac{4}{3} = \sqrt{\frac{36}{M_A}}$$

$$\Rightarrow \frac{16}{9} = \frac{36}{M_A} \Rightarrow M_A = \frac{81}{4} = 20.25$$

7. (b) According to Graham's law of diffusion

$$r \propto \sqrt{\frac{1}{d}} \sqrt{\frac{1}{M}} \Rightarrow \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{3r_1}{r_1} = \sqrt{\frac{M_2}{4}} \Rightarrow 9 = \frac{M_2}{4}$$

$$M_2 = 36 \text{ u}$$

$$8. \text{ (b)} \frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{V}{V} = \sqrt{\frac{M_B}{49}} \Rightarrow \frac{1}{2} = \sqrt{\frac{M_B}{49}}$$

$$10$$

$$M_B = \frac{1}{4} \times 49 = 12.25 \text{ u}$$

9. (a) Given

$$P_1 = 1.5 \text{ bar}, T_1 = 273 + 15 = 288 \text{ K}, V_1 = V \\ P_2 = 1.0 \text{ bar}, T_2 = 273 + 25 = 298 \text{ K}, V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{1.5 \times V}{288} = \frac{1 \times V_2}{298}$$

$V_2 = 1.55 V$  i.e., volume of bubble will be almost 1.6 times to initial volume of bubble.

10. (a) Rate of diffusion depends upon molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \Rightarrow r_1 = r_2 \text{ if } M_1 = M_2$$

Hence compounds are  $\text{N}_2\text{O}$  and  $\text{CO}_2$  as both have same molar mass i.e. 22

11. (a) Applying Boyle's law  $P_1 V_1 = P_2 V_2$  for both gases

$$\frac{500}{1000} \times 400 = P \times 3 \Rightarrow P = \frac{200}{3}$$

$$600 \times \frac{666.6}{1000} = P' \times 3 \Rightarrow P' = \frac{400}{3}$$

$$\Rightarrow P_T = P + P' - \frac{200}{3} + \frac{400}{3} - \frac{600}{3} = 200 \text{ torr}$$



**NOTES**

Real life application of Boyle's law: when we fill bike tire with air with pump, the gas molecules inside the tire get compressed and packed closer together. This increases the pressure of the gas and it starts to push against the wall of the tire and the tire becomes tighter.

12. (d)  $\frac{\text{Moles of H}_2}{\text{Moles of O}_2} = \frac{8}{1}$  (Given)

$$\left( \frac{\text{M.W. of O}_2}{\text{M.W. of H}_2} \right) \cdot \left( \frac{\text{weight of H}_2}{\text{weight of O}_2} \right) = \frac{8}{1}$$

$$\frac{\text{weight of H}_2}{\text{weight of O}_2} = \frac{8 \times 2}{32 \times 1} = \frac{1}{2}$$

13. (b) Given initial volume ( $V_1$ ) = 500 mL; Initial temperature ( $T_1$ ) =  $27^\circ\text{C} = 300 \text{ K}$  and final temperature ( $T_2$ ) =  $-5^\circ\text{C} = 268 \text{ K}$ . From Charles's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ or } \frac{500}{300} = \frac{V_2}{268}$$

Where  $V_2$  = New volume of gas

$$V_2 = \frac{500}{300} \times 268 = 446.66 \text{ ml}$$

14. (a) Given initial volume ( $V_1$ ) = 600 c.c.; Initial pressure ( $P_1$ ) = 750 mm and final volume ( $V_2$ ) = 500 c.c. According to Boyle's law,

$$\frac{P_1 V_1}{750 \times 600} = \frac{P_2 V_2}{P_2 \times 500}$$

$$\text{or } P_2 = \frac{750 \times 600}{500} = 900 \text{ mm.}$$

Therefore increase in pressure =  $(900 - 750) = 150 \text{ mm.}$

15. (b)  $R = 0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$ .
16. (d) According to Boyle's law at constant temperature,  $P \propto \frac{1}{V}$  or  $PV = \text{constant}$
17. (a) Charle's Law - The volume of the given mass of a gas increases or decreases by  $\frac{1}{273}$  of its volume at  $0^\circ\text{C}$  for each degree rise or fall of temperature at constant pressure.

$$V_t = V_0 \left(1 + \frac{t}{273}\right) \text{ at constant Pressure}$$

18. (d) Average velocity =  $\sqrt{\frac{8RT}{\pi M}}$   
i.e.,  $v \propto \sqrt{T}$   

$$\therefore \frac{V_2}{V_1} = \sqrt{\frac{2T}{T}} = 1.41$$

19. (c) At any constant temperature the K.E. of gaseous molecules remains same.



The molar kinetic energy of a gas is proportional to its temperature and the proportionality constant is  $\frac{3}{2}$  times the gas constant R.

$$E_m = \frac{3}{2} RT$$

20. (c) Average molar kinetic energy =  $\frac{3}{2} kT$   
As temperature is same hence average kinetic energy of CO and N<sub>2</sub> will be same.

21. (d)  $u \propto \sqrt{T}$  or  $u_1/u_2 = \sqrt{T_1/T_2}$   
 $= \sqrt{\frac{27+273}{927+273}} = \sqrt{\frac{300}{1200}} = \frac{1}{2}$   
 $\therefore u_2 = 2u_1$

22. (a) Average kinetic energy depends only on temperature  $\left(\text{K.E.} = \frac{3}{2} kT\right)$

23. (a)  $PV = \frac{1}{3} mn u^2 = \frac{1}{3} Mu^2$   
 $= \frac{2}{3} \cdot \frac{1}{2} Mu^2 = \frac{2}{3} E \text{ or } P = \frac{2}{3} E \text{ per unit vol.}$

24. (d) Most probable velocity ( $\alpha$ ) =  $\sqrt{\frac{2RT}{M}}$

$$\text{Mean velocity } (\bar{v}) = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Root mean square velocity } (u) = \sqrt{\frac{3RT}{M}}$$

$$\therefore \alpha : \bar{v} : u = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

25. (b) In vapour state, the molecules are free to move with highest average kinetic energy.  
 26. (c) The number of moles of gas do not change.



Volume is constant and the mass of H<sub>2</sub> is fixed so the number of moles of the gas do not change. As temperature increases the pressure also increases and the rate of collision among the gas molecules and their energy also increases.

27. (b)  $PV = \frac{1}{3} m N u^2 = \frac{1}{3} M u^2$   
or  $u = \sqrt{3PV/M}$ .

At STP,  $u \propto \sqrt{\frac{1}{M}}$

i.e. higher will be the molar mass, lower will be the value of  $u_{rms}$ .

Molecular masses of H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and HBr are 2, 28, 32 and 81. Hence the correct order of  $u_{rms}$  will be HBr < O<sub>2</sub> < N<sub>2</sub> < H<sub>2</sub>

28. (c) According to kinetic gas equation

$$PV = \frac{1}{3} m N u^2, u = \text{root mean square velocity}$$

$$\Rightarrow u^2 = \frac{3PV}{mN} \text{ or } u \propto \frac{1}{\sqrt{m}} \text{ i.e. } u \propto m^{-\frac{1}{2}}$$

29. (a) Absolute zero is the temperature at which kinetic energy of gas molecules becomes zero i.e. all molecular motion ceases.

30. (c) Compressibility factor,  $Z = \frac{PV}{nRT}$

Given: At 350 K and 15 bar,  
molar volume < volume of ideal gas

$$\therefore Z < 1$$

Therefore, attractive forces are dominant and the gas can be compressed easily.

31. (c) In real gas equation, van der Waal constant  
(a)  $\propto$  forces of attraction.
32. (a) van der Waal constant 'a', signifies intermolecular forces of attraction.  
Higher is the value of 'a', easier will be the liquefaction of gas.
33. (a) At high temperature and low pressure.
34. (c) Higher the critical temperature more easily will be the gas liquify. Now since most easily liquefiable gas show larger deviation,  $\text{NH}_3$  will show maximum deviation from ideal behaviour.

35. (d) Density =  $\frac{PM}{RT} = \frac{5 \times 28}{0.0821 \times 500} = 3.41 \text{ g/mL}$

36. (c) Set-I :  $\text{O}_2, \text{CO}_2, \text{H}_2, \text{He}$  for 'b' values  
Set-II :  $\text{CH}_4, \text{O}_2, \text{H}_2$ , for 'a' values  
Value of van der Waals constant 'b' increases with increase in molecular volume. Clearly, the increasing order of molecular volume (size of molecule) is:



Value of 'a' increases with increase in intermolecular attraction.  $\text{CH}_4$  is a polar molecule, thus, it will possess highest value of 'a'.  $\text{O}_2$  and  $\text{H}_2$ , both are non-polar molecules. The van der Waals force  $\propto$  molecular mass. Hence, the correct order of value of 'b' is :  $\text{CH}_4 > \text{O}_2 > \text{H}_2$ .

From the given options, (c) is most suitable.

37. (a) Given  $n_{\text{CO}} = n_{\text{N}_2}$

$$P_{\text{CO}} + P_{\text{N}_2} = 1 \text{ atm}$$

Partial pressure of a gas = mole fraction of gas  $\times$  total pressure

$$\begin{aligned} \therefore P_{\text{N}_2} &= \frac{n_{\text{N}_2}}{n_{\text{CO}} + n_{\text{N}_2}} \times 1 = \frac{n_{\text{N}_2}}{2n_{\text{N}_2}} \times 1 \\ &= \frac{1}{2} = 0.5 \text{ atm.} \end{aligned}$$

38. (d)  $P = \frac{nRT}{V} = \frac{w}{m} \frac{RT}{V}$   
 $= \frac{\frac{6}{16.05} \times 8.314 \times 402}{0.03} = 41648 \text{ Pa}$

39. (a) At higher temperature and low pressure real gas acts as an ideal gas.
40. (d) By Ideal gas equation

$$P_1 V = n_1 RT$$

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

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

41. (b) At low pressure and high temperature, real gas nearly behave like ideal gas. Hence, deviation is minimum from ideal behaviour.



At high temperature and low pressure, the correction terms ( $a/n^2$ ) and ( $b/V$ ) become negligible and thus, the deviation from ideal behaviour will be minimum.

42. (c)  $PV = nRT$  or  $P = \frac{n}{V} RT = CRT$ .

$$\text{Hence } 1 = 1 \times 0.082 \times T$$

$$\therefore T = \frac{1}{0.082} = 12K$$

43. (b) At low temperature and high pressure.
44. (c) Molecules of an ideal gas move with different speeds.
45. (d) In an ideal gas, the intermolecular forces of attraction are negligible and hence, it cannot be liquefied.
46. (c) In the equation  $PV = nRT$ ,  $n$  moles of the gas have volume  $V$ .



In van der Waals equation,  $n$  moles of gas occupies volume  $V$  and exert pressure  $P$  at a temperature  $T$ .

47. (d) At low pressure and high temperature correction for 1 mole of a gas is negligible, i.e. the effect of  $a/v^2$  and  $b$  becomes negligible.  
Thus, the gas equation becomes

$$PV = nRT$$

$$PV = RT \text{ or } \frac{PV}{RT} = 1 \text{ [Ideal gas equation]}$$

$\therefore Z = 1$ , and gas shows ideal behaviour.

48. (c) van der Waal's equation for 1 mole :

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

Here,  $\left( P + \frac{a}{V^2} \right)$  represent the intermolecular forces and  $(V - b)$  is the corrected volume.

49. (d)  $PV = nRT = \frac{m}{M} RT$

or  $PM = \frac{m}{V} RT = dRT \Rightarrow d = \frac{PM}{RT}$

50. (b)  $\frac{PV}{T} = \text{constant}$  or  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

51. (c) Due to intermolecular H-bonding the surface tension of  $H_2O$  is more than other given liquids. One  $H_2O$  molecule is joined with 4 another  $H_2O$  molecule through H-bond.

Hydrogen bonding is in order  $H_2O > C_2H_5OH > CH_3OH$ .

52. (a) By definition of Nernst distribution law. When a solute is shaken with two immiscible liquids, having solubility in both, the solute distributes itself between the two liquids in such a way that the ratio of its concentrations in two liquids is constant at a given temperature, provided the molecular state of the solute remains the same in both the liquids.
53. (d) A substance exists as a liquid above its m. pt. and below its b. pt.

# 6

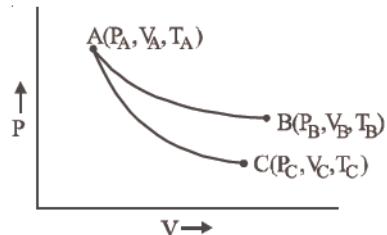
# Thermodynamics

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
First law and basic fundamentals of thermodynamics	first law of thermodynamics	1	A	1	A			1	A		
Laws of thermochemistry	bond dissociation energy					1	D				
Entropy and second law of thermodynamics	second law of thermodynamics	1	A								
	entropy			1	E						
Spontaneity and Gibb's free energy	spontaneity							1	A	1	E
LOD - Level of Difficulty	E - Easy	A - Average		D - Difficult		Qns - No. of Questions					

### Topic 1: First Law and Basic Fundamentals of Thermodynamics

- The correct option for free expansion of an ideal gas under adiabatic condition is **[2020]**
  - $q = 0, \Delta T < 0$  and  $w > 0$
  - $q < 0, \Delta T = 0$  and  $w = 0$
  - $q > 0, \Delta T > 0$  and  $w > 0$
  - $q = 0, \Delta T = 0$  and  $w = 0$
- An ideal gas expands isothermally from  $10^{-3} \text{ m}^3$  to  $10^{-2} \text{ m}^3$  at  $300 \text{ K}$  against a constant pressure of  $10^5 \text{ N m}^{-2}$ . The work done on the gas is **[NEET Odisha 2019]**
  - 900 kJ
  - +270 kJ
  - 900 J
  - +900 kJ
- Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure. **[NEET Odisha 2019]**



AB → Isothermal expansion

AC → Adiabatic expansion

Which of the following options is not correct?

(a)  $T_C > T_A$       (b)  $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$

(c)  $T_A = T_B$       (d)  $W_{\text{isothermal}} > W_{\text{adiabatic}}$

Under isothermal condition, a gas at  $300 \text{ K}$  expands from  $0.1 \text{ L}$  to  $0.25 \text{ L}$  against a constant external pressure of  $2 \text{ bar}$ . The work done by the gas is [Given that  $1 \text{ L bar} = 100 \text{ J}$ ] **[2019]**

(a) -30 J      (b) 5 kJ

(c) 25 J      (d) 30 J

4.



19. Consider the following processes :
- |                         | $\Delta H(\text{kJ/mol})$ |
|-------------------------|---------------------------|
| $1/2 A \rightarrow B$   | +150                      |
| $3B \rightarrow 2C + D$ | −125                      |
| $E + A \rightarrow 2D$  | +350                      |
- For  $B + D \rightarrow E + 2C$ ,  $\Delta H$  will be : [2011M]
- (a) 525 kJ/mol (b) −175 kJ/mol  
 (c) −325 kJ/mol (d) 325 kJ/mol
20. The following two reactions are known : [2010]
- $$\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g}); \quad \Delta H = -26.8 \text{ kJ}$$
- $$\text{FeO}(\text{s}) + \text{CO}(\text{g}) \longrightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g}); \quad \Delta H = -16.5 \text{ kJ}$$
- The value of  $\Delta H$  for the following reaction  $\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \longrightarrow 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$  is;
- (a) +6.2 kJ (b) +10.3 kJ  
 (c) −43.3 kJ (d) −10.3 kJ
21. From the following bond energies: [2009]
- H–H bond energy: 431.37 kJ mol<sup>−1</sup>  
 C=C bond energy: 606.10 kJ mol<sup>−1</sup>  
 C–C bond energy: 336.49 kJ mol<sup>−1</sup>  
 C–H bond energy: 410.50 kJ mol<sup>−1</sup>
- Enthalpy for the reaction,
- $$\begin{array}{ccc} \begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{C} = \text{C} & + \text{H} - \text{H} \end{array} & \longrightarrow & \begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H} - \text{C} & - \text{C} - \text{H} \\ | & | \\ \text{H} & \text{H} \end{array} \end{array}$$
- will be:
- (a) −243.6 kJ mol<sup>−1</sup> (b) −120.0 kJ mol<sup>−1</sup>  
 (c) 553.0 kJ mol<sup>−1</sup> (d) 1523.6 kJ mol<sup>−1</sup>
22. Bond dissociation enthalpy of H<sub>2</sub>, Cl<sub>2</sub> and HCl are 433, 242 and 431 kJ mol<sup>−1</sup> respectively. Enthalpy of formation of HCl is : [2008]
- (a) 93 kJ mol<sup>−1</sup> (b) −245 kJ mol<sup>−1</sup>  
 (c) −93 kJ mol<sup>−1</sup> (d) 245 kJ mol<sup>−1</sup>
23. Consider the following reactions: [2007]
- $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}), \quad \Delta H = -X_1 \text{ kJ mol}^{-1}$
  - $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}), \quad \Delta H = -X_2 \text{ kJ mol}^{-1}$
  - $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}, \quad \Delta H = -X_3 \text{ kJ mol}^{-1}$
  - $\text{C}_2\text{H}_2(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}), \quad \Delta H = +4X_4 \text{ kJ mol}^{-1}$

- Enthalpy of formation of H<sub>2</sub>O(l) is
- (a) + $X_3$  kJ mol<sup>−1</sup> (b) − $X_4$  kJ mol<sup>−1</sup>  
 (c) + $X_1$  kJ mol<sup>−1</sup> (d) − $X_2$  kJ mol<sup>−1</sup>
24. Given that bond energies of H–H and Cl–Cl are 430 kJ mol<sup>−1</sup> and 240 kJ mol<sup>−1</sup> respectively and  $\Delta H_f$  for HCl is −90 kJ mol<sup>−1</sup>, bond enthalpy of HCl is [2007]
- (a) 380 kJ mol<sup>−1</sup> (b) 425 kJ mol<sup>−1</sup>  
 (c) 245 kJ mol<sup>−1</sup> (d) 290 kJ mol<sup>−1</sup>
25. The enthalpy of hydrogenation of cyclohexene is −119.5 kJ mol<sup>−1</sup>. If resonance energy of benzene is −150.4 kJ mol<sup>−1</sup>, its enthalpy of hydrogenation would be [2006]
- (a) −208.1 kJ mol<sup>−1</sup> (b) −269.9 kJ mol<sup>−1</sup>  
 (c) −358.5 kJ mol<sup>−1</sup> (d) −508.9 kJ mol<sup>−1</sup>
26. Assume each reaction is carried out in an open container. For which reaction will  $\Delta H = \Delta E$ ? [2006]
- (a) C(s) + 2H<sub>2</sub>O(g) → 2H<sub>2</sub>(g) + CO<sub>2</sub>(g)  
 (b) PCl<sub>5</sub>(g) → PCl<sub>3</sub>(g) + Cl<sub>2</sub>(g)  
 (c) 2CO(g) + O<sub>2</sub>(g) → 2CO<sub>2</sub>(g)  
 (d) H<sub>2</sub>(g) + Br<sub>2</sub>(g) → 2HBr(g)
27. The absolute enthalpy of neutralisation of the reaction:  
 $\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$  will be: [2005]
- (a) −57.33 kJ mol<sup>−1</sup>  
 (b) Greater than −57.33 kJ mol<sup>−1</sup>  
 (c) Less than −57.33 kJ mol<sup>−1</sup>  
 (d) 57.33 kJ mol<sup>−1</sup>
28. If the bond energies of H–H, Br–Br, and H–Br are 433, 192 and 364 kJ mol<sup>−1</sup> respectively, the  $\Delta H^\circ$  for the reaction [2004]
- $$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$$
- is
- (a) −261 kJ (b) +103 kJ  
 (c) +261 kJ (d) −103 kJ
29. The work done during the expansion of a gas from a volume of 4 dm<sup>3</sup> to 6 dm<sup>3</sup> against a constant external pressure of 3 atm is (1 L atm = 101.32 J) [2004]
- (a) −6 J (b) −608 J  
 (c) +304 J (d) −304 J
30. The molar heat capacity of water at constant pressure is 75 JK<sup>−1</sup> mol<sup>−1</sup>. When 1 kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is [2003]
- (a) 6.6 K (b) 1.2 K  
 (c) 2.4 K (d) 4.8 K

31. The densities of graphite and diamond at 298 K are 2.25 and 3.31 g cm<sup>-3</sup>, respectively. If the standard free energy difference ( $\Delta G^\circ$ ) is equal to 1895 J mol<sup>-1</sup>, the pressure at which graphite will be transformed into diamond at 298 K is [2003]
- (a)  $9.92 \times 10^5$  Pa      (b)  $9.92 \times 10^8$  Pa  
 (c)  $9.92 \times 10^7$  Pa      (d)  $9.92 \times 10^6$  Pa
32. For which one of the following equations is  $\Delta H_{\text{react}}^\circ$  equal to  $\Delta H_f^\circ$  for the product? [2003]
- (a)  $2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$   
 (b)  $\text{N}_2(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$   
 (c)  $\text{CH}_4(\text{g}) + 2\text{Cl(g)} \rightarrow \text{CH}_2\text{Cl}_{2(l)} + 2\text{HCl(g)}$   
 (d)  $\text{Xe(g)} + 2\text{F}_2(\text{g}) \rightarrow \text{XeF}_4(\text{g})$
33. For the reaction  $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O(l)}$  at constant temperature,  $\Delta H - \Delta E$  is [2003]
- (a)  $-RT$       (b)  $+RT$   
 (c)  $-3RT$       (d)  $+3RT$
34. Heat of combustion  $\Delta H^\circ$  for C (s), H<sub>2</sub> (g) and CH<sub>4</sub> (g) are -94, -68 and -213 kcal/mol, then  $\Delta H^\circ$  for C(s) + 2H<sub>2</sub>(g) → CH<sub>4</sub>(g) is [2002]
- (a) -17 kcal      (b) -111 kcal  
 (c) -170 kcal      (d) -85 kcal
35. Enthalpy of  $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH}$  is negative. If enthalpy of combustion of CH<sub>4</sub> and CH<sub>3</sub>OH are x and y respectively, then which relation is correct [2001]
- (a)  $x > y$       (b)  $x < y$   
 (c)  $x = y$       (d)  $x \geq y$
36. What is the enthalpy change for,  $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g})$  if heat of formation of H<sub>2</sub>O<sub>2</sub> (l) and H<sub>2</sub>O (l) are -188 and -286 kJ/mol respectively? [2001]
- (a) -196 kJ/mol      (b) +948 kJ/mol  
 (c) +196 kJ/mol      (d) -948 kJ/mol
37. The values of heat of formation of SO<sub>2</sub> and SO<sub>3</sub> are -298.2 kJ and -98.2 kJ. The heat of formation of the reaction [2000]
- $\text{SO}_2 + (1/2)\text{O}_2 \rightarrow \text{SO}_3$  will be
- (a) -200 kJ      (b) -356.2 kJ  
 (c) +200 kJ      (d) -396.2 kJ
38. For a cyclic process, which of the following is not true? [1999]
- (a)  $\Delta H = 0$       (b)  $\Delta E = 0$   
 (c)  $\Delta G = 0$       (d) Total  $W = 0$
39. For a reaction in which all reactants and products are liquids, which one of the following equations is most applicable? [1999]
- (a)  $\Delta H < \Delta E$       (b)  $\Delta H = \Delta S$   
 (c)  $\Delta H = \Delta E$       (d)  $\Delta H = \Delta G$
40. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The  $\Delta E$  for this process is ( $R = 2 \text{ cal. mol}^{-1} \text{ K}^{-1}$ ) [1998]
- (a) 163.7 cal      (b) zero  
 (c) 1381.1 cal      (d) 9 lit. atm
41. Given that  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 : \Delta H^\circ = -x \text{ kJ}$   
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 : \Delta H^\circ = -y \text{ kJ}$   
 the enthalpy of formation of carbon monoxide will be [1997]
- (a)  $\frac{2x-y}{2}$       (b)  $\frac{y-2x}{2}$   
 (c)  $2x-y$       (d)  $y-2x$
42. Hydrogen has an ionisation energy of 1311 kJ mol<sup>-1</sup> and for chlorine it is 1256 kJ mol<sup>-1</sup>. Hydrogen forms H<sup>+</sup> (aq) ions but chlorine does not form Cl<sup>+</sup> (aq) ions because [1996]
- (a) H<sup>+</sup> has lower hydration enthalpy  
 (b) Cl<sup>+</sup> has lower hydration enthalpy  
 (c) Cl has high electron affinity  
 (d) Cl has high electronegativity
43. If enthalpies of formation of C<sub>2</sub>H<sub>4</sub>(g), CO<sub>2</sub>(g) and H<sub>2</sub>O(l) at 25°C and 1 atm pressure are 52, -394 and -286 kJ/mol respectively, the enthalpy of combustion of C<sub>2</sub>H<sub>4</sub> is equal to [1995]
- (a) -141.2 kJ/mol      (b) -1412 kJ/mol  
 (c) +14.2 kJ/mol      (d) +1412 kJ/mol
44. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true? [1994]
- (a)  $x = y$       (b)  $x = \frac{1}{2}y$   
 (c)  $x = 2y$       (d) None of these
45. For the reaction [1994]
- $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3, \Delta H = ?$
- (a)  $\Delta E + 2RT$       (b)  $\Delta E - 2RT$   
 (c)  $\Delta H = RT$       (d)  $\Delta E - RT$ .
46. During isothermal expansion of an ideal gas, its [1991, 94]
- (a) internal energy increases  
 (b) enthalpy decreases  
 (c) enthalpy remains unaffected  
 (d) enthalpy reduces to zero.

47. If  $\Delta H$  is the change in enthalpy and  $\Delta E$ , the change in internal energy accompanying a gaseous reaction, then [1990]
- $\Delta H$  is always greater than  $\Delta E$ ,
  - $\Delta H < \Delta E$  only if the number of moles of the products is greater than the number of moles of the reactants
  - $\Delta H$  is always less than  $\Delta E$
  - $\Delta H < \Delta E$  only if the number of moles of products is less than the number of moles of the reactants.

### Topic 3: Entropy and Second Law of Thermodynamics

48. For the reaction,  $2\text{Cl(g)} \rightarrow \text{Cl}_2\text{(g)}$ , the correct option is : [2020]
- $\Delta_rH > 0$  and  $\Delta_rS < 0$
  - $\Delta_rH < 0$  and  $\Delta_rS > 0$
  - $\Delta_rH < 0$  and  $\Delta_rS < 0$
  - $\Delta_rH > 0$  and  $\Delta_rS > 0$
49. In which case change in entropy is negative ? [2019]
- Evaporation of water
  - Expansion of a gas at constant temperature
  - Sublimation of solid to gas
  - $2\text{H(g)} \rightarrow \text{H}_2\text{(g)}$
50. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is : [2012]
- 10.52 cal / (mol K)
  - 21.04 cal / (mol K)
  - 5.260 cal / (mol K)
  - 0.526 cal / (mol K)
51. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol<sup>-1</sup> at 27°C, the entropy change for the process would be : [2011]
- 10 J mol<sup>-1</sup> K<sup>-1</sup>
  - 1.0 J mol<sup>-1</sup> K<sup>-1</sup>
  - 0.1 J mol<sup>-1</sup> K<sup>-1</sup>
  - 100 J mol<sup>-1</sup> K<sup>-1</sup>
52. Standard entropies of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and 50 JK<sup>-1</sup>mol<sup>-1</sup> respectively. For the reaction
- $$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3, \Delta H = -30 \text{ kJ}$$
- to be at equilibrium, the temperature should be: [2010]
- 750 K
  - 1000 K
  - 1250 K
  - 500 K
53. For the gas phase reaction, [2008]
- $$\text{PCl}_5\text{(g)} \rightleftharpoons \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$$
- which of the following conditions are correct ?
- $\Delta H = 0$  and  $\Delta S < 0$
  - $\Delta H > 0$  and  $\Delta S > 0$
  - $\Delta H < 0$  and  $\Delta S < 0$
  - $\Delta H > 0$  and  $\Delta S < 0$

54. What is the entropy change (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) when one mole of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol<sup>-1</sup> at 0°C) [2003]
- 21.98
  - 20.13
  - 2.013
  - 2.198
55. 2 mole of an ideal gas at 27°C temperature is expanded reversibly from 2 lit to 20 lit. Find the entropy change ( $R = 2 \text{ cal/mol K}$ ) [2002]
- 92.1
  - 0
  - 4
  - 9.2
56. Unit of entropy is [2002]
- $\text{JK}^{-1} \text{mol}^{-1}$
  - $\text{J mol}^{-1}$
  - $\text{J}^{-1} \text{K}^{-1} \text{mol}^{-1}$
  - $\text{JK mol}^{-1}$
57. The entropy change in the fusion of one mole of a solid melting at 27°C (Latent heat of fusion, 2930 J mol<sup>-1</sup>) is : [2000]
- 9.77  $\text{JK}^{-1} \text{mol}^{-1}$
  - 10.73  $\text{JK}^{-1} \text{mol}^{-1}$
  - 2930  $\text{JK}^{-1} \text{mol}^{-1}$
  - 108.5  $\text{JK}^{-1} \text{mol}^{-1}$
58. Identify the correct statement regarding entropy: [1998]
- At absolute zero of temperature, entropy of a perfectly crystalline substance is taken to be zero
  - At absolute zero of temperature, the entropy of a perfectly crystalline substance is +ve
  - At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero
  - At 0°C, the entropy of a perfectly crystalline substance is taken to be zero
59. According to the third law of thermodynamics which one of the following quantities for a perfectly crystalline solid is zero at absolute zero? [1996]
- Free energy
  - Entropy
  - Enthalpy
  - Internal energy
60. Given the following entropy values (in  $\text{JK}^{-1} \text{mol}^{-1}$ ) at 298 K and 1 atm :  $\text{H}_2\text{(g)}$  : 130.6,  $\text{Cl}_2\text{(g)}$  : 223.0,  $\text{HCl(g)}$  : 186.7. The entropy change (in  $\text{J K}^{-1} \text{mol}^{-1}$ ) for the reaction
- $$\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$$
- is [1996]
- +540.3
  - +727.0
  - 166.9
  - +19.8
61. A chemical reaction will be spontaneous if it is accompanied by a decrease of [1994]
- entropy of the system
  - enthalpy of the system
  - internal energy of the system
  - free energy of the system

**Topic 4: Spontaneity and Gibb's Free Energy**

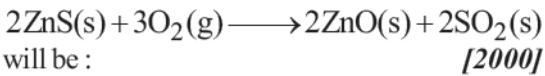
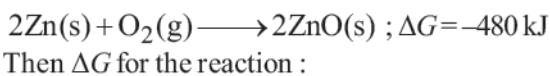
62. For a given reaction,  $\Delta H = 35.5 \text{ kJ mol}^{-1}$  and  $\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$ . The reaction is spontaneous at: (Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature) [2017]  
 (a)  $T > 425 \text{ K}$       (b) All temperatures  
 (c)  $T > 298 \text{ K}$       (d)  $T < 425 \text{ K}$
63. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is [2016]  
 (a)  $\Delta H > 0$  and  $\Delta S > 0$     (b)  $\Delta H > 0$  and  $\Delta S < 0$   
 (c)  $\Delta H < 0$  and  $\Delta S > 0$     (d)  $\Delta H < 0$  and  $\Delta S < 0$
64. For the reaction: [2014]  
 $X_2O_4(l) \rightarrow 2XO_2(g)$   
 $\Delta U = 2.1 \text{ k cal}$ ,  $\Delta S = 20 \text{ cal K}^{-1}$  at  $300 \text{ K}$   
 Hence  $\Delta G$  is:-  
 (a)  $2.7 \text{ k cal}$       (b)  $-2.7 \text{ k cal}$   
 (c)  $9.3 \text{ k cal}$       (d)  $-9.3 \text{ k cal}$
65. In which of the following reactions, standard entropy change ( $\Delta S^\circ$ ) is positive and standard Gibb's energy change ( $\Delta G^\circ$ ) decreases sharply with increasing temperature? [2012]  
 (a)  $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g)$   
 (b)  $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$   
 (c)  $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$   
 (d)  $\frac{1}{2}C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$
66. For vaporization of water at 1 atmospheric pressure, the values of  $\Delta H$  and  $\Delta S$  are  $40.63 \text{ kJ mol}^{-1}$  and  $108.8 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. The temperature when Gibbs energy change ( $\Delta G$ ) for this transformation will be zero, is: [2010]  
 (a)  $293.4 \text{ K}$       (b)  $273.4 \text{ K}$   
 (c)  $393.4 \text{ K}$       (d)  $373.4 \text{ K}$ .
67. Match List-I (Equations) with List-II (Type of processes) and select the correct option. [2010]
- | <b>List I</b>                       | <b>List II</b>                    |
|-------------------------------------|-----------------------------------|
| <b>Equations</b>                    | <b>Type of processes</b>          |
| (1) $K_p > Q$                       | (i) Non-spontaneous               |
| (2) $\Delta G^\circ < RT \ln Q$     | (ii) Equilibrium                  |
| (3) $K_p = Q$                       | (iii) Spontaneous and endothermic |
| (4) $T > \frac{\Delta H}{\Delta S}$ | (iv) Spontaneous                  |

**Options:**

- |           |      |       |       |
|-----------|------|-------|-------|
| (1)       | (2)  | (3)   | (4)   |
| (a) (ii)  | (i)  | (iv)  | (iii) |
| (b) (i)   | (ii) | (iii) | (iv)  |
| (c) (iii) | (iv) | (ii)  | (i)   |
| (d) (iv)  | (i)  | (ii)  | (iii) |

68. The values of  $\Delta H$  and  $\Delta S$  for the reaction,  $C(\text{graphite}) + CO_2(g) \rightarrow 2CO(g)$  are  $170 \text{ kJ}$  and  $170 \text{ JK}^{-1}$ , respectively. This reaction will be spontaneous at [2009]  
 (a)  $910 \text{ K}$       (b)  $1110 \text{ K}$   
 (c)  $510 \text{ K}$       (d)  $710 \text{ K}$
69. The enthalpy and entropy change for the reaction  $Br_2(l) + Cl_2(g) \rightarrow 2 BrCl(g)$  are  $30 \text{ kJ mol}^{-1}$  and  $105 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively. The temperature at which the reaction will be in equilibrium is [2006]  
 (a)  $273 \text{ K}$       (b)  $450 \text{ K}$   
 (c)  $300 \text{ K}$       (d)  $285.7 \text{ K}$
70. Identify the correct statement for change of Gibbs energy for a system ( $\Delta G_{\text{system}}$ ) at constant temperature and pressure: [2006]  
 (a) If  $\Delta G_{\text{system}} = 0$ , the system has attained equilibrium  
 (b) If  $\Delta G_{\text{system}} = 0$ , the system is still moving in a particular direction  
 (c) If  $\Delta G_{\text{system}} < 0$ , the process is not spontaneous  
 (d) If  $\Delta G_{\text{system}} > 0$ , the process is spontaneous
71. A reaction occurs spontaneously if [2005]  
 (a)  $T\Delta S < \Delta H$  and both  $\Delta H$  and  $\Delta S$  are + ve  
 (b)  $T\Delta S > \Delta H$  and  $\Delta H$  is + ve and  $\Delta S$  is - ve  
 (c)  $T\Delta S > \Delta H$  and both  $\Delta H$  and  $\Delta S$  are + ve  
 (d)  $T\Delta S = \Delta H$  and both  $\Delta H$  and  $\Delta S$  are + ve
72. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction? [2005]  
 (a) Exothermic and increasing disorder  
 (b) Exothermic and decreasing disorder  
 (c) Endothermic and increasing disorder  
 (d) Endothermic and decreasing disorder
73. Standard enthalpy and standard entropy changes for the oxidation of ammonia at  $298 \text{ K}$  are  $-382.64 \text{ kJ mol}^{-1}$  and  $-145.6 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively. Standard Gibb's energy change for the same reaction at  $298 \text{ K}$  is [2004]  
 (a)  $-22.1 \text{ kJ mol}^{-1}$       (b)  $-339.3 \text{ kJ mol}^{-1}$   
 (c)  $-439.3 \text{ kJ mol}^{-1}$       (d)  $-523.2 \text{ kJ mol}^{-1}$

74. Considering entropy ( $S$ ) as a thermodynamic parameter, the criterion for the spontaneity of any process is [2004]  
 (a)  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$   
 (b)  $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$   
 (c)  $\Delta S_{\text{system}} > 0$  only  
 (d)  $\Delta S_{\text{surroundings}} > 0$  only
75. The factor of  $\Delta G$  values is important in metallurgy. The  $\Delta G$  values for the following reactions at  $800^{\circ}\text{C}$  are given as :  
 $\text{S}_2(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) ; \Delta G = -544 \text{ kJ}$   
 $2\text{Zn}(\text{s}) + \text{S}_2(\text{s}) \rightarrow 2\text{ZnS}(\text{s}) ; \Delta G = -293 \text{ kJ}$



- (a)  $-357 \text{ kJ}$  (b)  $-731 \text{ kJ}$   
 (c)  $-773 \text{ kJ}$  (d)  $-229 \text{ kJ}$

76. Consider the following reaction occurring in an automobile [1994]



the sign of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  would be

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

### ANSWER KEY

1	(d)	9	(a)	17	(d)	25	(a)	33	(c)	41	(b)	49	(d)	57	(a)	65	(a)	73	(b)
2	(c)	10	(d)	18	(c)	26	(d)	34	(a)	42	(b)	50	(c)	58	(a)	66	(d)	74	(a)
3	(a)	11	(a)	19	(b)	27	(c)	35	(a)	43	(b)	51	(d)	59	(b)	67	(d)	75	(b)
4	(a)	12	(b)	20	(a)	28	(d)	36	(a)	44	(b)	52	(a)	60	(d)	68	(b)	76	(b)
5	(b)	13	(a)	21	(b)	29	(b)	37	(c)	45	(b)	53	(b)	61	(d)	69	(d)		
6	(a)	14	(d)	22	(c)	30	(c)	38	(d)	46	(c)	54	(a)	62	(a)	70	(a)		
7	(c)	15	(c)	23	(d)	31	(N)	39	(c)	47	(d)	55	(d)	63	(c)	71	(c)		
8	(c)	16	(a)	24	(b)	32	(d)	40	(b)	48	(c)	56	(a)	64	(b)	72	(a)		

## Hints & Solutions

1. (d) Free expansion of ideal gas  
 $P_{\text{ex}} = 0$   
 $\therefore w = -P_{\text{ex}} \Delta V = 0$   
 $\therefore$  Adiabatic process  $\Rightarrow q = 0$   
 $\Delta E = q + w$  (first law of thermodynamics)  
 $\therefore \Delta E = 0$   
 $\Delta E = nC_v dT \Rightarrow \Delta E = 0$   
 $\text{So, } q = 0, \Delta T = 0, w = 0.$
2. (c)  $W = -P_{\text{ext}}(V_f - V_i) = -10^5(10^{-2} - 10^{-3}) = -900 \text{ J}$
3. (a) Since graph A to C represents adiabatic reversible expansion, so work is done on the expense of internal energy, therefore, there is decrease in internal energy. So the temperature decreases.  
 i.e.,  $T_C < T_A$
4. (a)  $W = -P_{\text{ext}}(V_2 - V_1)$  (Irreversible isothermal expansion)  
 $= -2(0.25 - 0.1)$   
 $= -2(0.15) = -0.3 \text{ L Bar}$   
 $= -0.3 \times 100 \text{ J} = -30 \text{ J}$
5. (b) The system is in isolated state.  
 $\therefore$  For an adiabatic process,  $q = 0$   
 $\Delta U = q + w$   
 $\therefore \Delta U = w$   
 $= -p\Delta V$   
 $= -2.5 \text{ atm} \times (4.5 - 2.5) \text{ L}$   
 $= -2.5 \times 2 \text{ L-atm}$   
 $= -5 \times 101.3 \text{ J}$   
 $= -506.5 \text{ J} \approx -505 \text{ J}$
6. (a)  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2 + 393.5 \text{ kJ/mol}$   
 $12\text{g} \quad 44\text{g}$   
 $44\text{g CO}_2$  is formed from  $12\text{g}$  of carbon  
 $35.2\text{g}$  is formed from  $\frac{12 \times 35.2}{44} \text{ g}$  of C  
 $= 9.6 \text{ g of C} = 9.6/12 = 0.8 \text{ mole}$   
 $1 \text{ mole release heat } 393.5 \text{ kJ}$   
 $0.8 \text{ mole release heat} = 393.5 \times 0.8$   
 $= 314.8 \text{ kJ} \approx 315 \text{ kJ}$
7. (c)  $\text{CH}_4 + 2\text{O}_2 \xrightarrow{x} \text{CO}_2 + 2\text{H}_2\text{O}$   
 $\text{C}_3\text{H}_8 + 5\text{O}_2 \xrightarrow{(5-x)} 3\text{CO}_2 + 4\text{H}_2\text{O}$

$$2x + 5(5-x) = 16$$

$$\Rightarrow x = 3L$$

∴ Heat released

$$= \frac{3}{22.4} \times 890 + \frac{2}{22.4} \times 2220 = 317$$

8. (c) For adiabatic process  $\Delta Q = 0$   
In free expansion, external pressure is zero.  
Thus, work done  $W = 0$  and  $\Delta E = W = 0$ . If  
 $\Delta E = 0$ , then  $\Delta T = 0$ .
9. (a) Ideal gas during spontaneous expansion into vacuum does not do any external work.
10. (d) We know that  $q$  (heat) and work ( $w$ ) are not state functions but  $(q + w)$  is a state function.  
 $H - TS$  (i.e.,  $G$ ) is also a state function.
11. (a) Internal energy is dependent upon temperature and according to first law of thermodynamics total energy of an isolated system remains same, i.e., in a system of constant mass, energy can neither be created nor destroyed by any physical or chemical change but can be transformed from one form to another

$$\Delta E = q + w$$



For closed insulated container,  $q = 0$ , so,  
 $\Delta E = +W$ , as work is done on the system

12. (b) As volume is constant hence, work done in this process is zero hence, heat supplied is equal to change in internal energy.
13. (a)  $\Delta E = \Delta Q - W$   
For adiabatic expansion,  $\Delta Q = 0$   
 $\Rightarrow \Delta E = -W$

The negative sign shows decrease in Internal energy, which is equal to the work done by the system on the surroundings.

14. (d) Let B.E of  $X_2$ ,  $Y_2$  and  $XY$  are  $x \text{ kJ mol}^{-1}$ ,  $0.5 x \text{ kJ mol}^{-1}$  and  $x \text{ kJ mol}^{-1}$  respectively



$$\Delta H = -200 = \Sigma (\text{B.E})_{\text{Reactants}} - \Sigma (\text{B.E})_{\text{Product}}$$

$$= \left[ \frac{1}{2} \times (x) + \frac{1}{2} \times (0.5x) \right] - [1 \times (x)]$$

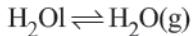
$$\text{On solving, } x = 800 \text{ kJ mol}^{-1}$$

15. (c) Applying Hess's law, equation (i) can be obtained by adding equations (ii) and (iii).  
 $\therefore x = y + z$

16. (a)  $\Delta_{\text{vap}}H^\circ = 40.66 \text{ kJ mol}^{-1}$   
 $T = 100 + 273 = 373 \text{ K}, \Delta E = ?$

$$\Delta H = \Delta E + \Delta n_g RT \Rightarrow \Delta E = \Delta H - \Delta n_g RT$$

$\Delta n_g$  = number of gaseous moles of products  
– number of gaseous moles of reactants



$$\Delta n_g = 1 - 0 = 1$$

$$\Delta E = \Delta H - RT$$

$$\Delta E = (40.66 \times 10^3) - (8.314 \times 373)$$

$$= 37559 \text{ J/mol or } 37.56 \text{ kJ/mol}$$

17. (d) For a monoatomic gas

$$C_v = \frac{3}{2}R$$

$$\therefore C_p = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$



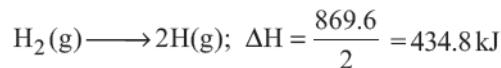
For monoatomic gases  $\frac{C_p}{C_v} = 1.67$

diatomic gases  $\frac{C_p}{C_v} = 1.40$

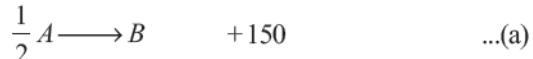
triatomic gases  $\frac{C_p}{C_v} = 1.29$  if degree of freedom = 7

$\frac{C_p}{C_v} = 1.33$  if degree of freedom = 6

18. (c) Given



19. (b) Given  $\Delta H$



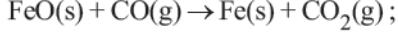
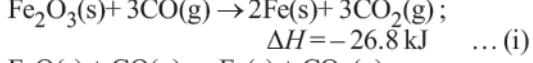
To calculate  $\Delta H$  operate

$$2 \times \text{eq. (a)} + \text{eq. (b)} - \text{eq. (c)}$$

$$\Delta H = 300 - 125 - 350 = -175$$

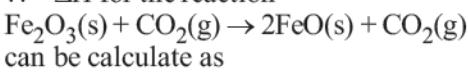
20. (a)  $\text{Fe}_2\text{O}_3\text{(s)} + \text{CO(g)} \rightarrow 2\text{FeO(s)} + \text{CO}_2\text{(g)}$

Given



$$\Delta H = -16.5 \text{ kJ} \quad \dots(ii)$$

$\therefore \Delta H$  for the reaction



$$\text{eqn (i)} - 2 \times \text{eqn (ii)}$$

$$\therefore \Delta H = -26.8 + 33.0 = +6.2 \text{ kJ}$$

21. (b) Enthalpy of reaction

$$= \Sigma \text{B.E.}_{(\text{Reactant})} - \Sigma \text{B.E.}_{(\text{Product})}$$

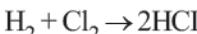
$$= \left[ \text{B.E.}_{(\text{C=C})} + 4 \text{B.E.}_{(\text{C-H})} + \text{B.E.}_{(\text{H-H})} \right]$$

$$- \left[ \text{B.E.}_{(\text{C-C})} + 6 \text{B.E.}_{(\text{C-H})} \right]$$

$$= [606.1 + (4 \times 410.5) + 431.37] - [336.49 + (6 \times 410.5)]$$

$$= -120.0 \text{ kJ mol}^{-1}$$

22. (c) The reaction for formation of HCl can be written as



Substituting the given values, we get enthalpy of formation of

$$\Delta H_f(\text{HCl}) = [(\text{B.E.})_{\text{H-H}} + (\text{B.E.})_{\text{Cl-Cl}}] - [2 \times \text{B.E.}_{(\text{H-Cl})}]$$

$$= 434 + 242 - 2 \times (431) = -186 \text{ kJ}$$

$\therefore$  Enthalpy of formation for

$$1 \text{ mol HCl} = \frac{-186}{2} \text{ kJ} = -93 \text{ kJ}$$

23. (d) This reaction shows the formation of  $\text{H}_2\text{O}$ , and the  $X_2$  represents the enthalpy of formation of  $\text{H}_2\text{O}$ .

**NOTES**

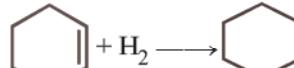
The enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent atoms.

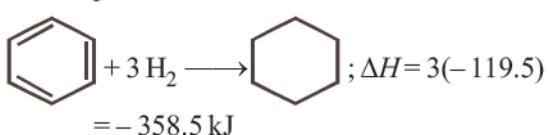
24. (b)  $\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \longrightarrow \text{HCl}$

$$\Delta H_{\text{HCl}} = \sum \text{B.E. of reactant} - \sum \text{B.E. of products}$$

$$-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$$

$$\therefore \text{B.E. of HCl} = 215 + 120 + 90 = 425 \text{ kJ mol}^{-1}$$

25. (a) 



The resonance energy provides extra stability to the benzene molecule so it has to overcome for hydrogenation to take place. So  $\Delta H = -358.5 - (-150.4) = -208.1 \text{ kJ}$



Resonance reduces the energy of molecule and thus, increases the stability. Hence, the magnitude of enthalpy of hydrogenation will be less than the expected value for benzene.

26. (d) We know that

$$\Delta H = \Delta E + P\Delta V$$

In the reaction,  $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$  this is no change in volume or  $\Delta V = 0$   
 $\text{So, } \Delta H = \Delta E$  for this reaction



If the container is closed then pressure is not constant and  $\Delta H = \Delta E + V \Delta P$

27. (c) As MgO is a oxide of weak base hence some energy is lost to break MgO (s). Hence enthalpy is less than  $-57.33 \text{ kJ mol}^{-1}$ .

28. (d)  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr(g)}$

$$\Delta H^\circ = (\text{B.E.})_{\text{reactant}} - (\text{B.E.})_{\text{product}}$$

$$= (433 + 192) - (2 \times 364)$$

$$= 625 - 728 = -103 \text{ kJ}$$

29. (b)  $W = -P\Delta V$

$$= -3(6 - 4) = -6 \text{ litre atmosphere}$$

$$= -6 \times 101.32 = -608 \text{ J}$$

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

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

$$Q = nC_p \Delta T$$

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

31. (N) Change in volume from 1 mole of graphite to 1 mole of diamond

$$\Delta V = \frac{12}{3.31} - \frac{12}{2.25} = -1.71 \text{ cm}^3$$

$$= -1.71 \times 10^{-6} \text{ m}^3$$

Gibb's free energy is the measure of useful work done at constant temperature and pressure.

$$\Delta G = -p\Delta V$$

$$\Rightarrow p = \frac{-\Delta G}{\Delta V} = \frac{1895 \text{ J}}{1.71 \times 10^{-6} \text{ m}^3} = 1.1 \times 10^9 \text{ Pa}$$

32. (d)  $\text{N}_2(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{N}_2\text{O}_3(\text{g})$

- The state of  $\text{N}_2\text{O}_3$  is liquid in NTP conditions. Thus, this reaction is not equal to  $\Delta H_f^\circ$  for the product.
- (d)  $\text{Xe(g)} + 2\text{F}_2(\text{g}) \longrightarrow \text{XeF}_4(\text{g})$   
 For this reaction  $\Delta H_r^\circ$  is equal to  $\Delta H_f^\circ$  of  $\text{XeF}_4(\text{g})$ .
33. (c)  $\Delta H = \Delta E + \Delta nRT$   
 $\Delta n = 3 - (1 + 5)$   
 $= 3 - 6 = -3$   
 $\Delta H - \Delta E = (-3RT)$
34. (a)  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
 $\Delta H = -94 \text{ kcal/mole} \dots (\text{i})$   
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g})$   
 $\Delta H = -68 \text{ kcal/mole} \dots (\text{ii})$   
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O},$   
 $\Delta H = -213 \text{ k cal/mole} \dots (\text{iii})$   
 $\text{C(s)} + 2\text{H}_2 \rightarrow \text{CH}_4(\text{g}), \Delta H = ? \dots (\text{iv})$   
 Eqn. (iv) can be obtained by  
 eq. (i) + eq. (ii)  $\times 2$  - eq. (iii)  
 $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
 $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$   
 $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g})$   
 $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$   
 So,  $\Delta H_{\text{CH}_4} = -94 + 2(-68) - (-213)$   
 $= -94 - 136 + 213 = -17 \text{ k cal/mole}$
35. (a) The enthalpy of combustion is always negative.  
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}; \Delta H_1 = -x \text{ kJ}$   
 $\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}; \Delta H_2 = -y \text{ kJ}$   
 $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_2\text{OH}; + \Delta H = \Delta H_1 - \Delta H_2$   
 It is given that  $\Delta H$  is negative.  
 Thus,  $-x - (-y) = -ve$   
 $y - x = -ve$   
 Hence,  $x > y$ .
36. (a)  $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \Delta H = ?$   
 $\Delta H = [2 \times \Delta H_f \text{ of } \text{H}_2\text{O(l)} + (\Delta H_f \text{ of } \text{O}_2) - (2 \times \Delta H_f \text{ of } \text{H}_2\text{O}_2\text{(l)})]$   
 $= [(2 \times (-286)) + (0) - (2 \times (-188))] = [-572 + 376] = -196 \text{ kJ/mole}$
37. (c)  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$   
 $\Delta H = \Delta H_f^\circ(\text{SO}_3) - \Delta H_f^\circ(\text{SO}_2)$   
 $= -98.2 + 298.2 = 200 \text{ kJ/Mole}$
38. (d) For a cyclic process  
 $\Delta E = 0, \Delta H = 0 \& \Delta G = 0$ . As all depend upon final state and initial state,  $W$  doesn't depend on path followed.
39. (c) As all reactant and product are liquid  
 $\Delta n(g) = 0$   
 $\Delta H = \Delta E - \Delta nRT$   
 $\Delta H = \Delta E \quad (\because \Delta n = 0)$
40. (b) For an isothermal process  $\Delta E = 0$
41. (b) Given  $\text{C} + \text{O}_2 = \text{CO}_2, \Delta H^\circ = -x \text{ kJ} \dots (\text{a})$   
 $2\text{CO}_2 = 2\text{CO} + \text{O}_2 \quad \Delta H^\circ = +y \text{ kJ} \dots (\text{b})$   
 or  $\text{CO}_2 = \text{CO} + \frac{1}{2}\text{O}_2, \Delta H^\circ = +y/2 \text{ kJ} \dots (\text{c})$   
 From eq. no. (a) and (c)  
 $\text{C} + \frac{1}{2}\text{O}_2 = \text{CO}, \Delta H^\circ = y/2 - x = \frac{y - 2x}{2} \text{ kJ}$
42. (b) Hydration energy of  $\text{Cl}^+$  is very less than  $\text{H}^+$ , hence it doesn't form  $\text{Cl}^+(\text{aq})$  ion.
43. (b) Enthalpy of formation of  $\text{C}_2\text{H}_4, \text{CO}_2$  and  $\text{H}_2\text{O}$  are 52, -394 and -286 kJ/mol respectively. (Given)  
 The reaction is  
 $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$ .  
 change in enthalpy,  
 $(\Delta H) = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$   
 $= 2 \times (-394) + 2 \times (-286) - (52 + 0)$   
 $= -1412 \text{ kJ/mol.}$
44. (b) 1 M  $\text{H}_2\text{SO}_4 = 2 \text{ g eq. of HCl}$   
 Hence  $y = 2x$  or  $x = \frac{1}{2}y$ .
45. (b)  $\Delta n_g = 2 - 4 = -2, \Delta H = \Delta E - 2RT$ .
46. (c) During isothermal expansion of ideal gas,  $\Delta T = 0$ . Now  $H = E + PV$   
 $\therefore \Delta H = \Delta E + \Delta(PV)$   
 $\therefore \Delta H = \Delta E + \Delta(nRT);$   
 Thus, if  $\Delta T = 0$ ,  $\Delta H = \Delta E$   
*i.e.*, remain unaffected.
47. (d) As  $\Delta H = \Delta E + \Delta n_g RT$   
 if  $n_p < n_r$ ;  $\Delta n_g = n_p - n_r = -ve$ .  
 Hence  $\Delta H < \Delta E$ .
48. (c) We know that,  $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$  is endothermic reaction because it required energy to break bond.

So reverse reaction,  $2\text{Cl(g)} \longrightarrow \text{Cl}_2(\text{g})$  will be exothermic,  $\Delta_r H < 0$ .

Also, two gaseous atom combine together to form 1 gaseous molecule.

49. (d) In  $2\text{H(g)} \rightarrow \text{H}_2(\text{g})$ , no. of moles decreases, therefore entropy decreases.

$$50. (\text{c}) \Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273}$$

$$= 5.260 \text{ cal/mol-K}$$

$$51. (\text{d}) \text{ Given } \Delta H = 30 \text{ kJ mol}^{-1} T = 273 + 27 = 300 \text{ K}$$

$$\Delta S_T = \frac{\Delta H_T}{T} = \frac{3 \times 10^4}{300} \text{ J mol}^{-1}$$

$$= 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

52. (a)  $\Delta S$  for the reaction  $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$

$$\Delta S = 50 - (30 + 60) = -40 \text{ J}$$

For equilibrium  $\Delta G = 0 = \Delta H - T \Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-40} = 750 \text{ K}$$

53. (b) For the reaction



The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, i.e.,  $\Delta H > 0$ .

Further

$$\Delta n = (1+1) - 1 = +1$$

Hence more number of molecules are present in products which shows more randomness i.e.  $\Delta S > 0$  ( $\Delta S$  is positive)

$$54. (\text{a}) \Delta S = \frac{\Delta H}{T}$$

$$\Delta S(\text{per mole}) = \frac{\Delta H \text{ per mole}}{T} = \frac{6000}{273}$$

$$= 21.98 \text{ JK}^{-1} \text{ mol}^{-1}$$

55. (d) For isothermal reversible expansion

$$w = q = nRT \times 2.303 \log \frac{V_2}{V_1}$$

$$= 2RT \times 2.303 \log \frac{20}{2}$$

$$= 2 \times 2 \times T \times 2.303 \times 1 = 9.2 T$$

$$\text{Entropy change, } \Delta S = \frac{q}{T} = \frac{9.2T}{T} = 9.2 \text{ cal.}$$

$$56. (\text{a}) \Delta S = \frac{q}{T}$$

$q \longrightarrow$  required heat per mole

$T \longrightarrow$  constant absolute temperature

Unit of entropy is  $\text{JK}^{-1} \text{ mol}^{-1}$

$$57. (\text{a}) \Delta S = \frac{\text{Latent heat of fusion}}{\text{Melting point}} = \frac{\Delta H_y}{T}$$

$$= \frac{2930}{300} \text{ JK}^{-1} \text{ mol}^{-1} = 9.77 \text{ JK}^{-1} \text{ mol}^{-1}$$

58. (a) We know from the third law of thermodynamics, the entropy of a perfectly crystalline substance at absolute zero temperature is taken to be zero.

59. (b) Entropy is zero for perfectly crystalline solid at absolute zero.



Entropy states the randomness or disorderness of the system. At absolute zero, the movement of molecules of the system or randomness of the system is zero, hence entropy is also zero.

60. (d) Entropy change

$$\Delta S = \Delta S_{\text{product}} - \Delta S_{\text{reactant}}$$

$$= 2(186.7) - (223 + 130.6)$$

$$= 373.4 - 353.6$$

$$= 19.8 \text{ JK}^{-1} \text{ mol}^{-1}$$

61. (d)  $\Delta G$  is negative for a spontaneous process.

62. (a) Given  $\Delta H = 35.5 \text{ kJ mol}^{-1}$

$$\Delta S = 83.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\therefore \Delta G = \Delta H - T \Delta S$$

For a reaction to be spontaneous,  $\Delta G = -ve$  i.e.,  $\Delta H < T \Delta S$

$$\therefore T > \frac{\Delta H}{\Delta S} = \frac{35.5 \times 10^3 \text{ J mol}^{-1}}{83.6 \text{ JK}^{-1}}$$

So, the given reaction will be spontaneous at  $T > 425 \text{ K}$

63. (c)  $\Delta G = \Delta H - T \cdot \Delta S$

For a spontaneous reaction  $\Delta G = -ve$  (always) which is possible only if

$$\Delta H < 0 \text{ and } \Delta S > 0$$

$\therefore$  spontaneous at all temperatures.

64. (b) Given  $\Delta U = 2.1 \text{ k cal}$ ,  $\Delta S = 20 \text{ cal. K}^{-1}$

$$T = 300 \text{ K}$$

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

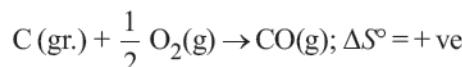
Putting the values given in the equation

$$\Delta H = 2.1 + 2 \times \frac{2}{1000} \times 300 \\ = 2.1 + 1.2 = 3.3 \text{ k cal.}$$

Now,  $\Delta G = \Delta H - T\Delta S$

$$= 3.3 - 300 \times \frac{20}{1000} = -2.7 \text{ k cal}$$

65. (a) Since, in the first reaction more ( $\Delta n > 0$ ) gaseous products are forming from solid carbon hence, entropy will increase i.e.  $\Delta S = +ve$ .



Since,  $\Delta G^\circ = \Delta H^\circ - T\Delta S$  hence the value of  $\Delta G$  decrease on increasing temperature.

66. (d)  $H_2O(l) \xrightleftharpoons[\Delta S]{\Delta H} H_2O(g)$

$$\Delta H = 40630 \text{ J mol}^{-1}$$

$$\Delta S = 108.8 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S$$

When  $\Delta G = 0$ ,  $\Delta H - T\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{40630 \text{ J mol}^{-1}}{108.8 \text{ JK}^{-1} \text{ mol}^{-1}} = 373.4 \text{ K.}$$

67. (d) When  $K_p > Q$ :

Rate of forward reaction > Rate of backward reaction

∴ Reaction is spontaneous

- (2) When  $\Delta G^\circ < RT \ln Q$

$$RT \ln K < RT \ln Q$$

$$\Rightarrow K < Q$$

The reaction will move in backward direction or the reaction is non-spontaneous.

- (3) When  $T\Delta S > \Delta H$ ,

$$\Delta G = \Delta H - T\Delta S$$

When  $\Delta H > 0$  and  $T\Delta S > \Delta H$  then  $\Delta G < 0$ .

Hence, reaction is endothermic and spontaneous.

68. (b)  $\Delta G = \Delta H - T\Delta S$

At equilibrium,  $\Delta G = 0$

$$\Rightarrow 0 = (170 \times 10^3 \text{ J}) - T(170 \text{ JK}^{-1})$$

$$\Rightarrow T = 1000 \text{ K}$$

For spontaneity,  $\Delta G$  is – ve, which is possible only if  $T > 1000 \text{ K}$ .

69. (d) We know that

$$\Delta G = \Delta H - T\Delta S$$

When the reaction is in equilibrium,  $\Delta G = 0$

$$0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{2 \times 30 \times 1000}{2 \times 105} = 285.7 \text{ K}$$

70. (a) If  $\Delta G_{\text{system}} = 0$  the system has attained equilibrium.

If  $\Delta G < 0$ , the process is spontaneous

If  $\Delta G > 0$ , the process does not occur in the forward direction. It may occur in the backward direction.

71. (c) For a spontaneous reaction  $\Delta G < 0$ , which is possible if  $\Delta S = +ve$ ,  $\Delta H = +ve$  and  $T\Delta S > \Delta H$  [As  $\Delta G = \Delta H - T\Delta S$ ]

72. (a) Measure of disorder of a system is nothing but Entropy. For a spontaneous reaction,  $\Delta G < 0$ . As per Gibbs Helmholtz equation,  $\Delta G = \Delta H - T\Delta S$

Thus  $\Delta G$  is – ve only

When  $\Delta H = -ve$  (exothermic) and  $\Delta S = +ve$  (increasing disorder)

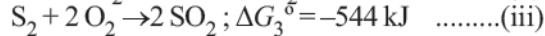
73. (b)  $\Delta G = \Delta H - T\Delta S$

$$= -382.64 - (-298 \times 145.6 \times 10^{-3})$$

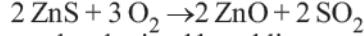
$$= -339.3 \text{ kJ mol}^{-1}$$

74. (a) For a spontaneous process,  $\Delta S_{\text{total}}$  is always positive

75. (b) For the reaction



$\Delta G^\circ$  for the reaction



can be obtained by adding eqn. (i), (ii) and (iii)

$$\Rightarrow \Delta G^\circ = 293 - 480 - 544 = -731 \text{ kJ}$$

76. (b) This is combustion reaction, which is always exothermic hence

$$\Delta H = -ve$$

As the no. of gaseous molecules are increasing hence entropy increases

now  $\Delta G = \Delta H - T\Delta S$

For a spontaneous reaction

$$\Delta G = -ve$$

Which is possible in this case as  $\Delta H = -ve$  and  $\Delta S = +ve$ .

# 7

# Equilibrium

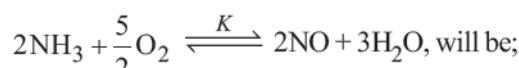
 Trend Analysis with Important Topics & Sub-Topics 

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Law of mass action,equilibrium constant and its application	equilibrium constant/ $K_p$ and $K_c$							2	A		
Relation between K,Q and G and factors affecting equilibrium	relation between K and G	1	A			1	D				
	Le-chatelier principle					1	A				
	Clausius and Clapeyron's equation									1	E
Theories of acid and bases,ionic product of water and pH scale	Bronsted acid and bases			1	E						
	pH scale			1	E	1	D				
Common ion effect,salt hydrolysis, buffer solution and solubility product	solubility	1	D							1	A
	$K_{sp}$			1	A	1	A	1	A		
LOD - Level of Difficulty		E - Easy		A - Average		D - Difficult		Qns - No. of Questions			

### Topic 1: Law of Mass Action, Equilibrium Constant ( $K_c$ and $K_p$ ) and its Application

1. The equilibrium constant of the following are :
- $$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \quad K_1 \quad [2017]$$
- $$\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \quad K_2$$
- $$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad K_3$$

The equilibrium constant ( $K$ ) of the reaction :

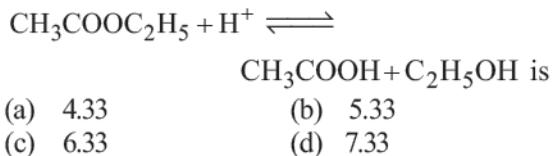


- (a)  $K_2K_3^3 / K_1$       (b)  $K_2K_3 / K_1$   
 (c)  $K_2^3K_3 / K_1$       (d)  $K_1K_3^3 / K_2$



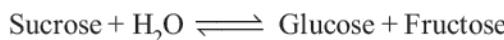


21. The rate constant for forward and backward reaction of hydrolysis of ester are  $1.1 \times 10^{-2}$  and  $1.5 \times 10^{-3}$  per minute respectively. Equilibrium constant for the reaction [1995]



### Topic 2: Relation between K, Q and G and Factors Effecting Equilibrium

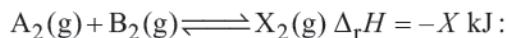
22. Hydrolysis of sucrose is given by the following reaction. [2020]



If the equilibrium constant ( $K_C$ ) is  $2 \times 10^{13}$  at 300 K, the value of  $\Delta_r G^\ominus$  at the same temperature will be :

- (a)  $8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$
- (b)  $8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(3 \times 10^{13})$
- (c)  $-8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(4 \times 10^{13})$
- (d)  $-8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$

23. Which one of the following conditions will favour maximum formation of the product in the reaction, [2018]



- (a) Low temperature and high pressure
- (b) Low temperature and low pressure
- (c) High temperature and low pressure
- (d) High temperature and high pressure

24. Consider the following liquid - vapour equilibrium. [2016]



Which of the following relations is correct ?

- (a)  $\frac{d\ln G}{dT^2} = \frac{\Delta H_v}{RT^2}$
- (b)  $\frac{d\ln P}{dT} = \frac{\Delta H_v}{RT}$
- (c)  $\frac{d\ln P}{dT^2} = \frac{-\Delta H_v}{T^2}$
- (d)  $\frac{d\ln P}{dT} = \frac{-\Delta H_v}{RT^2}$

25. Which of the following statements is correct for a reversible process in a state of equilibrium ? [2015]

- (a)  $\Delta G = 2.30 RT \log K$
- (b)  $\Delta G^\ominus = -2.30 RT \log K$
- (c)  $\Delta G^\ominus = 2.30 RT \log K$
- (d)  $\Delta G = -2.30 RT \log K$

26. For the reversible reaction, [2014]



The equilibrium shifts in forward direction

- (a) By increasing the concentration of  $\text{NH}_3(\text{g})$
- (b) By decreasing the pressure
- (c) By decreasing concentration of  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$
- (d) By increasing pressure and decreasing temperature.

27. For a given exothermic reaction,  $K_p$  and  $K'_p$  are the equilibrium constants at temperatures  $T_1$  and  $T_2$ , respectively. Assuming that heat of reaction is constant in temperature range between  $T_1$  and  $T_2$ , it is readily observed that: [2014]

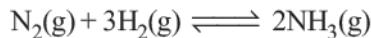
- (a)  $K_p > K'_p$
- (b)  $K_p < K'_p$
- (c)  $K_p = K'_p$
- (d)  $K_p = \frac{1}{K'_p}$

28. The dissociation constants for acetic acid and HCN at 25°C are  $1.5 \times 10^{-5}$  and  $4.5 \times 10^{-10}$  respectively. The equilibrium constant for the equilibrium



- (a)  $3.0 \times 10^{-5}$
- (b)  $3.0 \times 10^{-4}$
- (c)  $3.0 \times 10^4$
- (d)  $3.0 \times 10^5$

29. The reaction quotient ( $Q$ ) for the reaction



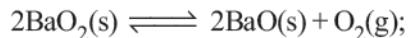
is given by  $Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ . The reaction will

proceed from right to left if [2003]

- (a)  $Q=0$
- (b)  $Q=K_c$
- (c)  $Q < K_c$
- (d)  $Q > K_c$

where  $K_c$  is the equilibrium constant

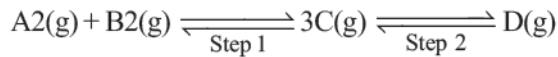
30. For the reaction



$\Delta H = +\text{ve}$ . In equilibrium condition, pressure of  $\text{O}_2$  is dependent on

- (a) mass of  $\text{BaO}_2$
- (b) mass of  $\text{BaO}$
- (c) temperature of equilibrium
- (d) mass of  $\text{BaO}_2$  and  $\text{BaO}$  both

31. In a two-step exothermic reaction



Steps 1 and 2 are favoured respectively by

[1997]

- (a) high pressure, high temperature and low pressure, low temperature  
 (b) high pressure, low temperature and low pressure, high temperature  
 (c) low pressure, high temperature and high pressure, high temperature  
 (d) low pressure, low temperature and high pressure, low temperature
32. The equilibrium constant for the reaction  $A_2 \rightleftharpoons 2A$  at 500 K and 700 K are  $1 \times 10^{-10}$  and  $1 \times 10^{-5}$  respectively. The given reaction is [1996]  
 (a) exothermic      (b) slow  
 (c) endothermic      (d) fast
33. Standard Gibb's free energy change for isomerization reaction [1995]  
 $\text{cis-2-pentene} \rightleftharpoons \text{trans-2-pentene}$   
 is  $-3.67 \text{ kJ/mol}$  at 400 K. If more trans-2-pentene is added to the reaction vessel, then  
 (a) more cis-2-pentene is formed  
 (b) equilibrium remains unaffected  
 (c) additional trans-2-pentene is formed  
 (d) equilibrium is shifted in forward direction
34. According to Le-chatelier's principle, adding heat to a solid  $\rightleftharpoons$  liquid equilibrium will cause the  
 (a) temperature to increase [1993]  
 (b) temperature to decrease  
 (c) amount of liquid to decrease  
 (d) amount of solid to decrease.
35. Which one of the following information can be obtained on the basis of Le Chatelier principle? [1992]  
 (a) Dissociation constant of a weak acid  
 (b) Entropy change in a reaction  
 (c) Equilibrium constant of a chemical reaction  
 (d) Shift in equilibrium position on changing value of a constraint.
- Topic 3: Theories of Acids and Bases, Ionic Product of Water and pH Scale**
36. The pH of 0.01 M NaOH (aq) solution will be [NEET Odisha 2019]  
 (a) 9      (b) 7.01  
 (c) 2      (d) 12
37. Which of the following cannot act both as Bronsted acid and as Bronsted base? [NEET Odisha 2019]  
 (a)  $\text{HSO}_4^-$       (b)  $\text{HCO}_3^-$   
 (c)  $\text{NH}_3$       (d) HCl
38. Conjugate base for Brönsted acids  $\text{H}_2\text{O}$  and HF are : [2019]  
 (a)  $\text{OH}^-$  and  $\text{H}_2\text{F}^+$ , respectively  
 (b)  $\text{H}_3\text{O}^+$  and  $\text{F}^-$ , respectively  
 (c)  $\text{OH}^-$  and  $\text{F}^-$ , respectively  
 (d)  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{F}^+$ , respectively
39. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations : [2018]  
 a.  $60 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 40 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$   
 b.  $55 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 45 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$   
 c.  $75 \text{ mL } \frac{\text{M}}{5} \text{ HCl} + 25 \text{ mL } \frac{\text{M}}{5} \text{ NaOH}$   
 d.  $100 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 100 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$   
 pH of which one of them will be equal to 1?  
 (a) b      (b) a  
 (c) c      (d) d
40. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed? [2015 RS]  
 (a) 12.65      (b) 2.0  
 (c) 7.0      (d) 1.04
41. Which of the following salts will give highest pH in water? [2014]  
 (a) KCl      (b) NaCl  
 (c)  $\text{Na}_2\text{CO}_3$       (d)  $\text{CuSO}_4$
42. Which of these is least likely to act as Lewis base? [NEET 2013]  
 (a)  $\text{F}^-$       (b)  $\text{BF}_3$   
 (c)  $\text{PF}_3$       (d) CO
43. Which of the following is least likely to behave as Lewis base? [2011]  
 (a)  $\text{H}_2\text{O}$       (b)  $\text{NH}_3$   
 (c)  $\text{BF}_3$       (d)  $\text{OH}^-$
44. Which one of the following molecular hydrides acts as a Lewis acid? [2010]  
 (a)  $\text{NH}_3$       (b)  $\text{H}_2\text{O}$   
 (c)  $\text{B}_2\text{H}_6$       (d)  $\text{CH}_4$
45. Which of the following molecules acts as a Lewis acid? [2009]  
 (a)  $(\text{CH}_3)_2\text{O}$       (b)  $(\text{CH}_3)_3\text{P}$   
 (c)  $(\text{CH}_3)_3\text{N}$       (d)  $(\text{CH}_3)_3\text{B}$

46. The ionization constant of ammonium hydroxide is  $1.77 \times 10^{-5}$  at 298 K. Hydrolysis constant of ammonium chloride is: [2009]  
 (a)  $6.50 \times 10^{-12}$       (b)  $5.65 \times 10^{-13}$   
 (c)  $5.65 \times 10^{-12}$       (d)  $5.65 \times 10^{-10}$
47. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H<sup>+</sup> ion concentration in the mixture? [2008]  
 (a)  $1.11 \times 10^{-4}$  M      (b)  $3.7 \times 10^{-4}$  M  
 (c)  $3.7 \times 10^{-3}$  M      (d)  $1.11 \times 10^{-3}$  M
48. Calculate the pOH of a solution at 25°C that contains  $1 \times 10^{-10}$  M of hydronium ions, i.e. H<sub>3</sub>O<sup>+</sup>. [2007]  
 (a) 4.000      (b) 9.0000  
 (c) 1.000      (d) 7.000
49. The hydrogen ion concentration of a  $10^{-8}$  M HCl aqueous solution at 298 K ( $K_w = 10^{-14}$ ) is [2006]  
 (a)  $11 \times 10^{-8}$  M      (b)  $9.525 \times 10^{-8}$  M  
 (c)  $1.0 \times 10^{-8}$  M      (d)  $1.0 \times 10^{-6}$  M
50. What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH<sub>1</sub>), sodium sulphide (pH<sub>2</sub>), sodium selenide (pH<sub>3</sub>) and sodium telluride (pH<sub>4</sub>)? [2005]  
 (a) pH<sub>1</sub> > pH<sub>2</sub> > pH<sub>3</sub> > pH<sub>4</sub>  
 (b) pH<sub>1</sub> > pH<sub>2</sub> ≈ pH<sub>3</sub> > pH<sub>4</sub>  
 (c) pH<sub>1</sub> < pH<sub>2</sub> < pH<sub>3</sub> < pH<sub>4</sub>  
 (d) pH<sub>1</sub> < pH<sub>2</sub> < pH<sub>3</sub> ≈ pH<sub>4</sub>
51. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In<sup>-</sup>) forms of the indicator by the expression [2004]  
 (a)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pK}_{\text{In}} - \text{pH}$   
 (b)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pK}_{\text{In}} - \text{pH}$   
 (c)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - \text{pK}_{\text{In}}$   
 (d)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} - \text{pK}_{\text{In}}$
52. Which one of the following orders of acid strength is correct? [2003]  
 (a) RCOOH > HC ≡ CH > HOH > ROH  
 (b) RCOOH > ROH > HOH > HC ≡ CH  
 (c) RCOOH > HOH > ROH > HC ≡ CH  
 (d) RCOOH > HOH > HC ≡ CH > ROH
53. Which one of the following compounds is *not a* protonic acid? [2003]  
 (a) SO<sub>2</sub>(OH)<sub>2</sub>      (b) B(OH)<sub>3</sub>  
 (c) PO(OH)<sub>3</sub>      (d) SO(OH)<sub>2</sub>
54. In HS<sup>-</sup>, I<sup>-</sup>, RNH<sub>2</sub> and NH<sub>3</sub>, order of proton accepting tendency will be [2001]  
 (a) I<sup>-</sup> > NH<sub>3</sub> > RNH<sub>2</sub> > HS<sup>-</sup>  
 (b) HS<sup>-</sup> > RNH<sub>2</sub> > NH<sub>3</sub> > I<sup>-</sup>  
 (c) RNH<sub>2</sub> > NH<sub>3</sub> > HS<sup>-</sup> > I<sup>-</sup>  
 (d) NH<sub>3</sub> > RNH<sub>2</sub> > HS<sup>-</sup> > I<sup>-</sup>
55. A base when dissolved in water yields a solution with a hydroxyl ion concentration of 0.05 mol litre<sup>-1</sup>. The solution is [2000]  
 (a) basic      (b) acidic  
 (c) neutral      (d) either 'b' or 'c'
56. Conjugate acid of NH<sub>2</sub><sup>-</sup> is: [2000]  
 (a) NH<sub>4</sub><sup>+</sup>      (b) NH<sub>3</sub>  
 (c) NH<sub>2</sub>      (d) NH
57. Which of the following statements about pH and H<sup>+</sup> ion concentration is incorrect? [2000]  
 (a) Addition of one drop of concentrated HCl in NH<sub>4</sub>OH solution decreases pH of the solution.  
 (b) A solution of the mixture of one equivalent of each of CH<sub>3</sub>COOH and NaOH has a pH of 7  
 (c) pH of pure neutral water is not zero  
 (d) A cold and concentrated H<sub>2</sub>SO<sub>4</sub> has lower H<sup>+</sup> ion concentration than a dilute solution of H<sub>2</sub>SO<sub>4</sub>
58. Among boron trifluoride, stannic chloride and stannous chloride, Lewis acid is represented by [1999]  
 (a) only stannic chloride  
 (b) boron trifluoride and stannic chloride  
 (c) boron trifluoride and stannous chloride  
 (d) only boron trifluoride
59. What is the H<sup>+</sup> ion concentration of a solution prepared by dissolving 4 g of NaOH (Atomic weight of Na = 23 amu) in 1000 mL? [1999]  
 (a)  $10^{-10}$  M      (b)  $10^{-4}$  M  
 (c)  $10^{-1}$  M      (d)  $10^{-13}$  M
60. The pH value of a 10 M solution of HCl is [1995]  
 (a) less than 0      (b) equal to 0  
 (c) equal to 1      (d) equal to 2

## Topic 4: Ionisation of Weak Acids and Bases and Relation between $K_a$ and $K_b$



## Topic 5: Common Ion Effect, Salt Hydrolysis, Buffer Solutions and Solubility Product

67. Find out the solubility of  $\text{Ni(OH)}_2$  in 0.1 M NaOH. Given that the ionic product of  $\text{Ni(OH)}_2$  is  $2 \times 10^{-15}$  [2020]  
 (a)  $2 \times 10^{-8} \text{ M}$       (b)  $1 \times 10^{-13} \text{ M}$   
 (c)  $1 \times 10^8 \text{ M}$       (d)  $2 \times 10^{-13} \text{ M}$

68. The molar solubility of  $\text{CaF}_2$  ( $K_{sp} = 5.3 \times 10^{-11}$ ) in 0.1 M solution of NaF will be  
**[NEET Odisha 2019]**  
(a)  $5.3 \times 10^{-10} \text{ mol L}^{-1}$   
(b)  $5.3 \times 10^{-11} \text{ mol L}^{-1}$   
(c)  $5.3 \times 10^{-8} \text{ mol L}^{-1}$   
(d)  $5.3 \times 10^{-9} \text{ mol L}^{-1}$

69. pH of a saturated solution of  $\text{Ca}(\text{OH})_2$  is 9. The solubility product ( $K_{sp}$ ) of  $\text{Ca}(\text{OH})_2$  is: **[2019]**  
(a)  $0.5 \times 10^{-15}$       (b)  $0.25 \times 10^{-10}$   
(c)  $0.125 \times 10^{-15}$       (d)  $0.5 \times 10^{-10}$

70. The solubility of  $\text{BaSO}_4$  in water is  $2.42 \times 10^{-3} \text{ g L}^{-1}$  at 298 K. The value of its solubility product ( $K_{sp}$ ) will be  
(Given molar mass of  $\text{BaSO}_4 = 233 \text{ g mol}^{-1}$ )  
(a)  $1.08 \times 10^{-10} \text{ mol}^2 \text{L}^{-2}$       **[2018]**  
(b)  $1.08 \times 10^{-12} \text{ mol}^2 \text{L}^{-2}$   
(c)  $1.08 \times 10^{-8} \text{ mol}^2 \text{L}^{-2}$   
(d)  $1.08 \times 10^{-14} \text{ mol}^2 \text{L}^{-2}$

71. Concentration of the  $\text{Ag}^+$  ions in a saturated solution of  $\text{Ag}_2\text{C}_2\text{O}_4$  is  $2.2 \times 10^{-4} \text{ mol L}^{-1}$ . Solubility product of  $\text{Ag}_2\text{C}_2\text{O}_4$  is: **[2017]**  
(a)  $2.66 \times 10^{-12}$       (b)  $4.5 \times 10^{-11}$   
(c)  $5.3 \times 10^{-12}$       (d)  $2.42 \times 10^{-8}$

72.  $MY$  and  $NY_3$ , two nearly insoluble salts, have the same  $K_{sp}$  values of  $6.2 \times 10^{-13}$  at room temperature. Which statement would be true in regard to  $MY$  and  $NY_3$ ? **[2016]**  
(a) The molar solubilities of  $MY$  and  $NY_3$  in water are identical.  
(b) The molar solubility of  $MY$  in water is less than that of  $NY_3$ .  
(c) The salts  $MY$  and  $NY_3$  are more soluble in 0.5 M  $KY$  than in pure water.  
(d) The addition of the salt of  $KY$  to solution of  $MY$  and  $NY_3$  will have no effect on their solubilities.

73. Consider the nitration of benzene using mixed conc of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . If a large amount of  $\text{KHSO}_4$  is added to the mixture, the rate of nitration will be **[2016]**  
(a) faster      (b) slower  
(c) unchanged      (d) doubled

74. The  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$ ,  $\text{AgCl}$ ,  $\text{AgBr}$  and  $\text{AgI}$  are respectively,  $1.1 \times 10^{-12}$ ,  $1.8 \times 10^{-10}$ ,  $5.0 \times 10^{-13}$ ,  $8.3 \times 10^{-17}$ . Which one of the following salts will precipitate last if  $\text{AgNO}_3$  solution is added to the solution containing equal moles of  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$  and  $\text{Na}_2\text{CrO}_4$ ? [2015]
- (a)  $\text{AgCl}$       (b)  $\text{AgBr}$   
 (c)  $\text{Ag}_2\text{CrO}_4$       (d)  $\text{AgI}$
75. Which one of the following pairs of solution is not an acidic buffer? [2015 RS]
- (a)  $\text{HClO}_4$  and  $\text{NaClO}_4$   
 (b)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$   
 (c)  $\text{H}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$   
 (d)  $\text{H}_3\text{PO}_4$  and  $\text{Na}_3\text{PO}_4$
76. Using the Gibbs energy change,  $\Delta G^\circ = +63.3\text{ kJ}$ , for the following reaction, [2014]
- $$\text{Ag}_2\text{CO}_3 \rightleftharpoons 2\text{Ag}^+ (\text{aq}) + \text{CO}_3^{2-} (\text{aq})$$
- the  $K_{sp}$  of  $\text{Ag}_2\text{CO}_3(\text{s})$  in water at  $25^\circ\text{C}$  is:-  
 $(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$
- (a)  $3.2 \times 10^{-26}$       (b)  $8.0 \times 10^{-12}$   
 (c)  $2.9 \times 10^{-3}$       (d)  $7.9 \times 10^{-2}$
77. Identify the correct order of solubility in aqueous medium: [NEET 2013]
- (a)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$       (b)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$   
 (c)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$       (d)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$
78. The values of  $K_{sp}$  of  $\text{CaCO}_3$  and  $\text{Ca}_2\text{O}_4$  are  $4.7 \times 10^{-9}$  and  $1.3 \times 10^{-9}$  respectively at  $25^\circ\text{C}$ . If the mixture of these two is washed with water, what is the concentration of  $\text{Ca}^{2+}$  ions in water? [NEET Kar. 2013]
- (a)  $7.746 \times 10^{-5} \text{ M}$       (b)  $5.831 \times 10^{-5} \text{ M}$   
 (c)  $6.856 \times 10^{-5} \text{ M}$       (d)  $3.606 \times 10^{-5} \text{ M}$
79. The dissociation constant of a weak acid is  $1 \times 10^{-4}$ . In order to prepare a buffer solution with a pH = 5 the  $[\text{Salt}]/[\text{Acid}]$  ratio should be [NEET Kar. 2013]
- (a) 1 : 10      (b) 4 : 5  
 (c) 10 : 1      (d) 5 : 4
80. pH of a saturated solution of  $\text{Ba}(\text{OH})_2$  is 12. The value of solubility product ( $K_{sp}$ ) of  $\text{Ba}(\text{OH})_2$  is: [2012]
- (a)  $3.3 \times 10^{-7}$       (b)  $5.0 \times 10^{-7}$   
 (c)  $4.0 \times 10^{-6}$       (d)  $5.0 \times 10^{-6}$
81. Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value? [2012]

- (a)  $\text{BaCl}_2$       (b)  $\text{AlCl}_3$   
 (c)  $\text{LiCl}$       (d)  $\text{BeCl}_2$
82. Buffer solutions have constant acidity and alkalinity because [2012]
- (a) these give unionised acid or base on reaction with added acid or alkali.  
 (b) acids and alkalies in these solutions are shielded from attack by other ions.  
 (c) they have large excess of  $\text{H}^+$  or  $\text{OH}^-$  ions  
 (d) they have fixed value of pH
83. A buffer solution is prepared in which the concentration of  $\text{NH}_3$  is 0.30 M and the concentration of  $\text{NH}_4^+$  is 0.20 M. If the equilibrium constant,  $K_b$  for  $\text{NH}_3$  equals  $1.8 \times 10^{-5}$ , what is the pH of this solution? ( $\log 2.7 = 0.433$ ). [2011]
- (a) 9.08      (b) 9.43  
 (c) 11.72      (d) 8.73
84. In qualitative analysis, the metals of Group I can be separated from other ions by precipitating them as chloride salts. A solution initially contains  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  at a concentration of 0.10 M. Aqueous HCl is added to this solution until the  $\text{Cl}^-$  concentration is 0.10 M. What will the concentrations of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  be at equilibrium?  
 $(K_{sp} \text{ for } \text{AgCl} = 1.8 \times 10^{-10}, K_{sp} \text{ for } \text{PbCl}_2 = 1.7 \times 10^{-5})$  [2011M]
- (a)  $[\text{Ag}^+] = 1.8 \times 10^{-7} \text{ M}; [\text{Pb}^{2+}] = 1.7 \times 10^{-6} \text{ M}$   
 (b)  $[\text{Ag}^+] = 1.8 \times 10^{-11} \text{ M}; [\text{Pb}^{2+}] = 8.5 \times 10^{-5} \text{ M}$   
 (c)  $[\text{Ag}^+] = 1.8 \times 10^{-9} \text{ M}; [\text{Pb}^{2+}] = 1.7 \times 10^{-3} \text{ M}$   
 (d)  $[\text{Ag}^+] = 1.8 \times 10^{-11} \text{ M}; [\text{Pb}^{2+}] = 8.5 \times 10^{-4} \text{ M}$
85. If pH of a saturated solution of  $\text{Ba}(\text{OH})_2$  is 12, the value of its  $K_{(sp)}$  is: [2010]
- (a)  $4.00 \times 10^{-6} \text{ M}^3$       (b)  $4.00 \times 10^{-7} \text{ M}^3$   
 (c)  $5.00 \times 10^{-6} \text{ M}^3$       (d)  $5.00 \times 10^{-7} \text{ M}^3$
86. What is  $[\text{H}^+]$  in mol/L of a solution that is 0.20 M in  $\text{CH}_3\text{COONa}$  and 0.10 M in  $\text{CH}_3\text{COOH}$ ?  $K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ . [2010]
- (a)  $3.5 \times 10^{-4}$       (b)  $1.1 \times 10^{-5}$   
 (c)  $1.8 \times 10^{-5}$       (d)  $9.0 \times 10^{-6}$
87. In a buffer solution containing equal concentration of  $\text{B}^-$  and  $\text{HB}$ , the  $K_b$  for  $\text{B}^-$  is  $10^{-10}$ . The pH of buffer solution is: [2010]
- (a) 10      (b) 7  
 (c) 6      (d) 4

88. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH? [2008]
- (a)  $\text{SrCl}_2$       (b)  $\text{BaCl}_2$   
 (c)  $\text{MgCl}_2$       (d)  $\text{CaCl}_2$
89. Which of the following pairs constitutes a buffer? [2006]
- (a)  $\text{NaOH}$  and  $\text{NaCl}$   
 (b)  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$   
 (c)  $\text{HCl}$  and  $\text{KCl}$   
 (d)  $\text{HNO}_2$  and  $\text{NaNO}_2$
90.  $\text{H}_2\text{S}$  gas when passed through a solution of cations containing  $\text{HCl}$ , precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because [2005]
- (a) presence of  $\text{HCl}$  decreases the sulphide ion concentration.  
 (b) solubility product of group II sulphides is more than that of group IV sulphides.  
 (c) presence of  $\text{HCl}$  increases the sulphide ion concentration.  
 (d) sulphides of group IV cations are unstable in  $\text{HCl}$ .
91. The solubility product of a sparingly soluble salt  $AX_2$  is  $3.2 \times 10^{-11}$ . Its solubility (in moles/litre) is [2004]
- (a)  $5.6 \times 10^{-6}$       (b)  $3.1 \times 10^{-4}$   
 (c)  $2 \times 10^{-4}$       (d)  $4 \times 10^{-4}$
92. The solubility product of  $\text{AgI}$  at  $25^\circ\text{C}$  is  $1.0 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$ . The solubility of  $\text{AgI}$  in  $10^{-4} \text{ N}$  solution of  $\text{KI}$  at  $25^\circ\text{C}$  is approximately (in  $\text{mol L}^{-1}$ ) [2003]
- (a)  $1.0 \times 10^{-8}$       (b)  $1.0 \times 10^{-16}$   
 (c)  $1.0 \times 10^{-12}$       (d)  $1.0 \times 10^{-10}$
93. Solubility of  $MX_2$ -type electrolytes is  $0.5 \times 10^{-4}$  mol/lit, then find out  $K_{sp}$  of electrolytes [2002]
- (a)  $5 \times 10^{-12}$       (b)  $25 \times 10^{-10}$   
 (c)  $1 \times 10^{-13}$       (d)  $5 \times 10^{-13}$
94. Which has the highest value of pH? [2002]
- (a)  $\text{CH}_3\text{COOK}$       (b)  $\text{Na}_2\text{CO}_3$   
 (c)  $\text{NH}_4\text{Cl}$       (d)  $\text{NaNO}_3$
95. Solution of  $0.1 \text{ N } \text{NH}_4\text{OH}$  and  $0.1 \text{ N } \text{NH}_4\text{Cl}$  has pH 9.25. Then find out  $pK_b$  of  $\text{NH}_4\text{OH}$  [2002]
- (a) 9.25      (b) 4.75  
 (c) 3.75      (d) 8.25
96. Solubility of a  $M_2\text{S}$  salt is  $3.5 \times 10^{-6}$ , then its solubility product will be [2001]
- (a)  $1.7 \times 10^{-16}$       (b)  $1.7 \times 10^{-6}$   
 (c)  $1.7 \times 10^{-18}$       (d)  $1.7 \times 10^{-12}$
97. The solubility product of a sparingly soluble salt  $BA_2$  is  $4 \times 10^{-12}$ . The solubility of  $BA_2$  is [1999]
- (a)  $4 \times 10^{-4}$       (b)  $4 \times 10^{-12}$   
 (c)  $4 \times 10^{-3}$       (d)  $1 \times 10^{-4}$
98. The solubility products of  $\text{CuS}$ ,  $\text{Ag}_2\text{S}$  and  $\text{HgS}$  are  $10^{-31}$ ,  $10^{-44}$ ,  $10^{-54}$  respectively. The solubilities of these sulphides are in the order [1997]
- (a)  $\text{Ag}_2\text{S} > \text{HgS} > \text{CuS}$  (b)  $\text{Ag}_2\text{S} > \text{CuS} > \text{HgS}$   
 (c)  $\text{HgS} > \text{Ag}_2\text{S} > \text{CuS}$  (d)  $\text{CuS} > \text{Ag}_2\text{S} > \text{HgS}$
99. A physician wishes to prepare a buffer solution of pH = 3.58 that efficiently resists a change in pH yet contains only small concentrations of the buffering agents. Which one of the following weak acids together with its sodium salt would be the best to use? [1997]
- (a) *m*-chlorobenzoic acid ( $\text{pK}_a = 3.98$ )  
 (b) *p*-chlorocinnamic acid ( $\text{pK}_a = 4.41$ )  
 (c) 2, 5-dihydroxy benzoic acid ( $\text{pK}_a = 2.97$ )  
 (d) Acetoacetic acid ( $\text{pK}_a = 3.58$ )
100. The pH value of blood does not appreciably change by a small addition of an acid or a base, because the blood [1995]
- (a) is a body fluid  
 (b) can be easily coagulated  
 (c) contains iron as a part of the molecule  
 (d) contains serum protein which acts as buffer
101. Which of the following is most soluble? [1994]
- (a)  $\text{Bi}_2\text{S}_3$  ( $K_{sp} = 1 \times 10^{-17}$ )  
 (b)  $\text{MnS}$  ( $K_{sp} = 7 \times 10^{-16}$ )  
 (c)  $\text{CuS}$  ( $K_{sp} = 8 \times 10^{-37}$ )  
 (d)  $\text{Ag}_2\text{S}$  ( $K_{sp} = 6 \times 10^{-51}$ ).
102. 0.1 M solution of which one of these substances will be basic? [1992]
- (a) Sodium borate  
 (b) Ammonium chloride  
 (c) Calcium nitrate  
 (d) Sodium sulphate.

103. In which of the following solvents, AgBr will have the highest solubility? *[1992]*
- (a)  $10^{-3}$  M NaBr      (b)  $10^{-3}$  M  $\text{NH}_4\text{OH}$   
 (c) Pure water      (d)  $10^{-3}$  M HBr
104. The compound whose aqueous solution has the highest pH is *[1988]*
- (a) NaCl      (b)  $\text{NaHCO}_3$   
 (c)  $\text{Na}_2\text{CO}_3$       (d)  $\text{NH}_4\text{Cl}$ .

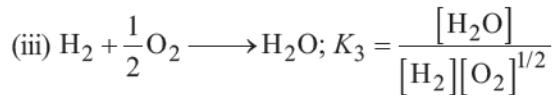
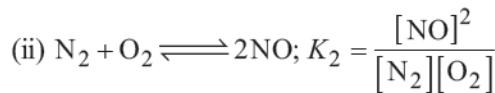
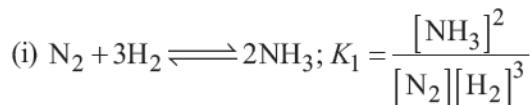
## ANSWER KEY

1	(a)	12	(c)	23	(a)	34	(d)	45	(d)	56	(b)	67	(d)	78	(a)	89	(d)	100	(d)
2	(d)	13	(b)	24	(d)	35	(d)	46	(d)	57	(b)	68	(d)	79	(c)	90	(a)	101	(a)
3	(b)	14	(d)	25	(b)	36	(d)	47	(b)	58	(c)	69	(a)	80	(b)	91	(c)	102	(a)
4	(a)	15	(a)	26	(d)	37	(d)	48	(a)	59	(d)	70	(a)	81	(a)	92	(c)	103	(b)
5	(c)	16	(a)	27	(a)	38	(c)	49	(a)	60	(a)	71	(c)	82	(a)	93	(d)	104	(c)
6	(c)	17	(a)	28	(c)	39	(c)	50	(a)	61	(a)	72	(b)	83	(b)	94	(b)		
7	(c)	18	(b)	29	(d)	40	(a)	51	(d)	62	(c)	73	(b)	84	(c)	95	(b)		
8	(d)	19	(d)	30	(c)	41	(c)	52	(c)	63	(a)	74	(c)	85	(d)	96	(a)		
9	(c)	20	(b)	31	(d)	42	(b)	53	(b)	64	(d)	75	(a)	86	(d)	97	(d)		
10	(c)	21	(d)	32	(b)	43	(c)	54	(c)	65	(c)	76	(b)	87	(d)	98	(b)		
11	(b)	22	(d)	33	(a)	44	(c)	55	(a)	66	(b)	77	(c)	88	(b)	99	(d)		

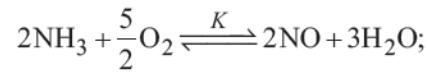
## Hints &amp; Solutions

WWW.JEEBOOKS.IN

1. (a)



Applying (II + 3 × III - I) we will get

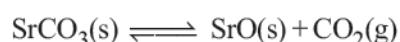


$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 \times [\text{O}_2]^{3/2}} \Big/ \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$\therefore K = K_2 \times K_3^3 / K_1$$

2. (d) Max. pressure of  $\text{CO}_2$  = Pressure of  $\text{CO}_2$  at equilibrium

For reaction,


 $K_p = P_{\text{CO}_2} = 1.6 \text{ atm} = \text{maximum pressure of CO}_2 \text{ volume of container at this stage.}$ 

$$V = \frac{nRT}{P} \quad \dots(i)$$

Since container is sealed and reaction was not earlier at equilibrium.

$$\therefore n = \text{constant.}$$

$$n = \frac{PV}{RT} = \frac{0.4 \times 20}{RT} \quad \dots(ii)$$

Put equation (ii) in equation (i)

$$V = \left[ \frac{0.4 \times 20}{RT} \right] \frac{RT}{1.6} = 5L$$

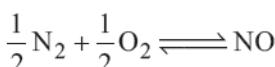
3. (b) Equilibrium constant for reaction:

$$K = 1.6 \times 10^{12} = \frac{[\text{Product}]}{[\text{Reactant}]}$$

The value of K is very high so the system will contain mostly products at equilibrium.

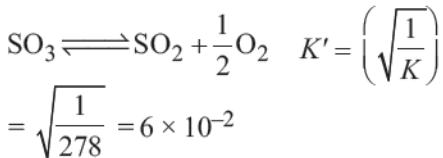
4. (a)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ 

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



$$K' = \frac{[NO]}{[N_2]^{1/2}[O_2]^{1/2}} = K^{1/2}$$

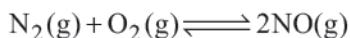
5. (c)  $2SO_2 + O_2 \rightleftharpoons 2SO_3$   $K = 278$  (given)



6. (c)  $A_2 + B_2 \rightleftharpoons 2AB$ ;  $K_c = \frac{[AB]^2}{[A_2][B_2]}$

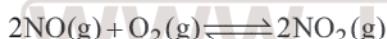
$$K_c = \frac{(2.8 \times 10^{-3})^2}{3 \times 10^{-3} \times 4.2 \times 10^{-3}} = \frac{(2.8)^2}{3 \times 4.2} = 0.62$$

7. (c) For the reaction



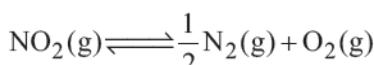
$$K_1 = \frac{[NO]^2}{[N_2][O_2]}$$

For the reaction



$$K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

For the reaction



$$K = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$$

$$\text{Hence, } K = \sqrt{\frac{1}{K_1} \times \frac{1}{K_2}}$$

$$K = \frac{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}}{[NO]^{\frac{1}{2}}} \times \frac{[NO][O_2]^{\frac{1}{2}}}{[NO_2]^{\frac{1}{2}}} = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$$

8. (d)  $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

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

$\therefore K_c$  and  $K_p$  are not equal.



If  $\Delta n = 0$ , then  $(RT)^{\Delta n} = 1$   
 $\Rightarrow K_c = K_p$

9. (c)  $2A_{(g)} + B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)}$

Mole ratio	2	1	3	1
------------	---	---	---	---

Molar concentration	1	1	0	0
---------------------	---	---	---	---

at t = 0				
----------	--	--	--	--

Molar concentration at equilibrium	0.50	0.75	0.75	0.25
------------------------------------	------	------	------	------

$$K_c = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}$$

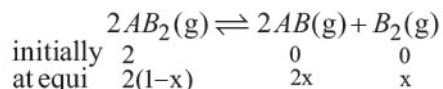
10. (c) For this reaction  $K_{eq}$  is given by

$$K = \frac{[Fe^{3+}][OH^-]^3}{[Fe(OH)_3]} = (Fe^{3+})(OH^-)^3 \quad [\because [solid]=1]$$

If  $(OH^-)$  is decreased by  $\frac{1}{4}$  times then for given reaction, equilibrium constant to remain constant, we have to increase the concentration of  $[Fe^{3+}]$  by a factor of  $4^3$  i.e.  $4 \times 4 \times 4 = 64$ . Thus, option (c) is correct answer.

To maintain the equilibrium constant if concentration of one of the product decreases by  $\frac{1}{n}$  times then the concentration of another product is increased by the factor of  $(n)^x$ , where  $x$  is the stoichiometric coefficient.

11. (b) For the reaction



The partial pressure at equilibrium are calculated on the basis of total number of moles at equilibrium.

Total number of moles

$$= 2(1-x) + 2x + x = (2+x)$$

$\therefore P_{AB_2} = \frac{2(1-x)}{(2+x)} \times P$  where  $P$  is the total pressure.

$$P_{AB} = \frac{2x}{(2+x)} \times P, \quad P_{B_2} = \frac{x}{(2+x)} \times P$$

Since  $x$  is very small so can be neglected in denominator

Thus, we get

$$P_{AB_2} = (1-x) \times P$$

$$P_{AB} = x \times P$$

$$P_{B_2} = \frac{x}{2} \times P$$

$$\text{Now, } K_P = \frac{(P_{AB})^2 (P_{B_2})}{(P_{AB_2})^2} = \frac{(x)^2 \times P^2 \cdot P \times \frac{x}{2}}{(1-x)^2 \times P^2}$$

$$= \frac{x^3 \cdot P^3}{2 \times 1 \times P^2} \quad [\because 1-x \approx 1]$$

$$= \frac{x^3 \cdot P}{2} \text{ or } x^3 = \frac{2 \cdot K_p}{P} \text{ or } x = \left(\frac{2 \cdot K_p}{P}\right)^{\frac{1}{3}}$$

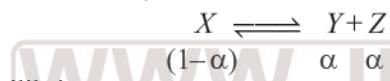
12. (c) Given reaction are



Let the total pressure for reaction (i) and (ii) be  $P_1$  and  $P_2$  respectively, then

$$\frac{K_{P_1}}{K_{P_2}} = \frac{9}{1} \quad (\text{given})$$

After dissociation,



At equilibrium

[Let 1 mole of  $X$  dissociate with  $\alpha$  as degree of dissociation]

Total number of moles =  $1 - \alpha + \alpha + \alpha = (1 + \alpha)$

$$\text{Thus } P_X = \left(\frac{1-\alpha}{1+\alpha}\right) \cdot P_1; P_Y = \left(\frac{\alpha}{1+\alpha}\right) P_1;$$

$$P_Z = \left(\frac{\alpha}{1+\alpha}\right) P_1$$

$$\therefore K_{P_1} = \left(\frac{\alpha}{1+\alpha}\right) P_1 \times \frac{\alpha}{(1+\alpha)}.$$

$$P_1 / \left(\frac{1-\alpha}{1+\alpha}\right) P_1 \quad \dots \text{(i)}$$

Similarly for  $A \rightleftharpoons{} 2B$

At equilibrium  $(1-\alpha) \quad 2\alpha$

We have,

$$K_{P_2} = \left(\frac{2\alpha P_2}{1+\alpha}\right)^2 / \left(\frac{1-\alpha}{1+\alpha}\right) P_2 \quad \dots \text{(ii)}$$

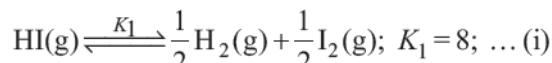
Dividing (i) by (ii), we get

$$\frac{K_{P_1}}{K_{P_2}} = \frac{\alpha^2 \cdot P_1}{4\alpha^2 \cdot P_2} \text{ or } \frac{K_{P_1}}{K_{P_2}} = \frac{1}{4} \cdot \frac{P_1}{P_2}$$

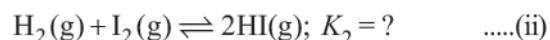
$$\text{or } 9 = \frac{1}{4} \cdot \frac{P_1}{P_2} \quad \left[ \therefore \frac{K_{P_1}}{K_{P_2}} = \frac{9}{1} \right]$$

$$\text{or } \frac{P_1}{P_2} = \frac{36}{1} \text{ or } P_1 : P_2 = 36 : 1$$

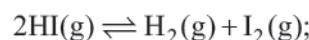
13. (b) Given : Equilibrium constant ( $K_1$ ) for the reaction:



To find equilibrium constant for the following reaction:

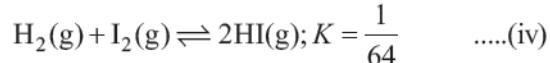


Multiply (i) by 2, we get



$$K_1 = 8^2 = 64. \quad \dots \text{(iii)}$$

Now reverse equation (iii), we get



Equation (iv) is the same as the required equation

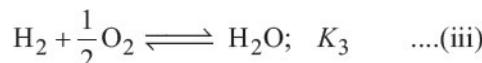
(ii), thus  $K_2$  for equation (ii) is  $\frac{1}{64}$  i.e. option (b) is correct.



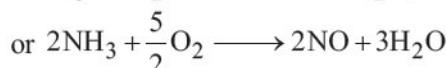
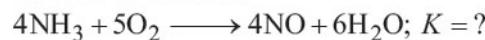
When the equation for an equilibrium is multiplied by a factor, the equilibrium constant must be raised to the power equal to the factor.

For a reversible reaction, the equilibrium constant of the backward reaction is inverse of the equilibrium constant for the forward reaction.

14. (d) Given,



We have to calculate



$$\text{For this equation, } K = \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}}$$

$$\text{but } K_1 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}, \quad K_2 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$\text{& } K_3 = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}} \text{ or } K_3^3 = \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 [\text{O}_2]^{3/2}}$$

$$\text{Now operate, } \frac{K_2 \cdot K_3^3}{K_1}$$

$$= \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} \times \frac{[\text{H}_2\text{O}]^3}{[\text{H}_2]^3 [\text{O}_2]^{3/2}} \cdot \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$= \frac{[\text{NO}]^2 [\text{H}_2\text{O}]^3}{[\text{NH}_3]^2 [\text{O}_2]^{5/2}} = K$$

$$\therefore K = \frac{K_2 \cdot K_3^3}{K_1}$$

15. (a) First option is incorrect as the value of  $K_p$  given is wrong. It should have been

$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CH}_4} \times [P_{\text{O}_2}]^2}$$

16. (a) For reaction (i)

$$K_1 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

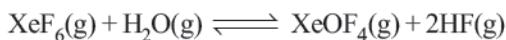
and for reaction (ii)

$$K_2 = \frac{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}{[\text{NO}]} \text{ therefore } K_1 = \frac{1}{K_2^2}$$

17. (a)  $\text{MgCO}_3(\text{s}) \rightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$   
 $\text{MgO}$  &  $\text{MgCO}_3$  are solid and they do not exert any pressure and hence only pressure exerted is by  $\text{CO}_2$ . Therefore  $K_p = P_{\text{CO}_2}$
18. (b) In polyprotic acids the loss of second proton occurs much less readily than the first. Usually the  $K_a$  values for successive loss of protons from these acids differ by at least a factor of  $10^{-3}$  i.e.,  $K_{a_1} > K_{a_2}$

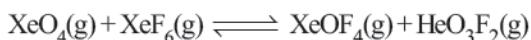


19. (d) For the reaction



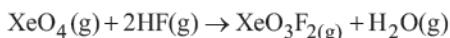
$$K_1 = \frac{[\text{XeOF}_4][\text{HF}]^2}{[\text{XeF}_6][\text{H}_2\text{O}]} \quad \dots(a)$$

and for the reaction



$$K_2 = \frac{[\text{XeOF}_4][\text{HeO}_3\text{F}_2]}{[\text{XeO}_4][\text{XeF}_6]} \quad \dots(b)$$

For reaction :

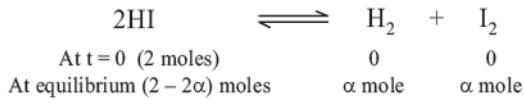


$$K = \frac{[\text{XeO}_3\text{F}_2][\text{H}_2\text{O}]}{[\text{XeO}_4][\text{HF}]^2}$$

∴ From eq. no. (a) and (b)

$$K = K_2 / K_1$$

20. (b) According to equation



Total moles at equilibrium =  $2 - 2\alpha + \alpha + \alpha = 2$  mole

21. (d) Rate constant of forward reaction ( $K_f$ ) =  $1.1 \times 10^{-2}$  and rate constant of backward reaction ( $K_b$ ) =  $1.5 \times 10^{-3}$  per minute. Equilibrium constant ( $K_c$ )

$$= \frac{K_f}{K_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33$$

22. (d)  $\Delta G = \Delta G^\circ + RT \ln Q$

At equilibrium  $\Delta G = 0$ ,  $Q = K_{eq}$

So,  $\Delta_r G^\circ = -RT \ln K_{eq}$

$$\Delta_r G^\circ = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

23. (a)  $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons \text{X}_2(\text{g})$ ;  $\Delta H = -X \text{ kJ}$   
 On increasing pressure equilibrium shifts in a direction where number of moles decreases i.e. forward direction.

On decreasing temperature, equilibrium shifts in exothermic direction i.e., forward direction.

So, high pressure and low temperature favours maximum formation of product.

24. (d) Clausius – Clapeyron's equation

$$\frac{d \ln P}{dT} = \frac{\Delta H_v}{RT^2}$$

25. (b)  $\Delta G^\circ = -2.30RT \log K$

because at equilibrium  $\Delta G = 0$

26. (d) Given reaction is exothermic reaction. Hence according to Le-Chatelier's principle low temperature favours the forward reaction and on increasing pressure equilibrium will shift, towards lesser number of moles i.e. forward direction.

27. (a) In exothermic reactions on increasing temperature value of  $K_p$  decreases

$$\therefore K_p > K'_p \quad (\text{Assuming } T_1 < T_2)$$

28. (c) Given,  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ ;

$$K_{a_1} = 1.5 \times 10^{-5} \quad \dots(i)$$



or  $\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}$ ;

$$K'_{a_2} = \frac{1}{K_{a_2}} = \frac{1}{4.5 \times 10^{-10}} \quad \dots(\text{ii})$$

$\therefore$  From (i) and (ii), we find that the equilibrium constant ( $K_a$ ) for the reaction,



$$K_a = K_{a_1} \times K'_{a_2}$$

$$= \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} = \frac{1}{3} \times 10^5 = 3.33 \times 10^4$$

29. (d) For reaction to proceed from right to left

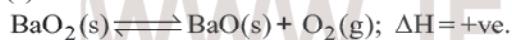
$$\frac{Q}{( \text{backward} )} > \frac{K_c}{( \text{forward} )} \text{ i.e the reaction will be fast}$$

in backward direction *i.e.*  $r_b > r_f$ .



When  $Q = K_c$ , the system is at equilibrium  
 $Q < K_c$ , reaction shift to the right from left.  
 $Q > K_c$ , reaction proceed from right to left.

30. (c) For the reaction



At equilibrium  $K_p = P_{\text{O}_2}$

[For solid and liquids concentration term is taken as unity]

Hence, the value of equilibrium constant depends only upon partial pressure of  $\text{O}_2$ . Further on increasing temperature, formation of  $\text{O}_2$  increases as this is an endothermic reaction.

31. (d)  $\text{A}_2(g) + \text{B}_2(g) \xrightleftharpoons[\text{Step 1}]{\text{Step 2}} 3\text{C}(g) \rightleftharpoons \text{D}(g)$

since the steps 1 and 2 are exothermic hence low temperature will favour both the reactions. In step - 1, moles are increasing hence low pressure will favour it. In step 2, moles are decreasing, hence high pressure will favour it.

32. (b)  $\text{A}_2 \rightleftharpoons 2\text{A}$  Equilibrium constant is given by

$$K_c = \frac{[\text{A}]^2}{[\text{A}_2]}$$

Since the value given is very small, hence conc. of products is less. It means the reaction is slow.

33. (a) If more trans-2-pentene is added, then its concentration in right hand side will increase. But in order to maintain the K constant, concentration of cis-2-pentene will also increase. Therefore more cis-2-pentene will be formed.

34. (d) Solid  $\rightleftharpoons$  Liquid

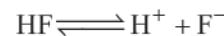
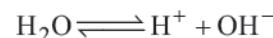
It is an endothermic process. So when temperature is raised, more liquid is formed. Hence adding heat will shift the equilibrium in the forward direction.

35. (d) According to Le-chatelier's principle whenever a constraint is applied to a system in equilibrium, the system tends to readjust so as to nullify the effect of the constraint.

36. (d)  $[\text{OH}^-] = 0.01 \text{ M} = 10^{-2} \text{ M}$   
 $\text{pOH} = -\log[\text{OH}^-] = -\log(10^{-2}) = 2$   
 $\text{pH} = 14 - \text{pOH} = 12$

37. (d)  $\text{HCl}$  cannot accept  $\text{H}^+$  therefore cannot act as Bronsted base.

38. (c) When a proton is removed from an acid, we obtain its conjugate base.



39. (c) Meq. of  $\text{HCl} = 75 \times \frac{1}{5} \times 1 = 15$

$$\text{Meq. of NaOH} = 25 \times \frac{1}{5} \times 1 = 5$$

Meq. of  $\text{HCl}$  in resulting solution = 10

$$\text{Molarity of } [\text{H}^+] \text{ in resulting mixture} = \frac{10}{100} = \frac{1}{10}$$

$$\text{pH} = -\log[\text{H}^+] = -\log\left[\frac{1}{10}\right] = 1.0$$

40. (a) g eq of  $\text{NaOH} = 0.1 \times V = 0.1V$   
g eq of  $\text{HCl} = 0.01 \times V = 0.01V$   
g eq of  $\text{NaOH} >$  g eq.  $\text{HCl}$   
hence, resultant solution should be basic, hence from the eqn

$$M_1 V_1 - M_2 V_2 = MV$$

$$0.1V - 0.01V = MV$$

$$M = \frac{0.09}{2} = 0.045 = 4.5 \times 10^{-2}$$

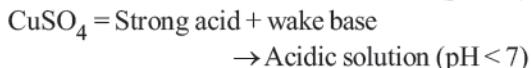
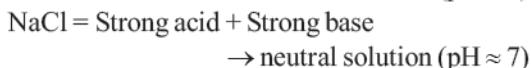
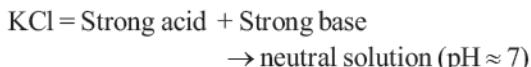
$$\text{Now, } \text{pOH} = -\log[\text{OH}^-]$$

$$= -\log 4.5 \times 10^{-2} = 1.34$$

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

$$\therefore \text{pH} = 14 - 1.34 = 12.65$$

41. (c)  $\text{Na}_2\text{CO}_3$  is a salt of strong base ( $\text{NaOH}$ ) and weak acid ( $\text{H}_2\text{CO}_3$ ). On hydrolysis this salt will produce strongly basic solution. *i.e.* pH will be highest ( $\text{pH} > 7$ ) for this solution. Others are combination of



42. (b)  $\text{BF}_3$  acts as Lewis acid.  
 43. (c)  $\text{BF}_3$  behaves as lewis acid as it is an electron deficient species.  
 44. (c) Boron in  $\text{B}_2\text{H}_6$  is electron deficient.  
 45. (d)  $(\text{CH}_3)_3\text{B}$  – is an electron deficient, thus behave as a lewis acid.  
 46. (d) Ammonium chloride is a salt of weak base and strong acid. In this case, hydrolysis constant,  $K_h$  can be calculated as

$$K_h = \frac{K_w}{K_b} = \frac{1 \times 10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$$

47. (b)  $[\text{H}_3\text{O}]^+$  for a solution having pH = 3 is given by  
 $[\text{H}_3\text{O}]^+ = 1 \times 10^{-3}$  moles/litre  $[\therefore [\text{H}_3\text{O}]^+ = 10^{-\text{pH}}]$   
 Similarly for solution having pH = 4,  
 $[\text{H}_3\text{O}]^+ = 1 \times 10^{-4}$  moles/ litre and for pH = 5  
 $[\text{H}_3\text{O}]^+ = 1 \times 10^{-5}$  moles/ litre  
 Let the volume of each solution in mixture be 1L, then total volume of mixture solution  
 $= (1 + 1 + 1) \text{ L} = 3\text{L}$

Total  $[\text{H}_3\text{O}]^+$  ion present in mixture solution  
 $= (10^{-3} + 10^{-4} + 10^{-5})$  moles

Then  $[\text{H}_3\text{O}]^+$  ion concentration of mixture solution

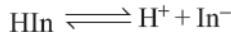
$$= \frac{10^{-3} + 10^{-4} + 10^{-5}}{3} \text{ M} = \frac{0.00111}{3} \text{ M}$$

$$= 0.00037 \text{ M} = 3.7 \times 10^{-4} \text{ M.}$$

48. (a) Given  $[\text{H}_3\text{O}^+] = 1 \times 10^{-10} \text{ M}$  at 25°C  $[\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-14}$   
 $\therefore [\text{OH}^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$   
 Now,  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4}$   
 $\therefore \text{pOH} = 4$   
 49. (a) For a solution of  $10^{-8} \text{ M HCl}$ ,  $[\text{H}^+] = 10^{-8}$   
 $[\text{H}^+]$  of water =  $10^{-7}$   
 $\text{Total } [\text{H}^+] = 10^{-7} + 10^{-8} = 10 \times 10^{-8} + 10^{-8}$   
 $10^{-8}(10 + 1) = 11 \times 10^{-8}$

50. (a) The solution formed from isomolar solutions of sodium oxide, sodium sulphide, sodium selenide and sodium telluride are  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  &  $\text{H}_2\text{Te}$  respectively. As the acidic strength increases from  $\text{H}_2\text{O}$  to  $\text{H}_2\text{Te}$  thus pH decreases and hence the correct order of pHs is  $\text{pH}_1 > \text{pH}_2 > \text{pH}_3 > \text{pH}_4$ .

51. (d) For an acid-base indicator



$$\therefore K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \text{ or } [\text{H}^+] = K_{\text{In}} \times \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{or } \log \text{H}^+ = \log K_{\text{In}} + \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

Taking negative on both sides

$$\log [\text{H}^+] - \log K_{\text{In}} = \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\text{or we can write } \text{pH} = \text{pK}_{\text{In}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

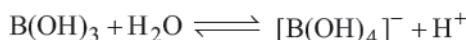
52. (c) The higher is the tendency to donate proton, stronger is the acid. Thus, the correct order is  $\text{R}-\text{COOH} > \text{HOH} > \text{R}-\text{OH} > \text{CH} \equiv \text{CH}$  depending upon the rate of donation of proton.



The stability order of conjugate base is



53. (b)  $\text{B}(\text{OH})_3$  does not provide  $\text{H}^+$  ions in water instead it accepts  $\text{OH}^-$  ion and hence it is Lewis acid



54. (c) Strong base has higher tendency to accept the proton. Increasing order of base and hence the order of accepting tendency of proton is



55. (a) Given : Hydroxyl ion concentration  $[\text{OH}^-] = 0.05 \text{ mol L}^{-1}$ . We know that the

$$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$\text{or } [\text{H}^+] = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol L}^{-1}$$

Since  $[\text{OH}^-] > [\text{H}^+]$

Therefore the solution is basic.

56. (b) Because  $\text{NH}_3$  after losing a proton ( $\text{H}^+$ ) gives  $\text{NH}_2^-$



(Conjugate acid-base pair differ only by a proton)

57. (b)  $\text{CH}_3\text{COOH}$  is weak acid while  $\text{NaOH}$  is strong base, so one equivalent of  $\text{NaOH}$  can not be neutralized with one equivalent of  $\text{CH}_3\text{COOH}$ . Hence the solution of one equivalent of each does not have pH value as 7. Its pH will be towards basic side as  $\text{NaOH}$  is a strong base hence conc. of  $\text{OH}^-$  will be more than the conc. of  $\text{H}^+$ .

58. (c) Because of electron deficiency, boron trifluoride and stannous chloride are lewis acid.

### NOTES

Vacant  $d$ -orbitals are available with stannic chloride, hence it can also accept pair of electrons and act as a lewis acid.

59. (d) No. of moles of  $\text{NaOH} = \frac{4}{40} = 0.1$

[Molecular weight of  $\text{NaOH} = 40$ ]

No. of moles of  $\text{OH}^- = 0.1$

Concentration of  $\text{OH}^- = \frac{0.1}{1 \text{ litre}} = 0.1 \text{ mol/L}$

As we know that,  $[\text{H}^+] [\text{OH}^-] = 10^{-14}$

$\therefore [\text{H}^+] = 10^{-13} \quad (\because [\text{OH}^-] = 10^{-1})$

60. (a) Molarity (M) = 10M.  $\text{HCl}$  is a strong acid and it is completely dissociated in aqueous solutions as :  $\text{HCl}(10) \rightleftharpoons \text{H}^+(10) + \text{Cl}^-$ .

So, for every moles of  $\text{HCl}$ , there is one  $\text{H}^+$ . Therefore  $[\text{H}^+] = [\text{HCl}]$  or  $[\text{H}^+] = 10$ .

$\text{pH} = -\log[\text{H}^+] = -\log[10] = -1$ .

61. (a)  $K_w$  at  $25^\circ\text{C} = 1 \times 10^{-14}$

At  $25^\circ\text{C}$

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

At  $100^\circ\text{C}$  (given)

$K_w = [\text{H}^+] [\text{OH}^-] = 55 \times 10^{-14}$

$\therefore$  for a neutral solution

$$[\text{H}^+] = [\text{OH}^-]$$

$\therefore [\text{H}^+]^2 = 55 \times 10^{-14}$

or  $[\text{H}^+] = (55 \times 10^{-14})^{1/2}$

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

On taking log on both side

$$-\log [\text{H}^+] = -\log(55 \times 10^{-14})^{1/2}$$

$$\text{pH} = \frac{1}{2}(-\log 55 + 14 \log 10)$$

$$\text{pH} = 6.13$$

**NOTES** Calculation of pOH in this question: value of pH and pOH must be same for a neutral solution. Thus,  $\text{pOH} = 6.13$ , also  $\text{pH} + \text{pOH} = -\log(55 \times 10^{-14})$

62. (c)  $\alpha = \sqrt{\frac{K_a}{C}} = 0.037 = \sqrt{\frac{K_a}{0.10}}$

$$K_a = (0.037)^2 \times 0.10 = 1.37 \times 10^{-4}$$

$$\approx 1.4 \times 10^{-4}$$

63. (a) Given  $K_a = 1.0 \times 10^{-5}$ ,  $C = 0.100 \text{ mol}$  for a weak electrolyte,  
degree of dissociation

$$\alpha = \sqrt{\frac{K_a}{C}} \sqrt{\frac{1 \times 10^{-5}}{0.100}} = 10^{-2} = 1\%$$

64. (d) Given  $K_b = 1.0 \times 10^{-12}$   
 $[\text{BOH}] = 0.01 \text{ M}$   $[\text{OH}^-] = ?$

$$\alpha = \sqrt{K_b / C}$$

$$= \sqrt{\frac{1 \times 10^{-12}}{0.01}} = 1.0 \times 10^{-5}$$

$$\text{Now } [\text{OH}^-] = c \cdot \alpha = 0.01 \times 10^{-5}$$

$$= 1 \times 10^{-7} \text{ mol L}^{-1}$$

65. (c)  $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Given that,

$$[\text{CH}_3\text{COO}^-] = [\text{H}^+] = 3.4 \times 10^{-4} \text{ M}$$

$$K_a \text{ for } \text{CH}_3\text{COOH} = 1.7 \times 10^{-5}$$

$\text{CH}_3\text{COOH}$  is weak acid, so in it  $[\text{CH}_3\text{COOH}]$  is equal to initial concentration. Hence

$$1.7 \times 10^{-5} = \frac{(3.4 \times 10^{-4})(3.4 \times 10^{-4})}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COOH}] = \frac{3.4 \times 10^{-4} \times 3.4 \times 10^{-4}}{1.7 \times 10^{-5}}$$

$$= 6.8 \times 10^{-3} \text{ M}$$

66. (b) An aqueous solution of acetic acid dissociates as



67. (d)  $\text{Ni(OH)}_2 \rightleftharpoons \underset{s}{\text{Ni}}^{2+} + 2\underset{s}{\text{OH}}^-$   
 $\text{NaOH} \longrightarrow \text{Na} + \text{OH}^-$

$$\text{Total } [\text{OH}^-] = 2s + 0.1 \approx 0.1$$

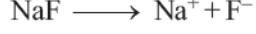
$$\text{Ionic product} = [\text{Ni}]^{2+}[\text{OH}]^2$$

$$2 \times 10^{-15} = s(0.1)^2$$

$$s = 2 \times 10^{-13}$$

$$\text{Solubility of } \text{Ni(OH)}_2 = 2 \times 10^{-13} \text{ M}$$

68. (d)  $\text{CaF}_2 \rightleftharpoons \underset{t=0}{\text{Ca}}^{2+} + \underset{0}{2\text{F}}^-$   
 $\underset{\text{At eqm.}}{\text{At eqm.}} \quad \underset{s}{\text{Ca}}^{2+} + \underset{2s}{2\text{F}}^-$



$$0.1 \quad 0.1 \quad 0.1$$

Due to common ion effect of NaF, solubility of CaF<sub>2</sub> is further suppressed. Therefore, the concentration of F<sup>-</sup> will be mainly due to NaF.

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

$$K_{sp} = (s)(0.1 + 2s)^2 \quad 0.1 + 2s \approx 0.1$$

$$s = \frac{K_{sp}}{(0.1)^2} = \frac{5.3 \times 10^{-11}}{(0.1)^2} = 5.3 \times 10^{-9} \text{ mol L}^{-1}$$

69. (a)  $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$

$$\text{pH} = 9, \text{pOH} = 14 - 9 = 5$$

$$[\text{OH}^-] = 10^{-5}$$

$$[\text{Ca}^{2+}] = \frac{10^{-5}}{2}$$

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = \left(\frac{10^{-5}}{2}\right) \times (10^{-5})^2$$

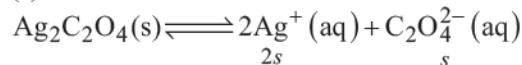
$$= 0.5 \times 10^{-15}$$

70. (a) Solubility of BaSO<sub>4</sub> =  $2.42 \times 10^{-3}$  g L<sup>-1</sup>

$$\therefore s = \frac{2.42 \times 10^{-3}}{233} = 1.038 \times 10^{-5} \text{ mol L}^{-1}$$

$$K_{sp} = s^2 = (1.038 \times 10^{-5})^2 = 1.08 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$$

71. (c)



$$K_{sp} = [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}]$$

$$[\text{Ag}^+] = 2.2 \times 10^{-4} \text{ M}$$

Given that:

∴ Concentration of C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions,

$$[\text{C}_2\text{O}_4^{2-}] = \frac{2.2 \times 10^{-4}}{2} \text{ M} = 1.1 \times 10^{-4} \text{ M}$$

$$\therefore K_{sp} = (2.2 \times 10^{-4})^2 (1.1 \times 10^{-4}) \\ = 5.324 \times 10^{-12}$$

72. (b)  $\text{MY} \rightleftharpoons \underset{|\text{M}^+ + \text{Y}^-|}{\text{M}} + \text{Y}^-$   
 $K_{sp} = s^2 = 6.2 \times 10^{-13}$

$$s = \sqrt{6.2 \times 10^{-13}}$$

$$s = 7.87 \times 10^{-7} \text{ mol L}^{-1}$$



$$K_{sp} = s \times (3s)^3 = 27s^4 = 6.2 \times 10^{-13}$$

$$s = \left(\frac{6.2 \times 10^{-13}}{27}\right)^{1/4}$$

$$s = 3.89 \times 10^{-4} \text{ mol L}^{-1}$$

∴ molar solubility of NY<sub>3</sub> is more than MY in water.

73. (b) The presence of large amount of KHSO<sub>4</sub> will decrease ionisation of H<sub>2</sub>SO<sub>4</sub> that result in lesser ionisation of nitric acid and lesser formation of nitronium ion [NO<sub>2</sub><sup>+</sup>]. Hence the rate of nitration will be slower.

74. (c) Ag<sub>2</sub>CrO<sub>4</sub>

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+] = \sqrt{\frac{1.1 \times 10^{-12}}{[\text{CrO}_4^{2-}]}}$$



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Ag}^+] = \frac{1.8 \times 10^{-10}}{[\text{Cl}^-]}$$



$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = 5.0 \times 10^{-13}$$

$$[\text{Ag}^+] = \frac{5.3 \times 10^{-13}}{[\text{Br}^-]}$$



$$K_{sp} = [\text{Ag}^+][\text{I}^-] = 8.3 \times 10^{-17}$$

$$[\text{Ag}^+] = \frac{8.3 \times 10^{-17}}{[\text{I}^-]}$$

If we take  $[\text{CrO}_4^{2-}] = [\text{Cl}^-] = [\text{Br}^-] = [\text{I}^-] = 1$

then maximum  $[\text{Ag}^+]$  will be required in case of Ag<sub>2</sub>CrO<sub>4</sub>.

75. (a) Among the given acids, HClO<sub>4</sub> is a very strong acid, completely dissociates

∴ [HA] → 0 in this case, hence cannot be used for acidic buffer.

76. (b)  $\Delta G = -2.303 \log K$

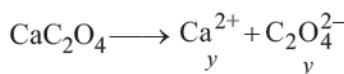
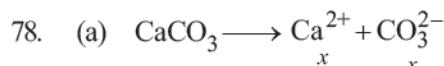
$$\text{here } K = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = K_{sp}$$

$$\therefore 63.3 \times 10^{-3} = -2.303 \times 8.314 \times 298 \log K_{sp}$$

$$\therefore \log K_{sp} = -\frac{63.3 \times 10^{-3}}{5705.8} = -11.09$$

$$\therefore K_{sp} = \text{Antilog}(-11.09) = 8 \times 10^{-12}$$

77. (c) Solubility of alkali metal is maximum among the following. Among ZnS ( $1.7 \times 10^{-5}$ ) & CuS ( $8 \times 10^{-7}$ ) ZnS has higher value of  $K_{sp}$ .



$$\therefore [\text{Ca}^{2+}] = x + y$$

$$\text{Now, } K_{sp}(\text{CaCO}_3) = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$\text{or } 4.7 \times 10^{-9} = (x + y)x$$

$$\text{similarly, } K_{sp}(\text{CaC}_2\text{O}_4) = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$$

$$\text{or } 1.3 \times 10^{-9} = (x + y)y$$

On solving, we get

$$[\text{Ca}^{2+}] = 7.746 \times 10^{-5} \text{ M}$$

79. (c) Given,  $K_a = 1 \times 10^{-4}$

$$\therefore pK_a = -\log(1 \times 10^{-4}) = 4$$

Now from Henderson equation

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Putting the values

$$5 = 4 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = 5 - 4 = 1$$

Taking antilog

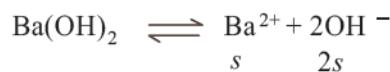
$$[\text{Salt}]/[\text{Acid}] = 10 = 10 : 1$$

80. (b) Given pH = 12

$$\text{or } [\text{H}^+] = 10^{-12}$$

$$\text{Since, } [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$\therefore [\text{OH}^-] = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$



$$[\text{OH}^-] = 10^{-2}$$

$$2s = 10^{-2}$$

$$s = \frac{10^{-2}}{2} = 5 \times 10^{-3} \text{ m}, K_{sp} = s \cdot (2s)^2$$

$$\Rightarrow K_{sp} = 5 \times 10^{-7}$$

81. (a) ( $\text{AlCl}_3, \text{LiCl} \& \text{BeCl}_2$ ) all these solutions are acidic due to cationic hydrolysis, whereas  $\text{BaCl}_2$ , is salt of strong base ( $\text{Ba(OH)}_2$ ) and strong acid ( $\text{HCl}$ ), hence it will have maximum pH.

82. (a) Constant acidity and alkalinity of buffer solution is due to the unionised acid or base.

**SOLVED** Lets take an example of an acidic buffer  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ .



when few drops of HCl are added to this buffer, the  $\text{H}^+$  of HCl immediately combine with  $\text{CH}_3\text{COO}^-$  ions to form undissociated acetic acid molecules. Thus there will be no  $\text{H}^+$  ions to combine with  $\text{CH}_3\text{COO}^-$  ions to form undissociated acetic acid molecules. Thus there will be no appreciable change in its pH value. Likewise if few drops of NaOH are added, the  $\text{OH}^-$  ions will combine with  $\text{H}^+$  ions to form unionised water molecule. Thus pH of solution will remain constant.

83. (b) Given :  $[\text{NH}_3] = 0.3 \text{ M}$ ,  $[\text{NH}_4^+] = 0.2 \text{ M}$ ,  $K_b = 1.8 \times 10^{-5}$ .

$$\text{pOH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$[pK_b = -\log K_b; pK_b = -\log 1.8 \times 10^{-5}]$$

$$\therefore pK_b = 4.74$$

$$\text{pOH} = 4.74 + \log \frac{0.2}{0.3}$$

$$= 4.74 + 0.3010 - 0.4771 = 4.56$$

$$\text{pH} = 14 - 4.56 = 9.436$$

84. (c)  $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

$$1.8 \times 10^{-10} = [\text{Ag}^+][0.1]$$

$$[\text{Ag}^+] = 1.8 \times 10^{-9} \text{ M}$$

$$K_{sp} = [\text{Pb}^{+2}][\text{Cl}^-]^2$$

$$1.7 \times 10^{-5} = [\text{Pb}^{+2}][0.1]^2$$

$$[\text{Pb}^{+2}] = 1.7 \times 10^{-3} \text{ M}$$

85. (d)  $\text{Ba}(\text{OH})_2(\text{s}) \longrightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$   
 $\text{pH} = 12$  or  $\text{pOH} = 2$   
 $[\text{OH}^-] = 10^{-2} \text{ M}$   
 $\text{Ba}(\text{OH})_2 \longrightarrow \text{Ba}^{2+} + 2\text{OH}^-$   
 $0.5 \times 10^{-2} \quad 10^{-2}$   
 $[\therefore \text{Concentration of Ba}^{2+} \text{ is half of OH}^-]$   
 $K_{sp} = [\text{Ba}^{2+}][\text{OH}^-]^2$   
 $= [0.5 \times 10^{-2}][1 \times 10^{-2}]^2$   
 $= 0.5 \times 10^{-6} = 5 \times 10^{-7} \text{ M}^3$

86. (d)  $\text{pH} = \text{p}K_a + \log \left[ \frac{\text{Salt}}{\text{Acid}} \right]$   
 $\log [\text{H}^+] = \log K_a - \log \left[ \frac{\text{Salt}}{\text{Acid}} \right]$   
 $\log [\text{H}^+] = \log K_a + \log \left[ \frac{\text{Acid}}{\text{Salt}} \right]$   
 $[\text{H}^+] = K_a \left[ \frac{\text{Acid}}{\text{Salt}} \right]$   
 $= 1.8 \times 10^{-5} \times \frac{0.1}{0.2} = 9 \times 10^{-6} \text{ M}$

87. (d)  $K_b = 10^{-10}; K_a = 10^{-4}$  or  $\text{p}K_a = 4$   
For the buffer solution containing equal concentration of  $\text{B}^-$  and  $\text{HB}$   
 $\text{pH} = \text{p}K_a + \log 1$   
 $\text{pH} = \text{p}K_a = 4$

88. (b) The highest pH will be recorded by the most basic solution. The basic nature of hydroxides of alkaline earth metals increase as we move from Mg to Ba and thus the solution of  $\text{BaCl}_2$  in water will be most basic and so it will have highest pH.

89. (d)  $\text{HNO}_2$  is a weak acid and  $\text{NaNO}_2$  is salt of that weak acid and strong base ( $\text{NaOH}$ ).

90. (a) IV<sup>th</sup> group needs higher  $\text{S}^{2-}$  ion concentration.

91. (c) For  $\text{AX}_2; K_{sp} = 4s^3 \therefore 3.2 \times 10^{-11} = 4s^3$   
or  $s = 3\sqrt{\frac{3.2 \times 10^{-11}}{4}} = 2 \times 10^{-4}$

92. (c)  $K_{sp}$  for  $\text{AgI} = 1 \times 10^{-16}$   
In solution of  $\text{KI}$ ,  $\text{I}^-$  would be due to the both  $\text{AgI}$  and  $\text{KI}$ ,  $10^{-4}$  solution  $\text{KI}$  would provide  $= 10^{-4} \text{ I}^-$   
 $\text{AgI}$  would provide, say  $= x \text{ I}^-$  ( $x$  is solubility of  $\text{AgI}$ )  
Total  $\text{I}^- = (10^{-4} + x)$ ,  $K_{sp}$  of  $\text{AgI} = (10^{-4} + x)x$   
 $\Rightarrow K_{sp} = 10^{-4}x + x^2$   
as  $x$  is very small  
 $\therefore x^2$  can be ignored  
 $\therefore 10^{-4}x = 10^{-16}$   
or  $\frac{x}{(\text{solubility})} = \frac{10^{-16}}{10^{-4}} = 10^{-12} (\text{mol L}^{-1})$

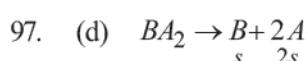
93. (d) Given  $s = 0.5 \times 10^{-4}$  moles/L  
 $[\text{MX}_2 \rightleftharpoons \text{M}^{2+} + 2\text{X}]$   
 $\therefore$  For  $\text{MX}_2, K_{sp} = s \times (2s)^2 = 4s^3$   
 $K_{sp} = 4 \times (0.5 \times 10^{-4})^3 = 4 \times 0.125 \times 10^{-12}$   
 $= 0.5 \times 10^{-12} = 5 \times 10^{-13}$

94. (b)  $\text{Na}_2\text{CO}_3$  is a salt of weak acid  $\text{H}_2\text{CO}_3$  and strong base  $\text{NaOH}$ , therefore, its aqueous solution will be basic hence has pH more than 7.  
 $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + 2\text{H}_2\text{CO}_3$   
strong base      weak acid

95. (b)  $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$   
or  $\text{p}K_b = \text{pOH} - \log \frac{[\text{salt}]}{[\text{Base}]}$   
but  $\text{pOH} + \text{pH} = 14$  or  $\text{pOH} = 14 - \text{pH}$   
 $\therefore 14 - \text{pH} - \log \frac{[\text{Salt}]}{[\text{Base}]} = \text{p}K_b$   
 $14 - 9.25 - \log \frac{0.1}{0.1} = \text{p}K_b$   
 $14 - 9.25 - 0 = \text{p}K_b$   
 $\text{p}K_b = 4.75$

In presence of HCl, the dissociation of  $\text{H}_2\text{S}$  decreases hence produces less amount of sulphide ions due to common ion effect, thus HCl decreases the solubility of  $\text{H}_2\text{S}$  which is sufficient to precipitate  $\text{II}^{\text{nd}}$  group radicals.





$$\text{Solubility product} = [s] [2s]^2 = 4s^3$$

$$4 \times 10^{-12} = 4s^3 \text{ or } s = \sqrt[3]{\frac{4 \times 10^{-12}}{4}}$$

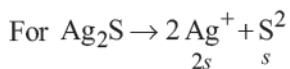
$$\therefore s = 10^{-4}$$

98. (b) For Binary salts like CuS & HgS, solubility,

$$s = \sqrt{K_{sp}}$$

$$\Rightarrow s_{\text{CuS}} = \sqrt{10^{-31}} = 3.16 \times 10^{-16},$$

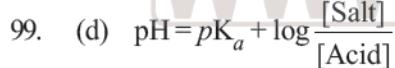
$$s_{\text{HgS}} = \sqrt{10^{-54}} = 10^{-27}$$



$$K_{sp} = 4s^3 \text{ or } s_{\text{Ag}_2\text{S}} = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{10^{-44}}{4}}$$

$$= \sqrt[3]{0.25 \times 10 \times 10^{-45}} = 13.54 \times 10^{-16}$$

$\therefore$  The order is  $\text{Ag}_2\text{S} > \text{CuS} > \text{HgS}$



For acetoacetic acid

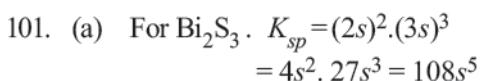
$$3.58 = 3.58 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\Rightarrow \log \frac{[\text{Salt}]}{[\text{Acid}]} = 0$$

$$\Rightarrow \frac{[\text{Salt}]}{[\text{Acid}]} = 1$$

This is the required condition for maximum buffer capacity.

100. (d) The buffer system present in serum is  $\text{H}_2\text{CO}_3 + \text{NaHCO}_3$  and as we known that a buffer solution resist the change in pH therefore pH value of blood does not change by a small addition of an acid or a base.



$$\text{or } s = \sqrt[5]{\frac{K_{sp}}{108}} = \sqrt[5]{\frac{1 \times 10^{-17}}{108}}$$

For  $\text{MnS}$ .  $K_{sp} = s^2$

$$\text{or } s = \sqrt{K_{sp}} = \sqrt{7 \times 10^{-16}}$$

$$\text{for CuS} \quad s = \sqrt{K_{sp}} = \sqrt{8 \times 10^{-37}}$$

$$\text{For Ag}_2\text{S} \quad K_{sp} = 2s^2 \cdot s = 4s^3$$

$$\text{or } s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{6 \times 10^{-51}}{4}}$$

thus  $\text{Bi}_2\text{S}_3$  has maximum solubility.



The solubility of  $\text{Bi}_2\text{S}_3$  will be in the order of 5<sup>th</sup> root of  $10^{-17}$ , thus, it is most soluble.

102. (a) Sodium borate is a salt of strong base ( $\text{NaOH}$ ) and weak acid ( $\text{H}_3\text{BO}_3$ ). Hence, its aqueous solution will be basic.

103. (b)  $\text{AgBr}$  has the highest solubility in  $10^{-3}$  M  $\text{NH}_4\text{OH}$ .  $\text{AgBr}$  is less soluble in  $\text{NaBr}$  and  $\text{HBr}$  due to presence of common ion ( $\text{Br}$ ). With  $\text{NH}_4\text{OH}$ ,  $\text{AgBr}$  will react as:



Hence, the highest solubility with  $\text{NH}_4\text{OH}$  solution.

104. (c)  $\text{NaCl}$  is a salt of strong acid and strong base hence its aqueous solution will be neutral i.e.  $\text{pH} = 7$ .  $\text{NaHCO}_3$  is an acidic salt hence  $\text{pH} < 7$ .  $\text{Na}_2\text{CO}_3$  is a salt of weak acid and strong base. Hence its aqueous solution will be strongly basic i.e.  $\text{pH} > 7$ .

$\text{NH}_4\text{Cl}$  is salt of weak base and strong acid, hence its aqueous solution will be strongly acidic i.e.  $\text{pH} < 7$ .

# 8

# Redox Reactions



## Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Oxidation number	oxidation number	1	E								
Disproportionation and balancing of redox reaction	disproportionation reaction			1	A	1	D				
	balancing of redox reaction					1	A				
LOD - Level of Difficulty	E - Easy	A - Average			D - Difficult			Qns - No. of Questions			

### Topic 1: Oxidation and Reduction Reactions

- Zn gives H<sub>2</sub> gas with H<sub>2</sub>SO<sub>4</sub> and HCl but not with HNO<sub>3</sub> because [2002]
  - Zn acts as an oxidising agent when it reacts with HNO<sub>3</sub>
  - HNO<sub>3</sub> is weaker acid than H<sub>2</sub>SO<sub>4</sub> and HCl
  - In electrochemical series, Zn is above hydrogen
  - NO<sub>3</sub><sup>-</sup> is reduced in preference to hydronium ion
- Which of the following involves a redox reaction?
  - Reaction of H<sub>2</sub>SO<sub>4</sub> with NaOH [1997]
  - Production of ozone from oxygen in the atmosphere by lightning
  - Production of nitrogen oxides from nitrogen and oxygen in the atmosphere by lightning
  - Evaporation of water
- The loss of electron is termed as [1995]
  - oxidation
  - reduction
  - combustion
  - neutralization

### Topic 2: Oxidation Number

- What is the change in oxidation number of carbon in the following reaction? [2020]
 
$$\text{CH}_4(g) + 4\text{Cl}_2(g) \longrightarrow \text{CCl}_4(l) + 4\text{HCl}(g)$$

- (a) 0 to +4 (b) -4 to +4  
(c) 0 to -4 (d) +4 to +4
5. The oxidation state of Cr in CrO<sub>6</sub> is [NEET Odisha 2019]
  - +4
  - 6
  - +12
  - +6
6. Oxidation numbers of P in PO<sub>4</sub><sup>3-</sup>, of S in SO<sub>4</sub><sup>2-</sup> and that of Cr in Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are respectively [2009]
  - +3, +6 and +5
  - +5, +3 and +6
  - 3, +6 and +6
  - +5, +6 and +6
7. The oxidation states of sulphur in the anions SO<sub>3</sub><sup>2-</sup>, S<sub>2</sub>O<sub>4</sub><sup>2-</sup> and S<sub>2</sub>O<sub>6</sub><sup>2-</sup> follow the order [2003]
  - S<sub>2</sub>O<sub>6</sub><sup>2-</sup> < S<sub>2</sub>O<sub>4</sub><sup>2-</sup> < SO<sub>3</sub><sup>2-</sup>
  - S<sub>2</sub>O<sub>4</sub><sup>2-</sup> < SO<sub>3</sub><sup>2-</sup> < S<sub>2</sub>O<sub>6</sub><sup>2-</sup>
  - SO<sub>3</sub><sup>2-</sup> < S<sub>2</sub>O<sub>4</sub><sup>2-</sup> < S<sub>2</sub>O<sub>6</sub><sup>2-</sup>
  - S<sub>2</sub>O<sub>4</sub><sup>2-</sup> < S<sub>2</sub>O<sub>6</sub><sup>2-</sup> < SO<sub>3</sub><sup>2-</sup>
8. A compound contains atoms of three elements A, B and C. If the oxidation number of A is +2, B is +5, and that of C is -2, the possible formula of the compound is : [2000]
  - A<sub>2</sub>(BC<sub>3</sub>)<sub>2</sub>
  - A<sub>3</sub>(BC<sub>4</sub>)<sub>2</sub>
  - A<sub>3</sub>(B<sub>4</sub>C)<sub>2</sub>
  - ABC<sub>2</sub>

## Topic 3: Disproportionation and Balancing of Redox Reactions

12. Which of the following reactions are disproportionation reaction? **[2019]**

  - $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$
  - $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$
  - $2\text{KMnO}_4 \xrightarrow{\Delta} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$
  - $2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \xrightarrow{\Delta} 5\text{MnO}_2 + 4\text{H}^+$

Select the **correct** option from the following:

  - (a) and (b) only
  - (a), (b) and (c)
  - (a), (c) and (d)
  - (a) and (d) only

13. For the redox reaction **[2018]**

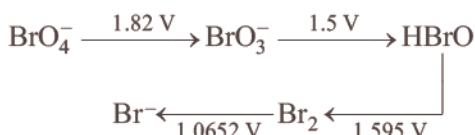
$$\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$$

The correct coefficients of the reactants for the

The correct coefficients of the reactants for the balanced equation are

	$\text{MnO}_4^-$	$\text{C}_2\text{O}_4^{2-}$	$\text{H}^+$
(a)	16	5	2
(b)	2	5	16
(c)	5	16	2
(d)	2	16	5

14. Consider the change in oxidation state of bromine corresponding to different emf values as shown in the diagram below : **[2018]**

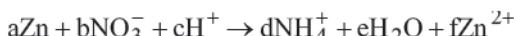


Then the species undergoing disproportionation is

- (a)  $\text{BrO}_3^-$       (b)  $\text{BrO}_4^-$   
 (c)  $\text{HBrO}$       (d)  $\text{Br}_2$



17. The following redox reaction is balanced by which set of coefficients ? **[1999]**

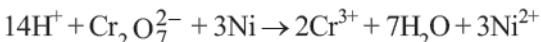


<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>e</b>	<b>f</b>
(a) 1	1	10	1	3	1
(b) 2	2	10	2	3	2
(c) 4	2	10	1	3	4
(d) 4	1	10	1	3	4

18. In which of the following reactions, there is no change in valency? [1994]

- (a)  $4 \text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$   
 (b)  $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$   
 (c)  $\text{BaO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + \text{H}_2\text{O}_2$   
 (d)  $3 \text{BaO} + \text{O}_2 \longrightarrow 2 \text{BaO}_2$

19. Which substance serves as a reducing agent in the following reaction? [1994]





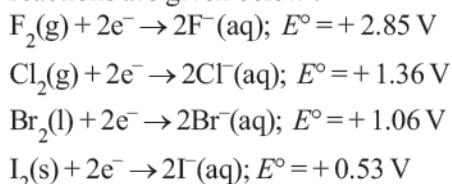



## Topic 4: Electrode Potential and Oxidising, Reducing Agents

20. The standard electrode potential ( $E^\circ$ ) values of  $\text{Al}^{3+}/\text{Al}$ ,  $\text{Ag}^+/\text{Ag}$ ,  $\text{K}^+/\text{K}$  and  $\text{Cr}^{3+}/\text{Cr}$  are  $-1.66\text{ V}$ ,  $0.80\text{ V}$ ,  $-2.93\text{ V}$  and  $-0.74\text{ V}$ , respectively. The correct decreasing order of reducing power of the metal is ***[NEET Odisha 2019]***

- (a) Al > K > Ag > Cr
  - (b) Ag > Cr > Al > K
  - (c) K > Al > Cr > Ag
  - (d) K > Al > Ag > Cr

21. Standard reduction potentials of the half reactions are given below :



The strongest oxidising and reducing agents respectively are : [2012 MJ]

- (a)  $\text{F}_2$  and  $\text{I}^-$       (b)  $\text{Br}_2$  and  $\text{Cl}^-$   
 (c)  $\text{Cl}_2$  and  $\text{Br}^-$       (d)  $\text{Cl}_2$  and  $\text{I}_2$

22. The oxide, which cannot act as a reducing agent, is [1995]

- (a)  $\text{NO}_2$       (b)  $\text{SO}_2$   
 (c)  $\text{CO}_2$       (d)  $\text{ClO}_2$

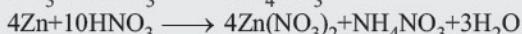
### ANSWER KEY

<b>1</b>	(d)	<b>4</b>	(b)	<b>7</b>	(b)	<b>10</b>	(a)	<b>13</b>	(b)	<b>16</b>	(b)	<b>19</b>	(b)	<b>22</b>	(c)
<b>2</b>	(c)	<b>5</b>	(d)	<b>8</b>	(b)	<b>11</b>	(a)	<b>14</b>	(c)	<b>17</b>	(d)	<b>20</b>	(c)		
<b>3</b>	(a)	<b>6</b>	(d)	<b>9</b>	(d)	<b>12</b>	(a)	<b>15</b>	(c)	<b>18</b>	(c)	<b>21</b>	(a)		

## Hints & Solutions



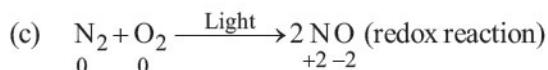
1. (d) Zinc gives  $\text{H}_2$  gas with dil  $\text{H}_2\text{SO}_4/\text{HCl}$  but not with  $\text{HNO}_3$  because in  $\text{HNO}_3$ ,  $\text{NO}_3^-$  ion is reduced and give  $\text{NH}_4\text{NO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$



Zn is above of hydrogen in electrochemical series. So, Zn displaces  $\text{H}_2$  from dilute  $\text{H}_2\text{SO}_4$  and HCl with liberation of  $\text{H}_2$ .



2. (c) (a)  $2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$  (neutralization)



here oxidation of  $\text{N}_2$  & reduction of  $\text{O}_2$  is taking place

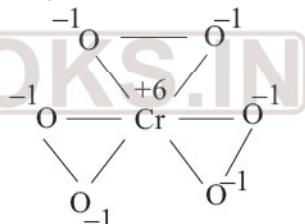


3. (a) Losing of electron is called oxidation.

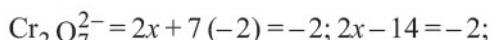
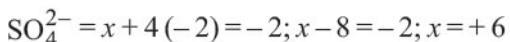
4. (b)  $\text{CH}_4(\text{g}) + 4\text{Cl}_2(\text{g}) \rightarrow \text{CCl}_4(\text{l}) + 4\text{HCl}(\text{g})$

Change in oxidation state of carbon is  $-4$  to  $+4$ .

5. (d)  $+6$  is the most appropriate oxidation state of Cr in  $\text{CrO}_6$ .

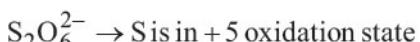
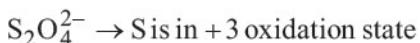


6. (d)  $\text{PO}_4^{3-} = x + 4(-2) = -3; x - 8 = -3; x = +5$



$$2x = 12; x = +6$$

7. (b)  $\text{SO}_3^{2-} \rightarrow$  S is in  $+4$  oxidation state



**NOTES** The structure of  $\text{S}_2\text{O}_4^{2-}$  and  $\text{S}_2\text{O}_6^{2-}$  are symmetrical. Thus, both sulphur atoms are in same oxidation state. This is not the case with  $\text{S}_2\text{O}_3^{2-}$  or  $\text{S}_4\text{O}_6^{2-}$  ions.

8. (b) Oxidation number of a compound must be 0. Using the values for A, B and C in the four options we find that  $A_3(BC_4)_2$  is the answer.

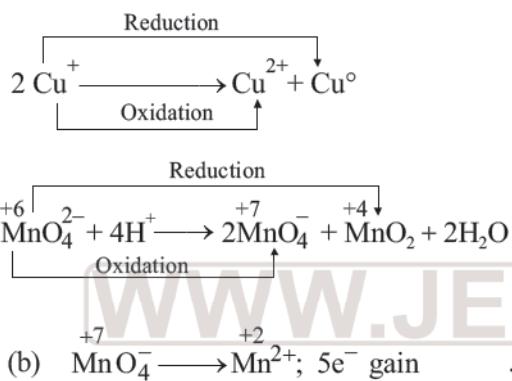
$$\text{Check : } (+2)3 + [(+5) + 4(-2)]2 = 6 + (5 - 8)2 = 0$$

9. (d) Pyrophosphoric acid  $H_4P_2O_7$   
 Let oxidation state of phosphorus is  $x$   
 $(4 \times 1 + (-2) \times 7 + 2x) = 0$   
 $\therefore 2x = 10$  or  $x = +5$

10. (a) Let  $x$  = oxidation no. of Cr in  $K_2Cr_2O_7$ .  
 $\therefore (2 \times 1) + (2 \times x) + 7(-2) = 0$   
 or  $2 + 2x - 14 = 0$  or  $x = +6$ .

11. (a) O.N. of P in  $H_3PO_3$  (phosphorous acid)  
 $3 \times 1 + x + 3 \times (-2) = 0$  or  $x = +3$   
 In orthophosphoric acid ( $H_3PO_4$ ) O.N. of P is +5, in hypophosphorous acid ( $H_3PO_2$ ) it is +1 while in metaphosphoric acid ( $HPO_3$ ), it is +5.

12. (a) In a disproportionation reaction, one species undergoes both oxidation and reduction.



13. (b)  $\text{MnO}_4^- \xrightarrow{\text{+1}} \text{Mn}^{2+}; 5\text{e}^- \text{ gain}$  ... (i)

$\text{C}_2\text{O}_4^{2-} \xrightarrow{\text{+3}} \text{CO}_2; 2\text{e}^- \text{ loss}$  ... (ii)

Multiplying (i) by 2 and (ii) by 5 to balance e<sup>-</sup>

$2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-} \longrightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2$

On balancing charge;

$2 \text{MnO}_4^- + 5 \text{C}_2\text{O}_4^{2-} + 16 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$

14. (c) Calculate  $E_{\text{cell}}^\circ$  corresponding to each compound undergoing disproportionation reaction. The reaction for which  $E_{\text{cell}}^\circ$  comes out + ve is spontaneous.

$\text{HBrO} \longrightarrow \text{Br}_2 E^\circ = 1.595 \text{ V, SRP (cathode)}$

$\text{HBrO} \longrightarrow \text{BrO}_3^- E^\circ = -1.5 \text{ V, SOP (anode)}$

$2\text{HBrO} \longrightarrow \text{Br}_2 + \text{BrO}_3^-$

$$E_{\text{cell}}^\circ = \text{SRP (cathode)} - \text{SRP (anode)}$$

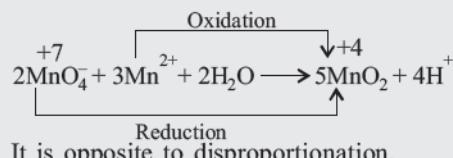
$$= 1.595 - 1.5$$

$$= 0.095 \text{ V}$$

$E_{\text{cell}}^\circ > 0 \Rightarrow \Delta G^\circ < 0$  [spontaneous]



Reaction in (d) involves comproportionation or synproportionation. When two reactants, each containing the same element but with a different oxidation number, form a product in which the element involved reach the same oxidation number.



**Reduction**  
It is opposite to disproportionation.

15. (c)  $\text{KClO}_3 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4$   
 $+ \text{KCl} + \text{CO}_2 + \text{H}_2\text{O}$   
*i.e.* maximum change in oxidation number is observed in Cl (+5 to -1).

16. (b) On reaction with hot and concentrated alkali a mixture of chloride and chlorate is formed  
 $3\text{Cl}_2 + 3 \text{NaOH}(\text{excess}) \xrightarrow{\text{Hot}}$   
 $5\text{NaCl} + \text{NaClO}_3 + 3\text{H}_2\text{O}$

17. (d)  $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$  .....(1)  
 $8\text{e}^- + 10\text{H}^+ + \text{NO}_3^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O}$  .....(2)  
 operate eq. (1)  $\times 4$  + eq. (2)  $\times 1$   
 $4\text{Zn} + 10\text{H}^+ + \text{NO}_3^- \rightarrow 4\text{Zn}^{+2} + \text{NH}_4^+ + 3\text{H}_2\text{O}$

18. (c)  $\overset{+2}{\text{Ba}} \overset{-1}{\text{O}_2} + \text{H}_2 \overset{+1}{\text{S}} \overset{+6}{\text{O}_4} \longrightarrow \overset{+2}{\text{Ba}} \overset{+6}{\text{S}} \overset{-2}{\text{O}_4} + \text{H}_2 \overset{+1}{\text{O}_2}$   
 In this reaction, none of the elements undergoes a change in oxidation number or valency.

19. (b) The element undergo oxidation itself and reduces others is known as reducing agent. In this reaction O. N. of Ni Changes from 0 to + 2 and hence Ni acts as a reducing agent.

20. (c) Lesser is the reduction potential greater is the reducing power.  
 Reducing power : K > Al > Cr > Ag

21. (a)  $\text{F}_2$  is the strongest oxidising agent as it has highest reduction potential while  $\text{I}^-$  is the strongest reducing agent since it has lowest reduction potential.



Higher the value of reduction potential, higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

22. (c) Carbon has the maximum oxidation state of + 4, therefore carbon dioxide ( $\text{CO}_2$ ) cannot act as a reducing agent.

# 9

# Hydrogen

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Preparation and properties of hydrogen	properties of hydrogen									1	A
Preparation and properties of water	hardness of water			1	A						
LOD - Level of Difficulty	E - Easy	A - Average		D - Difficult		Qns - No. of Questions					

### Topic 1: Preparation and Properties of Hydrogen

- Which of the following statements about hydrogen is incorrect? *[2016]*
  - hydrogen has three isotopes of which tritium is the most common.
  - Hydrogen never acts as cation in ionic salts
  - Hydronium ion,  $\text{H}_3\text{O}^+$  exists freely in solution
  - Dihydrogen does not act as a reducing agent
- When a substance *A* reacts with water, it produces a combustible gas *B* and a solution of substance *C* in water. When another substance *D* reacts with this solution of *C*, it also produces the same gas *B* on warming but *D* can produce gas *B* on reaction with dilute sulphuric acid at room temperature. *A* imparts a deep golden yellow colour to a smokeless flame of Bunsen burner. *A, B, C* and *D* respectively are *[1998]*
  - $\text{Na, H}_2, \text{NaOH, Zn}$
  - $\text{K, H}_2, \text{KOH, Al}$
  - $\text{Ca, H}_2, \text{Ca(OH)}_2, \text{Sn}$
  - $\text{CaC}_2, \text{C}_2\text{H}_2, \text{Ca(OH)}_2, \text{Fe}$
- Which one of the following pairs of substances on reaction will not evolve  $\text{H}_2$  gas? *[1998]*
  - Iron and  $\text{H}_2\text{SO}_4$  (aqueous)
  - Iron and steam
  - Copper and  $\text{HCl}$  (aqueous)
  - Sodium and ethyl alcohol

4. The hydride ion,  $\text{H}^-$ , is a stronger base than the hydroxide ion,  $\text{OH}^-$ . Which one of the following reactions will occur if sodium hydride ( $\text{NaH}$ ) is dissolved in water? *[1997]*

- $\text{H}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^-(\text{aq})$
- $\text{H}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$
- $\text{H}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{OH}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^-$
- $\text{H}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightarrow \text{reaction}$

5. The ionization of hydrogen atom would give rise to *[1990]*
- |                 |                   |
|-----------------|-------------------|
| (a) Hydride ion | (b) hydronium ion |
| (c) Proton      | (d) hydroxyl ion. |

### Topic 2: Preparation and Properties of Water

- The number of hydrogen bonded water molecules(s) associated with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is *[NEET 2019 Odisha]*
  - 5
  - 3
  - 1
  - 2
- The method used to remove temporary hardness of water is: *[2019]*
  - Calgon's method
  - Clark's method
  - Ion-exchange method
  - Synthetic resins method

8. Some statements about heavy water are given below:
- Heavy water is used as a moderator in nuclear reactors.
  - Heavy water is more associated than ordinary water.
  - Heavy water is more effective solvent than ordinary water.
- Which of the above statements are correct?
- (a) and (c)
  - (a) and (b) [2010]
  - (a), (b) and (c)
  - (b) and (c)
9. Which of the following groups of ions makes the water hard? [1994]
- Sodium and bicarbonate
  - Magnesium and chloride
  - Potassium and sulphate
  - Ammonium and chloride.
10. The dielectric constant of  $\text{H}_2\text{O}$  is 80. The electrostatic force of attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  will be [1994]
- reduced to 1/40 in water than in air
  - reduced to 1/80 in water than in air
  - will be increased to 80 in water than in air
  - will remain unchanged.
11. At its melting point, ice is lighter than water because [1992]
- $\text{H}_2\text{O}$  molecules are more closely packed in solid state
  - Ice crystals have hollow hexagonal arrangement of  $\text{H}_2\text{O}$  molecules.
  - On melting of ice the  $\text{H}_2\text{O}$  molecule shrinks in size
  - Ice forms mostly heavy water on first melting.
12. Calgon used as a water softener is [1989]
- $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$
  - $\text{Na}_4[\text{Na}_2(\text{PO}_3)_6]$

(c)  $\text{Na}_4[\text{Na}_4(\text{PO}_4)_5]$

(d)  $\text{Na}_4[\text{Na}_2(\text{PO}_4)_6]$

### Topic 3: Preparation and Properties of Hydrogen Peroxide

13. (i)  $\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{O}_2$   
(ii)  $\text{H}_2\text{O}_2 + \text{Ag}_2\text{O} \rightarrow 2\text{Ag} + \text{H}_2\text{O} + \text{O}_2$   
Role of hydrogen peroxide in the above reactions is respectively - [2014]
- Oxidizing in (i) and reducing in (ii)
  - Reducing in (i) and oxidizing in (ii)
  - Reducing in (i) and (ii)
  - Oxidizing in (i) and (ii)
14. When  $\text{H}_2\text{O}_2$  is oxidised, the product is [1999]
- $\text{OH}^-$
  - $\text{O}_2$
  - $\text{O}^{2-}$
  - $\text{HO}_2^-$
15. The volume strength of 1.5 N  $\text{H}_2\text{O}_2$  solution is
- 4.8L
  - 5.2L [1996]
  - 8.4L
  - 8.8L
16. The O—O—H bond angle in  $\text{H}_2\text{O}_2$  is [1994]
- $106^\circ$
  - $109^\circ 28'$
  - $120^\circ$
  - $97^\circ$
17. Which of the following is the true structure of  $\text{H}_2\text{O}_2$ ? [1989]
- (a)  $\text{H}-\text{O}-\text{O}-\text{H}$

(b)  $\begin{array}{c} \text{H} \\ | \\ \text{O}-\text{O} \\ | \\ \text{H} \end{array}$

(c)  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H}-\text{O}=\\ \diagdown \end{array}$

(d)  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H}-\text{O} \leftarrow \text{O} \\ \diagdown \end{array}$
18. The reaction of  $\text{H}_2\text{O}_2$  with sulphur is an example of ..... reaction [1988]
- Addition
  - Oxidation
  - Reduction
  - Redox

### ANSWER KEY

1	(a, d)	3	(c)	5	(c)	7	(b)	9	(b)	11	(b)	13	(c)	15	(c)	17	(b)
2	(a)	4	(b)	6	(c)	8	(b)	10	(b)	12	(a)	14	(b)	16	(d)	18	(d)

# Hints & Solutions

1. (a, d) Among the three isotopes of hydrogen, Protium ( ${}^1_1\text{H}$ ) is most common. It is an energetic reducing agent. It reduces oxides, chlorides and sulphides of certain metals and produce free metals at ordinary temperature.

$$\text{CuO} + 2\text{H} \rightarrow \text{Cu} + \text{H}_2\text{O}$$

2. (a)  $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 \uparrow$   
             'A'                          'C'                          'B'

$$\text{Zn} + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + \text{H}_2 \uparrow$$
  
             'D'                          'C'                          'B'
$$\text{Zn} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 \uparrow$$
  
             'D'                          'B'

Na produces golden yellow colour with smokeless flame of Bunsen burner.

3. (c)  $\text{Fe} + \text{dil. H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2 \uparrow$

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \uparrow$$
  
    Steam

$\text{Cu} + \text{dil. HCl} \rightarrow$  No reaction  
 Copper does not evolve  $\text{H}_2$  from acid as it is below hydrogen in electrochemical series.

$$2\text{Na} + \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C}_2\text{H}_5\text{ONa} + \text{H}_2 \uparrow$$

4. (b)  $\begin{matrix} \text{H}^- & (\text{aq}) + \text{H}_2\text{O}(\text{l}) \\ \text{base 1} & \end{matrix} \longrightarrow \begin{matrix} \text{OH}^- & (\text{aq}) + \text{H}_2(\text{g}) \\ \text{base 2} & \text{acid 2} \end{matrix}$

In this reaction  $\text{H}^-$  acts as bronsted base as it accepts one proton ( $\text{H}^+$ ) from  $\text{H}_2\text{O}$  to form  $\text{H}_2$ .

5. (c)  $\text{H}(\text{g}) \longrightarrow \text{H}^+(\text{g}) + \text{e}^-$ .

6. (c) The actual structure of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , so only one water molecule is associated with the molecule via hydrogen bond.

7. (b) In this method  $\text{Ca}(\text{OH})_2$  is used.

8. (b) Heavy water is used for slowing down the speed of neutrons and used as moderators. Boiling point of heavy water is more than that of ordinary water, so it is more associated. The dielectric constant of heavy water is slightly less than that of ordinary water. Hence, ordinary water is more effective solvent than heavy water.

9. (b) Temporary hardness is due to presence of bicarbonates of calcium and magnesium and permanent hardness is due to the sulphates or chlorides of both of calcium and magnesium.

10. (b) Electrostatic forces of attraction are reduced to  $1/80$ th in water.

**NOTES** Dielectric constant or relative permittivity is the factor by which the electric field between the charges is decreased relative to vacuum (or air as mentioned in this question).

11. (b) In liquid state, the  $\text{H}_2\text{O}$  molecules are held together by intermolecular H-bonds.

**NOTES** When water freezes at atmospheric pressure it crystallises in normal hexagonal form. In it, each oxygen atom is surrounded by 4 hydrogen atoms, two by strong covalent bonds and two by weak hydrogen bonds. Since hydrogen bonds are longer than covalent bonds. The molecules of water are not closely packed in crystal lattice. There exists a number of hollow spaces in the crystal lattice, which decreases the density of ice.

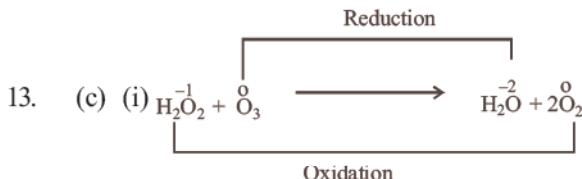
12. (a) The complex salt of metaphosphoric acid sodium hexametaphosphate  $(\text{NaPO}_3)_6$ , is known as calgon. It is represented as  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$

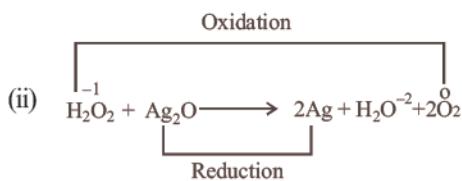
13. (c) (i)  $\begin{matrix} \text{H}_2\text{O}_2^{-1} & + \text{O}_3^0 \\ \text{Reduction} & \end{matrix} \longrightarrow \begin{matrix} \text{H}_2\text{O}^{-2} & + \text{O}_2^0 \\ \text{Oxidation} & \end{matrix}$

Dielectric constant or relative permittivity is the factor by which the electric field between the charges is decreased relative to vacuum (or air as mentioned in this question).

When water freezes at atmospheric pressure it crystallises in normal hexagonal form. In it, each oxygen atom is surrounded by 4 hydrogen atoms, two by strong covalent bonds and two by weak hydrogen bonds. Since hydrogen bonds are longer than covalent bonds. The molecules of water are not closely packed in crystal lattice. There exists a number of hollow spaces in the crystal lattice, which decreases the density of ice.

12. (a) The complex salt of metaphosphoric acid, sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub>, is known as calgon. It is represented as  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$



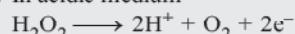


Hence, in both the reactions,  $\text{H}_2\text{O}_2$  is acting as an reducing agent.



Half equations for oxidation of  $\text{H}_2\text{O}_2$ :

(i) In acidic medium



(ii) In basic medium

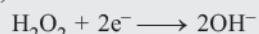


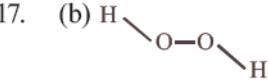
Half equations for reduction of  $\text{H}_2\text{O}_2$ :

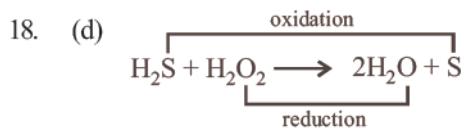
(i) In acidic medium



(ii) In basic medium



14. (b)  $\text{H}_2\text{O}_2 + [\text{O}] \xrightarrow{\text{Oxidation}} \text{H}_2\text{O} + \text{O}_2 \uparrow$
15. (c) Volume strength =  $5.6 \times \text{Normality} = 5.6 \times 1.5 = 8.4 \text{ L}$
16. (d) O – O – H bond angle in  $\text{H}_2\text{O}_2$  is  $97^\circ$ .
17. (b)  is the true structure of  $\text{H}_2\text{O}_2$ .



In this reaction,  $\text{H}_2\text{S}$  is oxidised to sulphur and  $\text{H}_2\text{O}_2$  is reduced to  $\text{H}_2\text{O}$ , hence this reaction show oxidation-reduction both i.e., redox reaction.

# 10

# The s-Block Elements



## Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Preparation and properties of alkali metals and their compounds	biological importance of alkali metals	1	E								
Some important compounds of sodium	properties of sodium chloride	1	E								
Preparation and properties of alkaline earth metal and their compounds	properties of alkaline earth metals compounds			1	A	2	A				
	biological importance of alkaline earth metals			1	E					1	E

WWW.IEEBOOKS.IN

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

Qns - No. of Questions

### Topic 1: Preparation and Properties of Alkali Metals and their Compounds

- The following metal ion activates many enzymes, participates in the oxidation of glucose to produce ATP and with Na, is responsible for the transmission of nerve signals. *[2020]*
  - Copper
  - Calcium
  - Potassium
  - Iron
- Which of the alkali metal chloride (MCl) forms its dihydrate salt ( $MCl \cdot 2H_2O$ ) easily? *[NEET Odisha 2019]*
  - KCl
  - LiCl
  - CsCl
  - RbCl
- The function of "Sodium pump" is a biological process operating in each and every cell of all animals. Which of the following biologically important ions is also a constituent of this pump: *[2015]*
  - $Mg^{2+}$
  - $K^+$
  - $Fe^{2+}$
  - $Ca^{2+}$

- Which one of the alkali metals, forms only, the normal oxide,  $M_2O$  on heating in air? *[2012]*
  - Rb
  - K
  - Li
  - Na
- The ease of adsorption of the hydrated alkali metal ions on an ion-exchange resins follows the order : *[2012]*
  - $Li^+ < K^+ < Na^+ < Rb^+$
  - $Rb^+ < K^+ < Na^+ < Li^+$
  - $K^+ < Na^+ < Rb^+ < Li^+$
  - $Na^+ < Li^+ < K^+ < Rb^+$
- In the replacement reaction  
 $\begin{array}{c} \diagup \\ Cl \end{array} + MF \longrightarrow \begin{array}{c} \diagup \\ CF \end{array} + MI$   
The reaction will be most favourable if M happens to be : *[2012 M]*
  - Na
  - K
  - Rb
  - Li
- The sequence of ionic mobility in aqueous solution is : *[2008]*
  - $K^+ > Na^+ > Rb^+ > Cs^+$
  - $Cs^+ > Rb^+ > K^+ > Na^+$

8. 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 ? [2008]

  - $\text{CsH} > \text{RbH} > \text{KH} > \text{NaH} > \text{LiH}$
  - $\text{KH} > \text{NaH} > \text{LiH} > \text{CsH} > \text{RbH}$
  - $\text{NaH} > \text{LiH} > \text{KH} > \text{RbH} > \text{CsH}$
  - $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH} > \text{CsH}$

9. The correct order of the mobility of the alkali metal ions in aqueous solutions is [2006]

  - $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+$
  - $\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Li}^+$
  - $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
  - $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$

10. In crystals of which one of the following ionic compounds would you expect maximum distance between centres of cations and anions? [1998]

  - $\text{LiF}$
  - $\text{CsF}$
  - $\text{CsI}$
  - $\text{LiI}$

11. Which of the following metal ions plays an important role in muscle contraction ? [1994]

  - $\text{K}^+$
  - $\text{Na}^+$
  - $\text{Mg}^{2+}$
  - $\text{Ca}^{2+}$

12. Which of the following statement is false ? [1994]

  - Strontium decomposes water readily than beryllium
  - Barium carbonate melts at a higher temperature than calcium carbonate
  - Barium hydroxide is more soluble in water than magnesium hydroxide
  - Beryllium hydroxide is more basic than barium hydroxide.

13. Which of the following has largest size ? [1993]

  - $\text{Na}$
  - $\text{Na}^+$
  - $\text{Na}^-$
  - Can't be predicted

14. Compared with the alkaline earth metals, the alkali metals exhibit [1990]

  - Smaller ionic radii
  - Highest boiling points
  - Greater hardness
  - Lower ionization energies.

15. Which one of the following properties of alkali metals increases in magnitude as the atomic number rises ? [1989]

  - Ionic radius
  - Melting point
  - Electronegativity
  - First ionization energy.

## **Topic 2: Some Important Compounds of Sodium**

23. Which of the following is known as fusion mixture? [1994]

(a) Mixture of  $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$   
 (b)  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$   
 (c) Mixture of  $\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$   
 (d)  $\text{NaHCO}_3$

24. Washing soda has formula [1990]

(a)  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$  (b)  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$   
 (c)  $\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$  (d)  $\text{Na}_2\text{CO}_3$

### Topic 3: Preparation and Properties of Alkaline Earth Metals and their Compounds

25. Which of the following is an amphoteric hydroxide ? [2019]

(a)  $\text{Sr}(\text{OH})_2$  (b)  $\text{Ca}(\text{OH})_2$   
 (c)  $\text{Mg}(\text{OH})_2$  (d)  $\text{Be}(\text{OH})_2$

26. Enzymes that utilize ATP in phosphate transfer require an alkaline earth metal ( $M$ ) as the cofactor.  $M$  is: [2019]

(a) Be (b) Mg  
 (c) Ca (d) Sr

27. Which of the following oxides is most acidic in nature? [2018]

(a)  $\text{MgO}$  (b)  $\text{BeO}$   
 (c)  $\text{CaO}$  (d)  $\text{BaO}$

28. Among  $\text{CaH}_2$ ,  $\text{BeH}_2$ ,  $\text{BaH}_2$ , the order of ionic character is [2018]

(a)  $\text{BeH}_2 < \text{CaH}_2 < \text{BaH}_2$   
 (b)  $\text{CaH}_2 < \text{BeH}_2 < \text{BaH}_2$   
 (c)  $\text{BaH}_2 < \text{BeH}_2 < \text{CaH}_2$   
 (d)  $\text{BeH}_2 < \text{BaH}_2 < \text{CaH}_2$

29. Which of the following statements is false ? [2016]

(a)  $\text{Mg}^{2+}$  ions form a complex with ATP  
 (b)  $\text{Ca}^{2+}$  ions are important in blood clotting  
 (c)  $\text{Ca}^{2+}$  ions are not important in maintaining the regular beating of the heart.  
 (d)  $\text{Mg}^{2+}$  ions are important in the green parts of plants.

30. Solubility of the alkaline earth's metal sulphates in water decreases in the sequence :- [2015]

(a)  $\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$  (b)  $\text{Sr} > \text{Ca} > \text{Mg} > \text{Ba}$   
 (c)  $\text{Ba} > \text{Mg} > \text{Sr} > \text{Ca}$  (d)  $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

31. Which of the following compounds has the lowest melting point ? [2011]

(a)  $\text{CaCl}_2$  (b)  $\text{CaBr}_2$   
 (c)  $\text{CaI}_2$  (d)  $\text{CaF}_2$

32. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy? [2010]

(a)  $\text{CaSO}_4$  (b)  $\text{BeSO}_4$   
 (c)  $\text{BaSO}_4$  (d)  $\text{SrSO}_4$

33. Property of the alkaline earth metals that increases with their atomic number [2010]

(a) Solubility of their hydroxides in water  
 (b) Solubility of their sulphates in water  
 (c) Ionization energy  
 (d) Electronegativity

34. The correct order of increasing thermal stability of  $\text{K}_2\text{CO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaCO}_3$  and  $\text{BeCO}_3$  is [2007]

(a)  $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{K}_2\text{CO}_3$   
 (b)  $\text{MgCO}_3 < \text{BeCO}_3 < \text{CaCO}_3 < \text{K}_2\text{CO}_3$   
 (c)  $\text{K}_2\text{CO}_3 < \text{MgCO}_3 < \text{CaCO}_3 < \text{BeCO}_3$   
 (d)  $\text{BeCO}_3 < \text{MgCO}_3 < \text{K}_2\text{CO}_3 < \text{CaCO}_3$

35. In which of the following the hydration energy is higher than the lattice energy? [2007]

(a)  $\text{MgSO}_4$  (b)  $\text{RaSO}_4$   
 (c)  $\text{SrSO}_4$  (d)  $\text{BaSO}_4$

36. Calcium is obtained by the [1997]

(a) electrolysis of solution of calcium chloride in water  
 (b) electrolysis of molten anhydrous calcium chloride or fused calcium chloride  
 (c) roasting of limestone  
 (d) reduction of calcium chloride with carbon

37. For two ionic solids  $\text{CaO}$  and  $\text{KI}$ , identify the wrong statement amongst the following : [1997]

(a) The lattice energy of  $\text{CaO}$  is much large than that of  $\text{KI}$   
 (b)  $\text{KI}$  is more soluble in water  
 (c)  $\text{KI}$  has higher melting point  
 (d)  $\text{CaO}$  has higher melting point

38. Which one is the correct statement with reference to solubility of  $\text{MgSO}_4$  in water? [1996]

(a)  $\text{SO}_4^{2-}$  ion mainly contributes towards hydration energy  
 (b) Sizes of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are similar  
 (c) Hydration energy of  $\text{MgSO}_4$  is higher in comparison to its lattice energy  
 (d) Ionic potential (charge/radius ratio) of  $\text{Mg}^{2+}$  is very low

39. Sodium is made by the electrolysis of a molten mixture of about 40% NaCl and 60% CaCl<sub>2</sub> because [1995]  
 (a) Ca<sup>2+</sup> can reduce NaCl to Na  
 (b) Ca<sup>2+</sup> can displace Na from NaCl  
 (c) CaCl<sub>2</sub> helps in conduction of electricity  
 (d) this mixture has a lower melting point than NaCl
40. All the following substances react with water. The pair that gives the same gaseous product is [1994]  
 (a) K and KO<sub>2</sub>      (b) Na and Na<sub>2</sub>O<sub>2</sub>  
 (c) Ca and CaH<sub>2</sub>      (d) Ba and BaO<sub>2</sub>
41. Which one of the following has minimum value of cation/anion ratio. [1993]  
 (a) NaCl      (b) KCl  
 (c) MgCl<sub>2</sub>      (d) CaF<sub>2</sub>
42. Electronic configuration of calcium atom can be written as [1992]  
 (a) [Ne], 4p<sup>2</sup>      (b) [Ar], 4s<sup>2</sup>  
 (c) [Ne], 4s<sup>2</sup>      (d) [Kr], 4p<sup>2</sup>
43. Which of the following atoms will have the smallest size? [1989]  
 (a) Mg      (b) Na  
 (c) Be      (d) Li

- Topic 4: Some Important Compounds of Calcium
44. On heating which of the following releases CO<sub>2</sub> most easily? [2015 RS]  
 (a) K<sub>2</sub>CO<sub>3</sub>      (b) Na<sub>2</sub>CO<sub>3</sub>  
 (c) MgCO<sub>3</sub>      (d) CaCO<sub>3</sub>
45. Which one of the following is present as an active ingredient in bleaching powder for bleaching action? [2011]  
 (a) CaOCl<sub>2</sub>      (b) Ca(OCl)<sub>2</sub>  
 (c) CaO<sub>2</sub>Cl      (d) CaCl<sub>2</sub>
46. Match List – I with List – II for the compositions of substances and select the correct answer using the code given below the lists : [2011M]

List - I Substances	List - II Composition			
(1) Plaster of paris	(i) CaSO <sub>4</sub> .2H <sub>2</sub> O			
(2) Epsomite	(ii) CaSO <sub>4</sub> .½H <sub>2</sub> O			
(3) Kieserite	(iii) MaSO <sub>4</sub> .7H <sub>2</sub> O			
(4) Gypsum	(iv) MgSO <sub>4</sub> .H <sub>2</sub> O			
	(v) CaSO <sub>4</sub>			
<b>Code :</b>				
(1)	(2)	(3)	(4)	
(a) (iii)	(iv)	(i)	(ii)	
(b) (ii)	(iii)	(iv)	(i)	
(c) (i)	(ii)	(iii)	(v)	
(d) (iv)	(iii)	(ii)	(i)	
47.	The compound A on heating gives a colourless gas and a residue that is dissolved in water to obtain B. Excess of CO <sub>2</sub> is bubbled through aqueous solution of B, C is formed which is recovered in the solid form. Solid C on gentle heating gives back A. The compound is [2010] (a) CaSO <sub>4</sub> .2H <sub>2</sub> O      (b) CaCO <sub>3</sub> (c) Na <sub>2</sub> CO <sub>3</sub> (d) K <sub>2</sub> CO <sub>3</sub>			
48.	A solid compound 'X' on heating gives CO <sub>2</sub> gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO <sub>2</sub> through 'Y' in water, a clear solution 'Z', is obtained. On boiling 'Z', a compound 'X' is reformed. The compound 'X' is [2004] (a) Ca(HCO <sub>3</sub> ) <sub>2</sub> (b) CaCO <sub>3</sub> (c) Na <sub>2</sub> CO <sub>3</sub> (d) K <sub>2</sub> CO <sub>3</sub>			
49.	Identify the correct statement [1995] (a) gypsum is obtained by heating plaster of Paris (b) plaster of Paris can be obtained by hydration of gypsum (c) plaster of paris is obtained by partial oxidation of gypsum (d) gypsum contains a lower percentage of calcium than plaster of Paris			

## ANSWER KEY

1	(c)	6	(c)	11	(d)	16	(a)	21	(a)	26	(b)	31	(c)	36	(b)	41	(c)	46	(b)
2	(b)	7	(b)	12	(d)	17	(b)	22	(b)	27	(b)	32	(b)	37	(c)	42	(b)	47	(b)
3	(b)	8	(d)	13	(c)	18	(d)	23	(c)	28	(a)	33	(a)	38	(c)	43	(c)	48	(b)
4	(c)	9	(c)	14	(d)	19	(c)	24	(b)	29	(c)	34	(a)	39	(d)	44	(c)	49	(d)
5	(b)	10	(c)	15	(a)	20	(a)	25	(d)	30	(d)	35	(a)	40	(c)	45	(b)		

## Hints & Solutions

1. (c) Potassium (K) activates many enzymes to participate in oxidation of glucose to produce ATP and helps in the transmission of nerve signal along with Na.
2. (b) Only LiCl forms a dihydrate, other metal chlorides do not form hydrates.
3. (b) In sodium pump, high concentration of potassium ions and a low concentration of sodium ions are maintained within a cell by a plasma membrane protein.
4. (c) All the alkali metals when heated with oxygen form different types of oxides for example lithium forms lithium oxide ( $\text{Li}_2\text{O}$ ), sodium forms sodium peroxide ( $\text{Na}_2\text{O}_2$ ), while K, Rb and Cs form their respective superoxides.



$\text{Li}^+$  being smallest, combines with small anion  $\text{O}^{2-}$  to form stable  $\text{Li}_2\text{O}$ .

The  $\text{Na}^+$  being relatively larger than  $\text{Li}^+$  and weaker positive field than  $\text{Li}^+$ , combines with  $\text{O}_2^{2-}$  (peroxide ion) to form  $\text{Na}_2\text{O}_2$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  being relative larger than  $\text{Na}^+$  and with weaker positive field than  $\text{Na}^+$  combines with  $\text{O}_2^-$  (superoxide ion) to for  $\text{KO}_2$ ,  $\text{RbO}_2$  and  $\text{CsO}_2$  respectively.

5. (b) All alkali metal salts are ionic (except Lithium) and soluble in water due to the fact that cations get hydrated by water molecules. The degree of hydration depends upon the size of the cation. Smaller the size of a cation, greater is its hydration energy.

Relative ionic radii :



Relative ionic radii in water or relative degree of hydration:



6. (c) Tertiary halide can show ionic reaction with MF so, MF should be most ionic for reaction to proceed forward. Hence 'M' should be 'Rb'.
7. (b) Smaller the ion more is its ionic mobility in aqueous solution. Ionic radii of the given alkali metals is in the order  $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$  and thus expected ionic mobility will be in the same

order  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$ . However due to high degree of solvation (or hydration) and because of lower size or high charge density, the hydrated ion size follows the same order  $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$  and thus conductivity order is  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+$ .

8. (d) The stability of alkali metal hydrides decreases from Li to Cs. It is due to the fact that M-H bonds becomes 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



9. (c) Hydrated Ionic radii of alkali metals in water follows the order  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$  Thus in aqueous solution due to larger ionic radius  $\text{Li}^+$  has lowest mobility and hence the correct order of ionic mobility is



10. (c) As  $\text{Cs}^+$  ion has larger size than  $\text{Li}^+$  and  $\text{I}^-$  has larger size than  $\text{F}^-$ , therefore maximum distance between centres of cations and anions is in  $\text{CsI}$ .
11. (d)  $\text{Ca}^{2+}$  ions is an essential element for the contraction of muscles.
12. (d)  $\text{Be}(\text{OH})_2$  is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases gradually.
13. (c) A cation is always much smaller than the corresponding atom, whereas an anion is always larger than the corresponding atom, hence the size decreases in the order



14. (d) Because of larger size and smaller nuclear charge, alkali metals have low ionization potential relative to alkaline earth metals.
15. (a) Within a group, ionic radius increases with increase in atomic number. The melting point decrease down the group due to weakening of metallic bond. The electronegativity and the 1<sup>st</sup> ionization energy also decreases down the group.

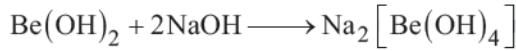
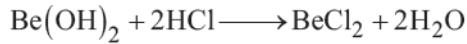
16. (a) When HCl is passed through the solution  $\text{Cl}^-$  ion concentration increases. Hence ionic product becomes more than solubility product. Only NaCl is crystallised due to less solubility than  $\text{MgCl}_2$  and  $\text{CaCl}_2$ .
17. (b) Crude sodium chloride which is obtained by crystallisation of brine solution contains  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are present as impurities in crude.
18. (d) In castner kellner cell, sodium amalgam is formed at mercury cathode.



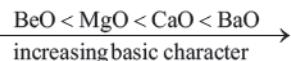
NOTES

Sodium is discharged from brine at a mercury cathode in preference to hydrogen because of the high hydrogen overpotential at mercury surface. This is the reason of using mercury cathode instead of graphite or platinum in castner-kellner cell.

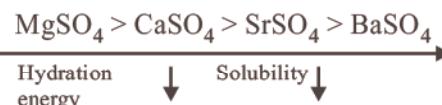
19. (c)  $2\text{Al(s)} + 2\text{NaOH(aq)} + 2\text{H}_2\text{O(l)} \longrightarrow 2\text{NaAlO}_2 + 3\text{H}_2$   
sod. meta aluminate
20. (a) NaOH is a strong alkali. It combines with acidic and amphoteric oxides to form salts. Since CaO is a basic oxide hence does not react with NaOH.
21. (a) In Castner process, for production of (Na) sodium metal, sodium hydroxide (NaOH) is electrolysed at  $330^\circ\text{C}$ .
22. (b)  $\text{Na}_2\text{CO}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{NaNO}_2 + \text{CO}_2$
23. (c) Mixture of  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  is called as fusion mixture.
24. (b) Washing soda is  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ .
25. (d) Amphoteric hydroxide means it can react with both acid and base.



26. (b) Enzyme that utilise ATP in phosphate transfer require an alkaline earth metal (M) Mg as the cofactor.
27. (b) In metals, moving down the group, metallic character increases, so basic nature increases hence most acidic will be BeO.



28. (a)  $\text{BeH}_2 < \text{CaH}_2 < \text{BaH}_2$   
Smaller the size of cation, more will be its polarising power. Hence,  $\text{BeH}_2$  will be least ionic.
29. (c) Calcium regulates muscle contraction, including beating of heart muscle, so that it can contract and pump out blood to all our body.
30. (d) Solubility of alkaline earth metal sulphates decreases down the group due to decrease in hydration energy.



31. (c) Melting point of metal halides decreases as the size of the halogen increases. The correct order is
- $$\text{CaF}_2 > \text{CaCl}_2 > \text{CaBr}_2 > \text{CaI}_2$$
32. (b)  $\text{Be}^{2+}$  is very small, hence its hydration enthalpy is greater than its lattice enthalpy. Also, hydration energy decreases down the group.
33. (a) The magnitude of hydration energy for the hydroxides of alkaline earth metals remains almost same whereas lattice energy decreases appreciably down the group. Hence, solubility increases down the group.
34. (a) As the cation size increases down the group, the metal carbonates become more ionic in nature. Hence, the thermal stability increases as:  $\text{BeCO}_3 < \text{MgCO}_3 < \text{CaCO}_3$ .  
The ionic character of group 1 carbonates is more than that of group 2, thus they possess more thermal stability. Hence, the correct order of thermal stability :  $\text{BeCO}_3 < \text{MgCO}_3 < \text{CuCO}_3 < \text{K}_2\text{CO}_3$ .
35. (a) The solubility and the hydration energy of sulphates of alkaline earth metals decreases as we move down the group from Be to Ba due to the reason that ionic size increases down the group. The lattice energy remains constant because sulphate ion is so large, so that small change in cationic sizes do not make any difference. Thus the order will be:
- $$\text{BeSO}_4 > \text{MgSO}_4 > \text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$$

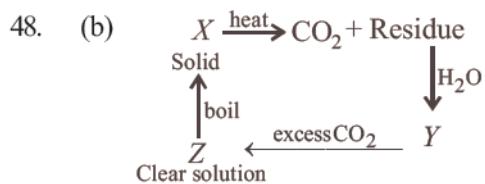
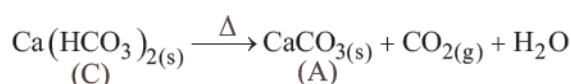
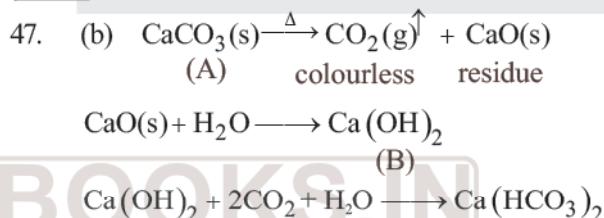
36. (b) Calcium is obtained by electrolysis of a fused mass consisting six parts calcium chloride and one part calcium fluoride at about  $700^{\circ}\text{C}$  in an electrolytic cell.
37. (c)  $\text{CaO}$  has higher lattice energy because of higher charge on  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ , which results in higher attraction.  $\text{KI}$  is more soluble in water because of low lattice energy and higher hydration energy. Clearly (c) is wrong because  $\text{CaO}$  has higher melting point as compared to  $\text{KI}$ .
38. (c)  $\text{MgSO}_4$  is the only alkaline earth metal sulphate which is soluble in water and for solubility hydration energy should be greater than lattice energy.
39. (d) Sodium is obtained by electrolytic reduction of its chloride. Melting point of chloride of sodium is high ( $803^{\circ}\text{C}$ ) so in order to lower its melting point ( $600^{\circ}\text{C}$ ), calcium chloride is added to it.
40. (c)  $\text{Ca}$  and  $\text{CaH}_2$  both react with water to form  $\text{H}_2$  gas,
- $$\text{Ca} + 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + \text{H}_2$$
- $$\text{CaH}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ca}(\text{OH})_2 + 2\text{H}_2$$
- whereas
- $\text{K}$  gives  $\text{H}_2$  while  $\text{KO}_2$  gives  $\text{O}_2$  and  $\text{H}_2\text{O}_2$
- $$2\text{K} + 2\text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{H}_2$$
- $$2\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{O}_2 + \text{H}_2\text{O}_2$$
- $$2\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{KOH} + \text{O}_2 + \text{H}_2\text{O}_2$$
- Similarly,  $\text{Na}$  gives  $\text{H}_2$  while  $\text{Na}_2\text{O}_2$  gives  $\text{H}_2\text{O}_2$
- $$2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2$$
- $$\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$$
- Also,  $\text{Ba}$  gives  $\text{H}_2$  while  $\text{BaO}_2$  gives  $\text{H}_2\text{O}_2$
- $$\text{Ba} + 2\text{H}_2\text{O} \longrightarrow \text{Ba}(\text{OH})_2 + \text{H}_2$$
- $$\text{BaO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Ba}(\text{OH})_2 + \text{H}_2\text{O}_2$$
41. (c) Atomic size of  $\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$  and that of  $\text{Cl}^- > \text{F}^-$ . Therefore,  $\text{Mg}^{2+}/\text{Cl}^-$  ratio has the minimum value.
42. (b)  ${}_{20}\text{Ca} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 = [\text{Ar}] 4s^2$
43. (c) Within a period, the atomic size decreases from left to right. Further atomic size increases down the group. Hence the correct order is i.e.  $\text{Na} > \text{Mg} > \text{Li} > \text{Be}$ .

44. (c) Carbonates becomes more thermally stable down the group, therefore  $\text{MgCO}_3$  will leave  $\text{CO}_2$  easily.
45. (b) Active ingredient in bleaching powder for bleaching action is  $\text{Ca(OCl)}_2$ .

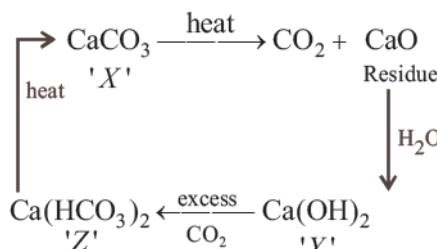
**NOTES**  
Bleaching powder is a mixture of calcium hypochlorite  $\text{Ca(OCl)}_2$ , dibasic calcium hypochlorite  $\text{Ca(OCl)}_2 \cdot 2\text{Ca(OH)}_2$  and dibasic calcium chloride  $\text{CaCl}_2 \cdot 2\text{Ca(OH)}_2$ .

46. (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 =  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

**NOTES**  
Plaster of paris can be more accurately written as  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$



The given properties coincide with  $\text{CaCO}_3$



49. (d) Gypsum is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and plaster of Paris is  $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ . Therefore, gypsum contains a lower percentage of calcium than plaster of Paris.

# 11

# The *p*-Block Elements (Group 13 & 14)

 Trend Analysis with Important Topics & Sub-Topics 

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Boron family	multiple concept (structure, formulae)	1	A								
	physical/chemical properties of elements of gp 13					1	E				
Carbon family	oxides of carbon	1	A								
	multiple concept (zeolites, allotropes, oxides of carbon)	1	A								
	inert pair effect							1	A		
	properties of halides of gp 14			2	A						

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

Qns - No. of Questions

## Topic 1: Boron Family

1. Match the following and identify the correct option. *[2020]*

- |   |  |
|---|--|
| (A) $\text{CO(g)} + \text{H}_2\text{(g)}$ | (i) $\text{Mg}(\text{HCO}_3)_2^+$<br>$\text{Ca}(\text{HCO}_3)_2$ |
| (B) Temporary hardness of water           | (ii) An electron deficient hydride                               |
| (C) $\text{B}_2\text{H}_6$                | (iii) Synthesis gas  |
| (D) $\text{H}_2\text{O}_2$                | (iv) Non-planar structure  |
| (A)    (B)    (C)    (D)                  |  |
| (a) (iii)    (ii)    (i)    (iv)          |  |
| (b) (iii)    (iv)    (ii)    (i)          |  |
| (c) (i)    (iii)    (ii)    (iv)          |  |
| (d) (iii)    (i)    (ii)    (iv)          |  |

2. Aluminium chloride in acidified aqueous solution forms a complex ‘A’, in which hybridisation state of Al is ‘B’. What are ‘A’ and ‘B’, respectively? *[NEET Odisha 2019]*

- (a)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $d_2sp^3$
- (b)  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ,  $sp^3d^2$
- (c)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ ,  $sp^3$
- (d)  $[\text{Al}(\text{H}_2\text{O})_4]^{3+}$ ,  $dsp^2$

3. Which one of the following elements is unable to form ion? *[2018]*

- (a) Ga
- (b) Al
- (c) In
- (d) B

4. The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence : *[2015 RS]*

- (a)  $\text{Ga} < \text{In} < \text{Al} < \text{Tl}$
- (b)  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
- (c)  $\text{Tl} < \text{In} < \text{Ga} < \text{Al}$
- (d)  $\text{In} < \text{Tl} < \text{Ga} < \text{Al}$

## Topic 2: Carbon Family

19. Which of these is not a monomer for a high molecular mass silicone polymer? [NEET 2013]  
 (a)  $\text{Me}_2\text{SiCl}_2$       (b)  $\text{Me}_3\text{SiCl}$   
 (c)  $\text{PhSiCl}_3$       (d)  $\text{MeSiCl}_3$
20. The basic structural unit of silicates is : [NEET 2013]  
 (a)  $\text{SiO}_4^{4-}$       (b)  $\text{SiO}_3^{2-}$   
 (c)  $\text{SiO}_4^{2-}$       (d)  $\text{SiO}$
21. Which statement is wrong? [NEET Kar. 2013]  
 (a) Feldspars are not aluminosilicates  
 (b) Beryl is an example of cyclic silicate  
 (c)  $\text{Mg}_2\text{SiO}_4$  is orthosilicate  
 (d) Basic structural unit in silicates is the  $\text{SiO}_4$  tetrahedron
22. Name the type of the structure of silicate in which one oxygen atom of  $[\text{SiO}_4]^{4-}$  is shared? [2011]  
 (a) Linear chain silicate  
 (b) Sheet silicate  
 (c) Pyrosilicate  
 (d) Three dimensional
23. The straight chain polymer is formed by [2009]  
 (a) hydrolysis of  $\text{CH}_3\text{SiCl}_3$  followed by condensation polymerisation  
 (b) hydrolysis of  $(\text{CH}_3)_4\text{Si}$  by addition polymerisation  
 (c) hydrolysis of  $(\text{CH}_3)_2\text{SiCl}_2$  followed by condensation polymerisation  
 (d) hydrolysis of  $(\text{CH}_3)_3\text{SiCl}$  followed by condensation polymerisation
24. Which one of the following statements about the zeolites is **false**? [2004]  
 (a) They are used as cation exchangers  
 (b) They have open structure which enables them to take up small molecules
- (c) Zeolites are aluminosilicates having three dimensional network  
 (d) Some of the  $\text{SiO}_4^{4-}$  units are replaced by  $\text{AlO}_4^{5-}$  and  $\text{AlO}_6^{9-}$  ions in zeolites
25. Glass reacts with HF to produce [2000]  
 (a)  $\text{SiF}_4$       (b)  $\text{H}_2\text{SiF}_6$   
 (c)  $\text{H}_2\text{SiO}_3$       (d)  $\text{Na}_3\text{AlF}_6$
26. In graphite, electrons are [1993, 1994]  
 (a) Localised on every third C-atom  
 (b) Present in anti-bonding orbital  
 (c) Localised on each C-atom  
 (d) Spread out between the structure
27. Which of the following types of forces bind together the carbon atoms in diamond? [1992]  
 (a) Ionic      (b) Covalent  
 (c) Dipolar      (d) van der Waals.
28. Water gas is produced by [1992]  
 (a) Passing steam through a red hot coke bed  
 (b) Saturating hydrogen with moisture  
 (c) Mixing oxygen and hydrogen in the ratio of 1 : 2  
 (d) Heating a mixture of  $\text{CO}_2$  and  $\text{CH}_4$  in petroleum refineries.
29. Glass is a [1991]  
 (a) Liquid  
 (b) Solid  
 (c) Supercooled liquid  
 (d) Transparent organic polymer
30. The substance used as a smoke screen in warfare is [1989]  
 (a)  $\text{SiCl}_4$       (b)  $\text{PH}_3$   
 (c)  $\text{PCl}_5$       (d) Acetylene

## ANSWER KEY

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

## Hints & Solutions

1. (d)
    - A. Mixture of CO and H<sub>2</sub> gases is known as water gas or synthesis gas.
    - B. Temporary hardness of water is due to bicarbonates of calcium and magnesium.
    - C. Diborane (B<sub>2</sub>H<sub>6</sub>) is an electron deficient hydride.
    - D. H<sub>2</sub>O<sub>2</sub> is non-planar molecule having open book like structure.
  2. (b) AlCl<sub>3</sub>  $\xrightarrow{\text{Acidified aq. sol.}}$  [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>  
*sp<sup>3</sup>d<sup>2</sup>*
  3. (d) MF<sub>6</sub><sup>3-</sup>  
Boron belongs to 2<sup>nd</sup> period and it does not have vacant d-orbital.
  4. (b) Lower oxidation state become more stable on moving down the group  
 $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
  5. (d) Boron nitride (BN) is known as inorganic graphite. The most stable form is hexagonal one. It has layered structure similar to graphite.
  6. (c) Fused alumina (Al<sub>2</sub>O<sub>3</sub>) is a bad conductor of electricity. Therefore, cryolite (Na<sub>3</sub>AlF<sub>6</sub>) and fluorspar (CaF<sub>2</sub>) are added to purified alumina which not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K.
  7. (b) In BF<sub>3</sub>, p-p overlap between B and F is maximum due to identical size and energy of p-orbitals, so electron deficiency in boron of BF<sub>3</sub> is neutralized partially to the maximum extent by back donation. Also, the tendency to back donate decreases from F to I. So the order will be:  
 $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$
  8. (b) Al<sub>2</sub>O<sub>3</sub> can be converted to anhydrous AlCl<sub>3</sub> by heating a mixture of Al<sub>2</sub>O<sub>3</sub> and carbon in dry Cl<sub>2</sub> gas.
- $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 \xrightarrow[1000^\circ\text{C}]{\substack{\text{vapours} \\ \text{cooled}}} 2\text{AlCl}_3 + 3\text{CO}$   
Solid anhydrous aluminium chloride
9. (b) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. 10H<sub>2</sub>O  $\xrightarrow[-10\text{H}_2\text{O}]^{\Delta} \text{Na}_2\text{B}_4\text{O}_7 \longrightarrow 2\text{NaBO}_2 + \text{B}_2\text{O}_3$   
anhydrous sod.metaborate Boric anhydride
  10. (a) H<sub>3</sub>BO<sub>3</sub> is a weak monobasic acid.
  11. (a) On a commercial scale, chlorine is prepared by electrolysis of an aqueous solution of sodium chloride (brine solution). Cl<sub>2</sub> is evolved at the anode.  
(b) Br<sub>2</sub> is prepared by passing Cl<sub>2</sub> gas through sea water containing NaBr, kBr etc.  
(c) Al is extracted by electrolysis of fused mixture of alumina, cryolite and fluorspar.
- NOTES** Products of electrolysis depend on the concentration of electrolyte, overvoltage factor and the electrodes used. Also, the commercial viability is an important factor.
12. (d) Potash Alum, K<sub>2</sub>SO<sub>4</sub>. Al<sub>2</sub>(SO<sub>4</sub>). 24H<sub>2</sub>O is a double salt.
  13. (b) The carboxyhaemoglobin (haemoglobin bound to CO), is about 300 times more stable than oxyhaemoglobin.
  14. (c)
    - A. Dry ice, CO<sub>2</sub>(s), is used as refrigerant
    - B. C<sub>60</sub> contains 20 six membered rings, 12 five membered rings
- NOTES** Zeolites are crystalline, 3D aluminosilicates. ZSM-5 contain two sets of perpendicular, intersecting channel, one is 10 membered another is 8 membered.
15. (d) Silicones are used in cosmetic surgery.
  16. (a) PbF<sub>4</sub> is ionic in nature due to high electronegativity difference.
  17. (d) [SiCl<sub>6</sub>]<sup>2-</sup> does not exist because six large chloride ions cannot be accommodated around Si<sup>4+</sup>, due to its small size.

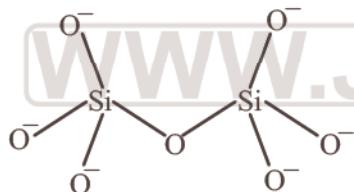
18. (d) Due to inert pair effect, Pb(II) is more stable than Pb(IV)  
 Sn(IV) is more stable than Sn(II)  
 $\therefore$  Pb(IV) is easily reduced to Pb(II) and can act as an oxidising agent whereas Sn(II) is easily oxidised to Sn(IV) and can act as a reducing agent.



Inertness of  $ns^2$  electrons of the valence shell to participate in bonding on moving down the group in heavier p-block elements is called inert pair effect. It occurs due to poor shielding of the  $ns^2$  electrons of the valence shell by the intervening d and f electrons.

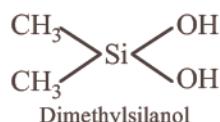
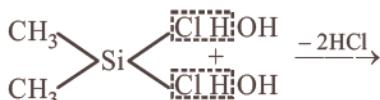
19. (b) Since  $\text{Me}_3\text{SiCl}$  contains only one Cl, therefore it can't form high molecular mass silicon polymer. It can form only dimer.  
 20. (a)  $\text{SiO}_4^{4-}$  is basic structural unit of silicates.  
 21. (a) Feldspars are 3-dimensional aluminosilicates.

22. (c)

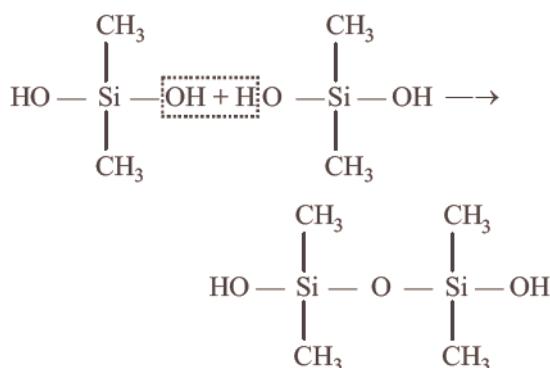


Pyrosilicate ( $\text{Si}_2\text{O}_7$ ) $^{6-}$

23. (c) Hydrolysis of substituted chlorosilanes yield corresponding silanols which undergo polymerisation.



Polymerisation of dimethylsilanol yields linear thermoplastic polymer.

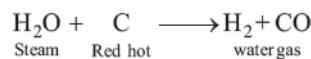


24. (c) Zeolites are crystalline solid structures made up of silicon, aluminium and oxygen making a framework with cavities.



Zeolites have  $\text{SiO}_4^{4-}$  and  $\text{AlO}_4^{5-}$  tetrahedrons linked together in a 3-D open structure in which 4 or 6 membered rings predominate. Due to open structure they have cavities and can take up water and other small molecules.

25. (b)  $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$   
 26. (d) In graphite, each carbon is  $sp^2$ -hybridized and the single occupied unhybridized p-orbital of C-atoms overlap side ways to give  $\pi$ -electron cloud which is delocalized and thus the electrons are spread out between the structure.  
 27. (b) In diamond, each carbon atom is  $sp^3$  hybridized and thus, forms covalent bonds with four other carbon atoms lying at the corners of a regular tetrahedron.  
 28. (a) Water gas is made by blowing steam through the layer of incandescent coal.



29. (c) Glass is a super cooled liquid.



Supercooling is the process of lowering the temperature of a liquid or gas below its freezing point without becoming a solid.

30. (a)  $\text{SiCl}_4$  gets hydrolysed in moist air and gives white fumes which are used as a smoke screen in warfare.

# 12

# Organic Chemistry - Some Basic Principles and Techniques

Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Classification and nomenclature of organic compounds	IUPAC nomenclature							1	E		
Concept of reaction mechanism in organic compounds	stability of carbocation/ carbanion	1	A			1	D			1	A
	chromatography/ distillation	1	E					1	A		
	electrophilic substitution reactions			1	A			1	A		
	inductive effect					1	A				

LOD - Level of Difficulty

E - Easy

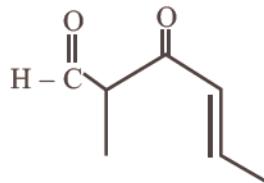
A - Average

D - Difficult

Qns - No. of Questions

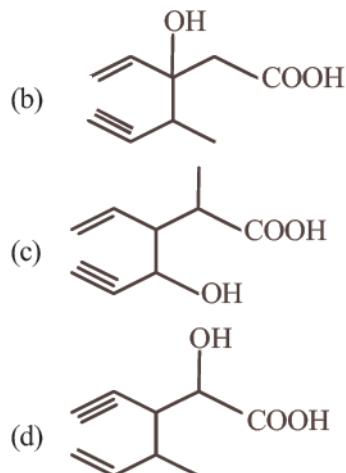
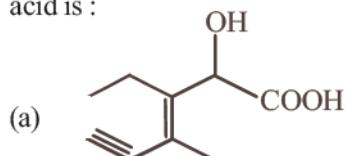
## Topic 1: Classification and Nomenclature of Organic Compounds

1. The IUPAC name of the compound is : [2017]



- (a) 5-formylhex-2-en-3-one
- (b) 5-methyl-4-oxohex-2-en-5-al
- (c) 3-keto-2-methylhex-5-enal
- (d) 3-keto-2-methylhex-4-enal

2. Structure of the compound whose IUPAC name is 3-ethyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid is : [NEET 2013]



3. The structure of isobutyl group in an organic compound is : [NEET 2013]

- (a)  $\text{CH}_3 - \underset{|}{\text{CH}} - \text{CH}_2 - \text{CH}_3$
- (b)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 -$

- (c)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \\ | \\ \text{CH}_3 \end{array}$

(d)  $\begin{array}{c} \text{CH}_3 \\ \backslash \\ (\text{CH}_3) \text{CH} - \text{CH}_2 - \end{array}$

4. Which nomenclature is not according to IUPAC system? [2012]

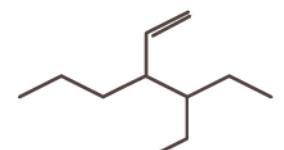
(a)  $\text{Br} - \text{CH}_2 - \text{CH} = \text{CH}_2$ ,  
1-Bromo-prop-2-ene

(b)  $\begin{array}{ccccc} & \text{CH}_3 & & & \\ & | & & & \\ \text{CH}_3 - & \text{CH}_2 - & \text{C} - & \text{CH}_2 - & \text{CHCH}_3 \\ & | & & & | \\ & \text{Br} & & & \text{CH}_3 \end{array}$   
4-Bromo-2, 4-dimethylhexane

(c)  $\begin{array}{ccccc} \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 - \text{CH}_3 \\ | & & | & & | \\ \text{CH}_3 & - & \text{CH} & - & \text{CH}_2 - \text{CH}_3 \\ | & & | & & | \\ \text{CH}_3 & & \text{C}_6\text{H}_5 & & \text{CH}_3 \end{array}$   
2-Methyl-3-phenylpentane

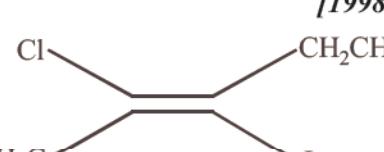
(d)  $\begin{array}{ccccc} \text{CH}_3 & - & \text{C} & - & \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{COOH} \\ || & & & & | \\ \text{O} & & & & \text{O} \end{array}$   
5-oxohexanoic acid

5. The correct IUPAC name of the compound [2011]



(a) 4-Ethyl-3-propyl hex-1-ene  
(b) 3-Ethyl-4-ethenyl heptane  
(c) 3-Ethyl-4-propyl hex-1-ene  
(d) 3-(1-ethylpropyl) hex-1-ene

6. The IUPAC name of the following compound is [1998, 2011 M]



(a) trans-2-chloro-3-iodo-2-pentene  
(b) cis-3-iodo-4-chloro-3-pentene  
(c) trans-3-iodo-4-chloro-3-pentene  
(d) cis-2-chloro-3-iodo-2-pentene

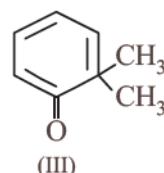
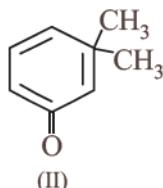
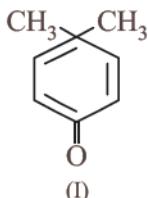
- (c)  $\text{CH}_3 - \text{CH}_2 - \underset{\substack{\parallel \\ \text{CH}_2}}{\text{C}} - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \text{CH}_3$   
2-Ethyl-3-methylbut-1-ene
- (d)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH} - (\text{CH}_3)_2$   
4-Methyl-2-pentyne
13. Name of the compound given below is [2003]
- 
- (a) 5-ethyl-6-methyloctane  
(b) 4-ethyl-3-methyloctane  
(c) 3-methyl-4-ethyloctane  
(d) 2, 3-diethylheptane
14. IUPAC name of the following is [2002]  
 $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{C} \equiv \text{CH}$
- (a) 1, 5-hexenyne    (b) 1-hexene- 5-yne  
(c) 1-hexyne- 5-ene    (d) 1, 5-hexynene
15. The incorrect IUPAC name is [2001]
- (a)  $\text{CH}_3 - \underset{\substack{\parallel \\ \text{O}}}{{\text{C}}}-\text{CH} - \text{CH}_3$   
2-Methyl-3-butanone
- (b)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \underset{\substack{| \\ \text{CH}_2\text{CH}_3}}{\text{CH}} - \text{CH}_3$   
2,3-Dimethylpentane
- (c)  $\text{CH}_3\text{CH} - \underset{\substack{| \\ \text{Cl}}}{{\text{CH}}}-\underset{\substack{| \\ \text{Br}}}{{\text{CH}}}-\text{CH}_3$   
2-Bromo-3-chlorobutane
- (d)  $\text{CH}_3 - \text{C} \equiv \text{CCH}(\text{CH}_3)_2$   
4-Methyl-2-pentyne
16. The structural formula of a compound is  $\text{CH}_3 - \text{CH} = \text{C} = \text{CH}_2$ . The types of hybridization at the four carbons from left to right are
- (a)  $sp^2, sp^2, sp^2, sp^3$     (b)  $sp^2, sp^3, sp^2, sp^2$   
(c)  $sp^3, sp^2, sp, sp^2$     (d)  $sp^3, sp^2, sp^2, sp^2$
17. The IUPAC name of [1996]
- 
- is
- (a) 1, 3-isopropyl-3-methylpropane  
(b) 2, 3, 6-trimethylheptane  
(c) 2, 5, 6-trimethylheptane  
(d) 2, 6, 3-trimethylheptane
18. Huckel's rule states that a monocyclic conjugated compound will be aromatic if it contains [1996]
- (a)  $(4n + 2\pi)$  electrons  
(b)  $(4\pi + 2n)$  electrons  
(c)  $4\pi$  electrons  
(d)  $(4n + 2)\pi$  electrons
19. The first organic compound, synthesized in the laboratory, was [1995]
- (a) alcohol    (b) acetic acid  
(c) urea    (d) none of these
20. Which of the following IUPAC names is correct for the compound? [1994]
- $\text{H}_3\text{C} - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \underset{\substack{| \\ \text{CH}_2\text{CH}_3}}{\text{CH}} - \text{CH}_2 - \text{CH}_3$
- (a) 2-Methyl-3-ethylpentane  
(b) 3-Ethyl-2-methylpentane  
(c) 2-Ethyl-3-methylpentane  
(d) 3-Methyl-2-ethylpentane
21. Which is the correct symbol relating the two Kekule structures of benzene? [1993]
- (a)  $\rightleftharpoons$     (b)  $\longleftrightarrow$   
(c)  $=$     (d)  $\leftrightarrow$
22. When the hybridization state of carbon atom changes from  $sp^3$  to  $sp^2$  and finally to  $sp$ , the angle between the hybridized orbitals [1993]
- (a) decreases gradually  
(b) decreases considerably  
(c) is not affected  
(d) increases progressively.
23. The IUPAC name of [1992]
- $\text{CH}_3 - \text{CH} - \text{CH} = \text{C} - \text{CHO}$
- $\begin{array}{c} | & | \\ \text{OH} & \text{CH}_3 \end{array}$
- (a) 4-Hydroxy-1-methylpentanal  
(b) 4-Hydroxy-2-methylpent-2-en-1-al  
(c) 2-Hydroxy-4-methylpent-3-en-5-al  
(d) 2-Hydroxy-3-methylpent-2-en-5-al
24. 2-Methyl-2-butene will be represented as [1992]
- $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{CH} - \text{CH}_2\text{CH}_3 \end{array}$
- (b)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{C}} = \text{CH} - \text{CH}_3$

- (c)  $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\underset{|}{\text{C}}} = \text{CH}_2$
- (d)  $\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH} = \text{CH}_2$
25. A straight chain hydrocarbon has the molecular formula  $\text{C}_8\text{H}_{10}$ . The hybridization of the carbon atoms from one end of the chain to the other are respectively  $sp^3$ ,  $sp^2$ ,  $sp^2$ ,  $sp^3$ ,  $sp^2$ ,  $sp^2$ ,  $sp$  and  $sp$ . The structural formula of the hydrocarbon would be : [1991]
- (a)  $\text{CH}_3\text{C} \equiv \text{CCH}_2 - \text{CH} = \text{CHCH} = \text{CH}_2$   
 (b)  $\text{CH}_3\text{CH}_2 - \text{CH} = \text{CHCH} = \text{CHC} \equiv \text{CH}$   
 (c)  $\text{CH}_3\text{CH} = \text{CHCH}_2 - \text{C} \equiv \text{CCH} = \text{CH}_2$   
 (d)  $\text{CH}_3\text{CH} = \text{CHCH}_2 - \text{CH} = \text{CH} - \text{C} \equiv \text{CH}$ .
26. An  $sp^3$  hybrid orbital contains [1991]  
 (a) 1/4 s-character      (b) 1/2 s-character  
 (c) 1/3 s-character      (d) 2/3 s-character.
27. The shortest C – C bond distance is found in [1991]  
 (a) Diamond      (b) Ethane  
 (c) Benzene      (d) Acetylene
28. An organic compound  $X$  (molecular formula  $\text{C}_6\text{H}_7\text{O}_2\text{N}$ ) has six carbon atoms in a ring system, two double bonds and a nitro group as substituent,  $X$  is [1990]  
 (a) Homocyclic but not aromatic  
 (b) Aromatic but not homocyclic  
 (c) Homocyclic and aromatic  
 (d) Heterocyclic and aromatic
29. Which of the following possesses a  $sp$ -carbon in its structure ? [1989]  
 (a)  $\text{CH}_2 = \text{CCl} - \text{CH} = \text{CH}_2$   
 (b)  $\text{CCl}_2 = \text{CCl}_2$   
 (c)  $\text{CH}_2 = \text{C} = \text{CH}_2$   
 (d)  $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$
30. Cyclic hydrocarbon ‘A’ has all the carbon and hydrogen atoms in a single plane. All the carbon carbon bonds have the same length, less than 1.54 Å, but more than 1.34 Å. The C – C – C bond angle will be [1989]  
 (a)  $109^\circ 28'$       (b)  $100^\circ$   
 (c)  $180^\circ$       (d)  $120^\circ$
31. The Cl – C – Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about [1988]

- (a)  $120^\circ$  and  $120^\circ$       (b)  $90^\circ$  and  $109.5^\circ$   
 (c)  $109.5^\circ$  and  $90^\circ$       (d)  $120^\circ$  and  $109.5^\circ$

### Topic 2: Isomerism in Organic Compounds

32. Given



Which of the given compounds can exhibit tautomerism? [2015]

- (a) I and III      (b) II and III  
 (c) I, II and III      (d) I and II

33. Which one of the following pairs represents stereoisomerism? [2005]

- (a) Structural isomerism and Geometrical isomerism  
 (b) Optical isomerism and Geometrical isomerism  
 (c) Chain isomerism and Rotational isomerism.  
 (d) Linkage isomerism and Geometrical isomerism

34.  $\text{CH}_2 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$  and  $\text{CH}_2 = \text{C} - \text{CH}_3$  are [2002]

- (a) Resonating structures  
 (b) Tautomers  
 (c) Geometrical isomers  
 (d) Optical isomers

35. Tautomerism will be exhibited by [1997]

- (a)  $(\text{CH}_3)_2\text{NH}$       (b)  $(\text{CH}_3)_3\text{CNO}$   
 (c)  $\text{R}_3\text{CNO}_2$       (d)  $\text{RCH}_2\text{NO}_2$

36. The number of possible isomers of the compound with molecular formula  $\text{C}_7\text{H}_8\text{O}$  is [1995]

- (a) 3      (b) 5  
 (c) 7      (d) 9

37. Isomers of a substance must have the same [1991]

- (a) Structural formula  
 (b) Physical properties  
 (c) Chemical properties  
 (d) Molecular formula

38. How many chain isomers could be obtained from the alkane  $\text{C}_6\text{H}_{14}$ ? [1988]

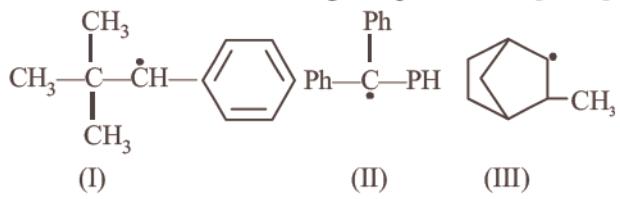
- (a) Four      (b) Five  
 (c) Six      (d) Seven

**Topic 3: Concept of Reaction Mechanism in Organic Compounds**

39. A tertiary butyl carbocation is more stable than a secondary butyl carbocation because of which of the following? [2020]
- + R effect of  $-\text{CH}_3$  groups
  - R effect of  $-\text{CH}_3$  groups
  - Hyperconjugation
  - I effect of  $-\text{CH}_3$  groups
40. Paper chromatography is an example of [2020]
- Partition chromatography
  - Thin layer chromatography
  - Column chromatography
  - Adsorption chromatography
41. The most stable carbocation, among the following, is [NEET Odisha, 2019]
- $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{CH}}$
  - $(\text{CH}_3)_3\text{C}-\overset{\oplus}{\text{CH}}-\text{CH}_3$
  - $\text{CH}_3-\text{CH}_2-\overset{\oplus}{\text{CH}}-\text{CH}_2-\text{CH}_3$
  - $\text{CH}_3-\overset{\oplus}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
42. Among the following, the reaction that proceeds through an electrophilic substitution, is: [2019]
- - 
  - 
  -

43. Which of the following carbocations is expected to be most stable? [2018]
- (a)
- (b)
- (c)
- (d)
44. Which of the following is correct with respect to - I effect of the substituents? (R = alkyl) [2018]
- $-\text{NH}_2 < -\text{OR} < -\text{F}$
  - $-\text{NR}_2 < -\text{OR} < -\text{F}$
  - $-\text{NR}_2 > -\text{OR} > -\text{F}$
  - $-\text{NH}_2 > -\text{OR} > -\text{F}$
45. The most suitable method of separation of 1 : 1 mixture of ortho and para-nitrophenols is: [1994, 2017]
- Chromatography
  - Crystallisation
  - Steam distillation
  - Sublimation
46. The correct statement regarding electrophile is:- [2017]
- Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from another electrophile
  - Electrophiles are generally neutral species and can form a bond by accepting a pair of electrons from a nucleophile
  - Electrophile can be either neutral or positively charged species and can form a bond by accepting a pair of electrons from a nucleophile
  - Electrophile is a negatively charged species and can form a bond by accepting a pair of electrons from a nucleophile
47. The pair of electron in the given carbanion,  $\text{CH}_3\text{C}\equiv\text{C}^-$ , is present in which of the following orbitals? [2016]
- $2p$
  - $sp^3$
  - $sp^2$
  - $sp$
48. Which of the following statements is not correct for a nucleophile? [2015 RS]
- Nucleophile is a Lewis acid
  - Ammonia is a nucleophile
  - Nucleophiles attack on less  $e^-$  density sites
  - Nucleophiles are not electron seeking.

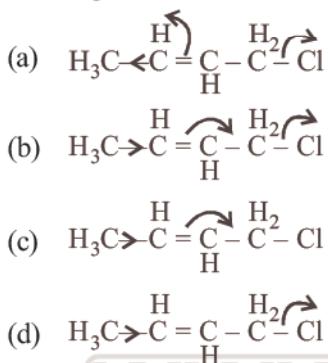
49. Consider the following compounds [2015]



Hyperconjugation occurs in :



50. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? **[2015]**



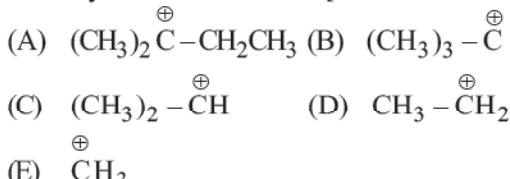
51. In Duma's method for estimation of nitrogen, 0.25 g of an organic compound gave 40 mL of nitrogen collected at 300 K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is : **[2015I]**



52. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M  $\text{H}_2\text{SO}_4$ . The percentage of nitrogen in the soil is : [2014]



53. Arrange the following in increasing order of stability **[NEET Kar. 2013]**



- (a) E < D < C < B < A (b) E < D < C < A < B  
 (c) D < E < C < A < B (d) A < E < D < C < B

54. Homolytic fission of the following alkanes forms free radicals  $\text{CH}_3 - \text{CH}_3$ ,  $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ ,  $(\text{CH}_3)_2 \text{CH} - \text{CH}_3$ ,  $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$ . Increasing order of stability of the radicals is

[NEET Kar. 2013]

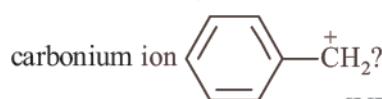
- (a)  $(CH_3)_3 \dot{C} < (CH_3)_2 \dot{C} - CH_2CH_3 <$   
 $CH_3 - \dot{C} H - CH_3 < CH_3 - \dot{C} H_2$

(b)  $(CH_3)_2 \dot{C} - CH_2CH_3 < CH_3 - \dot{C} H - CH_3 <$   
 $CH_3 - \dot{C} H_2 < (CH_3)_3 \dot{C}$

(c)  $CH_3 - \dot{C} H_2 < CH_3 - \dot{C} H - CH_3 <$   
 $(CH_3)_2 \dot{C} - CH_2 - CH_3 < (CH_3)_3 \dot{C}$

(d)  $CH_3 - \dot{C} H_2 < CH_3 - \dot{C} H - CH_3 < (CH_3)_3 \dot{C} < (CH_3)_2 \dot{C} - CH_2CH_3$

55. What is the hybridisation state of benzyl?



[NEET Kar. 2013]



56. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed corresponds to which of the following formulae?

- (a)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_3$       (b)  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$   
 (c)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_2$       (d)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$

- The correct order of increasing bond length

57. The correct order of increasing bond length of C–H, C–O, C–C and C=C is: [2011]

- (a) C – H < C = C < C – O < C – C  
 (b) C – C < C = C < C – O < C – H  
 (c) C – O < C – H < C – C < C = C  
 (d) C – H < C – O < C – C < C = C

58. In Duma's method of estimation of nitrogen, 0.35 g of an organic compound gave 55 mL of nitrogen collected at 300 K temperature and 715 mm pressure. The percentage composition of nitrogen in the compound would be :

- (Aqueous tension at 300 K = 15 mm) [2011]

59. The Lassaigne's extract is boiled with conc.  
 $\text{HNO}_3$  while testing for halogens. By doing so it

- (a) decomposes  $\text{Na}_2\text{S}$  and  $\text{NaCN}$ , if formed.
  - (b) helps in the precipitation of  $\text{AgCl}$ .
  - (c) increases the solubility product of  $\text{AgCl}$ .
  - (d) increases the concentration of  $\text{NO}_3^-$  ions.

60. The stability of carbanions in the following :



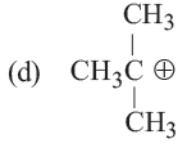
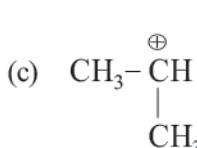
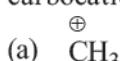
is in the order of :

[2008]

- (a) (a) > (b) > (c) > (d) (b) (b) > (c) > (d) > (a)

- (c) (d) > (b) > (c) > (a) (d) (a) > (c) > (b) > (d)

61. Which amongst the following is the most stable carbocation? [2005]



62. The best method for the separation of naphthalene and benzoic acid from their mixture is [2005]

- (a) distillation (b) sublimation
- 
- (c) chromatography (d) crystallisation

63. In steam distillation of toluene, the pressure for toluene in vapour is [2001]

- (a) Equal to pressure of barometer
- 
- (b) Less than pressure of barometer
- 
- (c) Equal to vapour pressure of toluene in simple distillation
- 
- (d) More than vapour pressure of toluene in simple distillation

64. Which one of the following order is correct regarding the – I effect of the substituents ? [1998]

- (a)
- $-\text{NR}_2 < -\text{OR} > -\text{F}$
- (b)
- $-\text{NR}_2 > -\text{OR} > -\text{F}$
- 
- (c)
- $-\text{NR}_2 < -\text{OR} < -\text{F}$
- (d)
- $-\text{NR}_2 > -\text{OR} < -\text{F}$

65. Which one of the following is a technique most suitable for purification of cyclohexanone from a mixture containing benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone? [1997]

- (a) Crystallization
- 
- (b) Sublimation
- 
- (c) IR spectroscopy
- 
- (d) Gas chromatography

66. Lassaigne's test for the detection of nitrogen fails in [1994]

- (a)
- $\text{NH}_2\text{CONHNH}_2\cdot\text{HCl}$
- (b)
- $\text{NH}_2\text{NH}_2\cdot\text{HCl}$

- (c)
- $\text{NH}_2\text{CONH}_2$
- (d)
- $\text{C}_6\text{H}_5\text{NHNH}_2\cdot\text{HCl}$

67. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of a mixture of A and B can be carried out easily by using a solution of [1992]

- (a) Sodium hydroxide (b) Sodium sulphate
- 
- (c) calcium chloride (d) Sodium bicarbonate

68. Which of the following is the most stable carbocation (carbonium ion)? [1991]



69. In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into [1991]

- (a) Sodaamide (b) Sodium cyanide
- 
- (c) Sodium nitrite (d) Sodium nitrate

70. Kjeldahl's method is used in the estimation of [1990]

- (a) Nitrogen (b) Halogens
- 
- (c) Sulphur (d) Oxygen

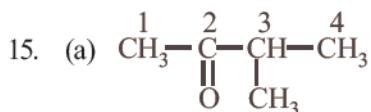
71. Lassaigne's test is used in qualitative analysis to detect [1989]

- (a) Nitrogen (b) Sulphur
- 
- (c) Chlorine (d) All of these

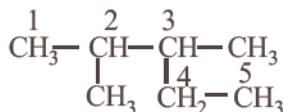
## ANSWER KEY

1	(d)	9	(c)	17	(b)	25	(d)	33	(b)	41	(d)	49	(b)	57	(a)	65	(c)
2	(a)	10	(c)	18	(d)	26	(a)	34	(a)	42	(b)	50	(b)	58	(b)	66	(b)
3	(d)	11	(a)	19	(c)	27	(d)	35	(d)	43	(d)	51	(b)	59	(a)	67	(d)
4	(a)	12	(a)	20	(b)	28	(a)	36	(b)	44	(a)	52	(a)	60	(a)	68	(c)
5	(a)	13	(b)	21	(d)	29	(c)	37	(d)	45	(c)	53	(b)	61	(d)	69	(b)
6	(a)	14	(b)	22	(d)	30	(d)	38	(b)	46	(c)	54	(c)	62	(b)	70	(a)
7	(d)	15	(a)	23	(b)	31	(d)	39	(c)	47	(d)	55	(b)	63	(b)	71	(d)
8	(b)	16	(c)	24	(b)	32	(c)	40	(a)	48	(a)	56	(c)	64	(c)		

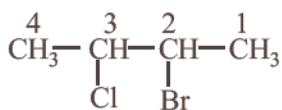




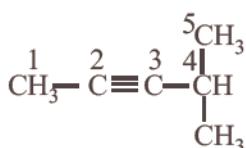
3 Methyl-2- butanone



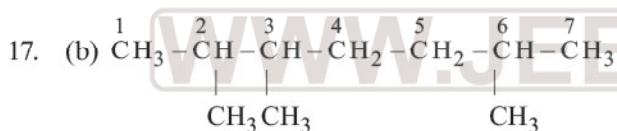
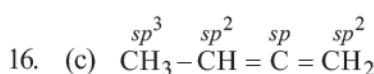
2, 3 dimethyl pentane



2 Bromo-3-chlorobutane

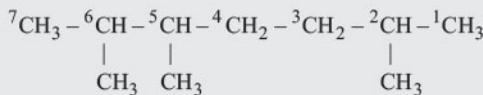


4-Methyl-2-pentyne

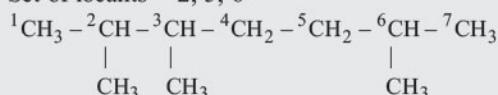


2, 3, 6 – trimethylheptane

**NOTES**  
When many substituents are present, the numbering is done from the end where the first point of difference is the lowest number.



Set of locants = 2, 5, 6



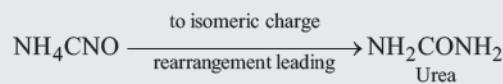
Set of locants = 2, 3, 6

The first point of difference 3 is lower than the number 5 of first set. Thus, the correct name is 2, 3, 6-trimethylheptane.

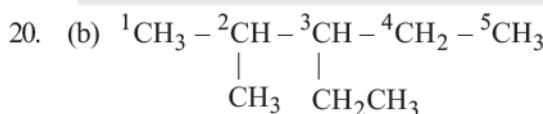
18. (d) Huckel's rule states that for aromaticity there must be  $(4n + 2)\pi$  electrons present in a compound, where  $n$  is an integer.  
 19. (c) Urea is the first organic compound synthesized in the laboratory by wohler.



The vital force theory suffered first death blow in 1828 when Wohler synthesized the Ist organic compound urea in the laboratory from inorganic compounds reported below :



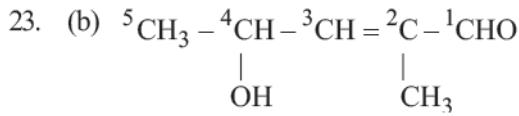
Later on a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.



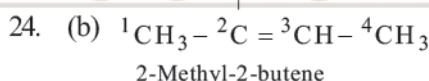
3-Ethyl-2-methylpentane

21. (d) Resonance structures are separated by a double headed arrow ( $\longleftrightarrow$ )

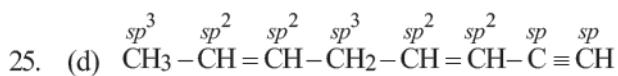
22. (d) Angle increases progressively  
 $sp^3$  ( $109^\circ 28'$ ),  $sp^2$  ( $120^\circ$ ),  $sp$  ( $180^\circ$ )



4-Hydroxy-2-methylpent-2-en-1-ol

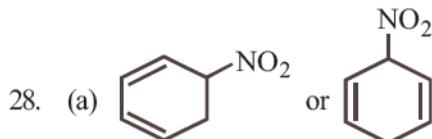
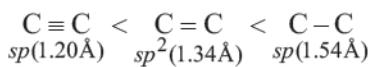


2-Methyl-2-butene



26. (a)  $sp^3$  orbital has 1/4(25%) s-character & 75% p-character.

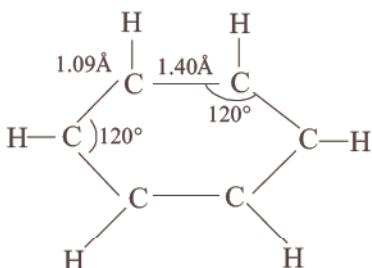
27. (d) Shortest C – C distance ( $1.20 \text{ \AA}$ ) is in acetylene, as acetylene has  $sp$  hybridisation. The bond length increases in the order



Hence it is homocyclic (as the ring system is made of one type of atoms, i.e. carbon) but not aromatic. As it does not follow  $(4n + 2)\pi$  electron rule of aromaticity.

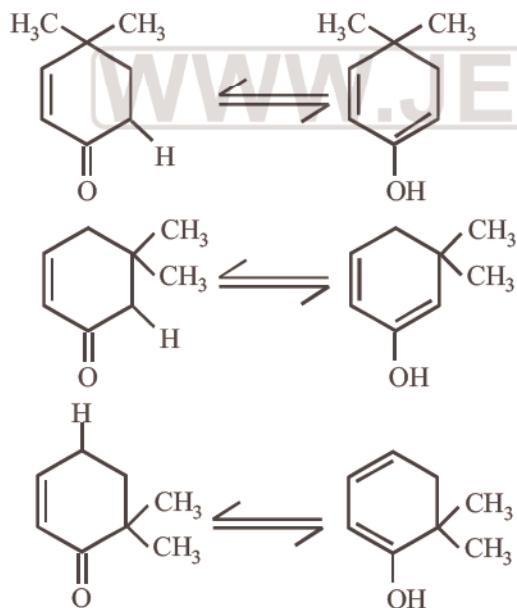
29. (c)  $\text{CH}_2 = \overset{sp^2}{\text{C}} = \overset{sp^2}{\text{C}} = \text{CH}_2$

30. (d) All the properties mentioned in the question suggest that it is a benzene molecule. Since in benzene all carbons are  $sp^2$ -hybridized, therefore, C – C – C angle is  $120^\circ$ .

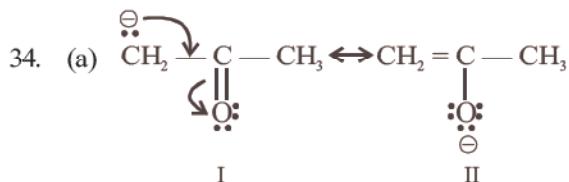


31. (d) Tetrachloroethene being an alkene has  $sp^2$ -hybridized C– atoms and hence the angle Cl–C–Cl is  $120^\circ$  while in tetrachloromethane, carbon is  $sp^3$  hybridized, therefore the angle Cl–C–Cl is  $109.5^\circ$ .

32. (c) All of these compounds show tautomerism

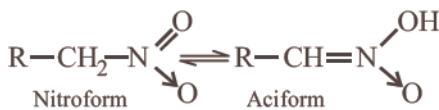


33. b) Optical and geometrical isomerism pair up to exhibit stereoisomerism. This is because the isomers differ only in their orientation in space.



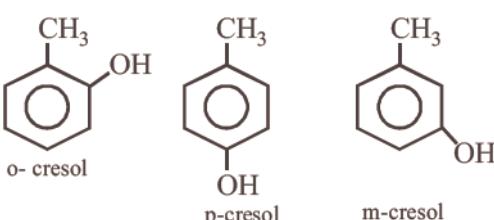
both are resonating structures.

35. (d) As option (d) has  $\alpha$ -hydrogen atom. Therefore it shows tautomerism whereas other structures do not.

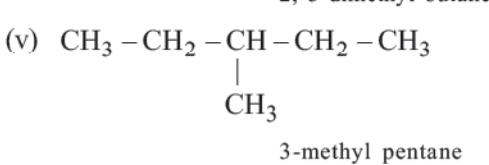
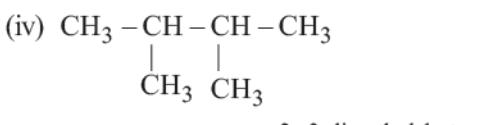
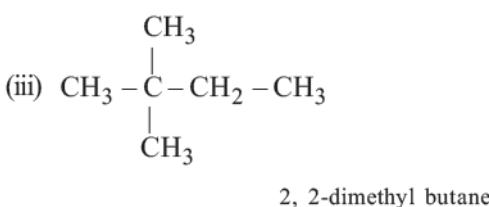
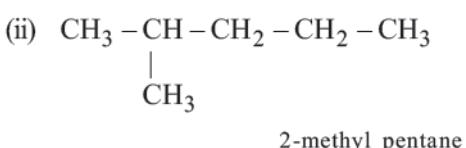


Tautomerism is exhibited by the oscillation of hydrogen atom between two polyvalent atoms present in the molecule.

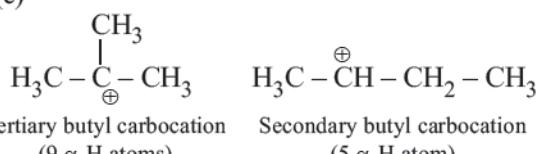
36. (b) The possible isomers of the compound with molecular formula  $C_7H_8O$  is 5. These are  $C_6H_5OCH_3$ ,  $C_6H_5CH_2OH$  and



37. (d) Organic compounds having same molecular formula but differ from each other in physical or chemical properties or structural formula are



39. (c)

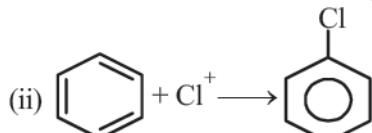


*t*-Butyl carbocation is more stable due to hyperconjugation.

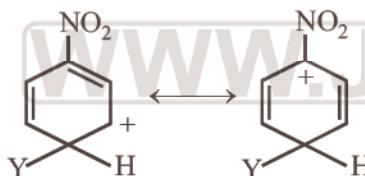
40. (a) Paper chromatography is a type of partition chromatography.

41. (d) Stability of carbocation  $\propto$  No. of  $\alpha$ -H  
 Among the given carbocations,  
 $\begin{array}{c} \oplus \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \end{array}$  is the most  
 stable carbocation (5  $\alpha$ -H)

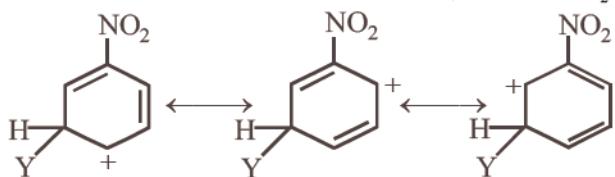
42. (b) (i)  $\text{AlCl}_3 + \text{Cl} - \text{Cl} \rightarrow [\text{AlCl}_4]^- + \text{Cl}^+$   
 Electrophile



43. (d)  $-\text{NO}_2$  group is meta-directing group



(Less stable due to more  $e^-$  withdrawing effect of  $-\text{NO}_2$ )



(More stable due to less  $e^-$  withdrawing effect of  $-\text{NO}_2$ ) greater no. of resonating structures.

44. (a)  $-I$  effect increases on increasing electronegativity of atom. So, correct order of  $-I$  effect is  $-\text{NH}_2 < -\text{OR} < -\text{F}$ .

45. (c) The *o*-isomer is steam volatile due to intramolecular H-bonding. The *p*-isomer is not steam volatile due to intermolecular H-bonding or association of molecules. Thus, both can be separated by steam distillation.

46. (c) Electrophile is an electron deficient species and can accept pair of electrons from nucleophile

47. (d)  $\text{CH}_3-\text{C}\equiv\text{C}^\ominus$

No. of  $\sigma$  bp  $-1 \left[ \frac{1}{lp-1} \right]$  2 & hybridisation is  $sp$

48. (a) Nucleophiles are usually lewis bases.

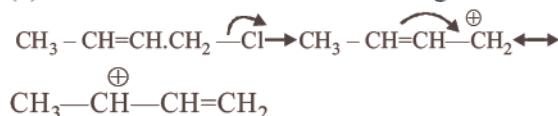


Nucleophile is a species that provide electron while species which are deficient of electrons are termed as lewis acid.

49. (b) Only structure (III) has H in conjugation with free radical.

So, hyperconjugation is possible in III only.

50. (b)  $\pi$  bond is transferred after leaving  $\text{Cl}^-$



Hyperinflation results from the interaction of  $\sigma$  bond electrons with an adjacent empty or partially filled *p*-orbital or a orbital to give an extended molecular orbital that increase the stability.

51. (b) Wt. of organic substance = 0.25 g

$$V_1 = 40 \text{ mL}, T_1 = 300 \text{ K}$$

$$P_1 = 725 - 25 = 700 \text{ mm of Hg}$$

$$P_2 = 760 \text{ mm of Hg (at STP)}$$

$$T_2 = 273 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$V_2$  (Volume of nitrogen at STP)

$$= \frac{273 \times 700 \times 40}{300 \times 760} = 33.52 \text{ mL}$$

Percentage of nitrogen

$$= \frac{28 \times \text{volume of } \text{N}_2 \text{ at STP} \times 100}{22400 \times \text{wt. of organic substance}}$$

$$= \frac{28 \times 33.52 \times 100}{22400 \times 0.25} = 16.76\%$$

52. (a) 10 mL, 1 M  $\text{H}_2\text{SO}_4 = 20 \text{ mL, 1 M NH}_3$

$\therefore$  wt of N in one mole  $\text{NH}_3 = 14$

$$\therefore 20 \times 10^{-3} \text{ mol NH}_3 \longrightarrow$$

$$20 \times 10^{-3} \times 14 \text{ nitrogen}$$

$\therefore 0.75 \text{ g of sample contains}$

$$= \frac{14 \times 20 \times 10^{-3}}{0.75} \times 100 = 37.33\%$$

53. (b) Greater the number of  $e^-$  donating alkyl groups (+I effect), greater will be the stability of carbocations.

54. (c) Stability depends on number of hyperconjugative structure.
55. (b) In the carbonium ion the carbon atom carrying the positive charge is  $sp^2$  hybridized.
56. (c) The prussian blue colour is of  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$  ferric ferrocyanide
57. (a) Bond length order is



58. (b) Given wt of compound taken ( $w$ ) = 0.35 g

Volume of nitrogen collected ( $V$ ) = 55 mL

Room temperature ( $t$  K) = 300 K

Atmospheric pressure ( $P$ ) = 715 mm

Aq. tension ( $\rho$ ) = 15 mm

Calculation -

$$\text{Volume of N}_2 \text{ at NTP} = \frac{(P - \rho) \times V}{t} \times \frac{273}{760} \text{ mL}$$

$$= \frac{(715 - 15) \times 55}{300} \times \frac{273}{760} = 46.098 \text{ mL}$$

% of nitrogen

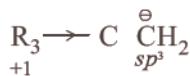
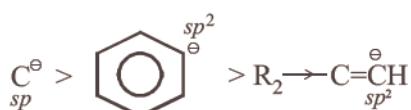
$$= \frac{28 \times \text{vol. of N}_2 \text{ at NTP} \times 100}{22400 \times \text{wt of organic compound}}$$

$$= \frac{28 \times 46.098 \times 100}{22400 \times 0.35} = 16.46\%$$

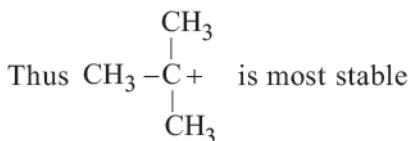
59. (a) Conc.  $\text{HNO}_3$  decomposes  $\text{NaCN}$  and  $\text{Na}_2\text{S}$  to avoid their interference.



60. (a) As 's' character increases, stability of carbanion increases. Also, electron donating groups decreases the stability of carbanion. Hence, the correct stability, order:



61. (d) More the number of alkyl groups, greater will be the dispersal of positive charge and therefore more the stability of carbocation.



62. (b) Among the given compounds naphthalene is volatile but benzoic acid is non-volatile (it forms a dimer). So, the best method for their separation is sublimation



**NOTES**  
Sublimation method is applicable to compounds which can be converted directly into the vapour phase from its solid state on heating and back to the solid state on cooling.

63. (b) The principle of steam distillation is based on Dalton's law of partial pressures. Suppose  $p_1$  and  $p_2$  be the vapour pressures of water vapour and the toluene at the distillation temperature. Toluene boils when total pressure is equal to atmospheric pressure  $p$  i.e.  $p = p_1 + p_2$  or  $p_2 = p - p_1$

As a result, when toluene boil in the presence of steam its partial pressure  $p_2$  is less than atmospheric pressure.

64. (c) As electronegativity of N, O & F follow the order  $\text{N} < \text{O} < \text{F}$  hence based upon electronegative character order of-I effect is  $-\text{NR}_2 < -\text{OR} < -\text{F}$ .



**NOTES**  
The atom or group which has more power to attract electrons in comparison to hydrogen is said to have -I effect. Thus higher the electronegativity of atom, stronger will be the -I effect.

65. (c) IR spectroscopy is used for the purification of cyclohexanone from a mixture of benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone. Because in this method, each functional group appear at a certain peak. So, cyclohexanone can be identified by carbonyl peak.



An amyl alcohol is any one of 8 alcohols with the formula  $\text{C}_5\text{H}_{12}\text{O}$  (alkanol with 5 carbons).

66. (b) Hydrazine ( $\text{NH}_2\text{NH}_2$ ) does not contain carbon and hence on fusion with Na metal, it cannot form  $\text{NaCN}$ ; so it does not show Lassaigne's test for nitrogen.

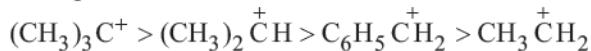


This test fails in case of diazo compounds, dinitro compounds and compounds containing nitrogen in the ring.

67. (d) Carboxylic acids dissolve in  $\text{NaHCO}_3$  and evolve  $\text{CO}_2$  gas but phenols do not.



68. (c) Higher the  $+I$  effect greater is stability of the species. Thus,



Also, primary benzyl carbocation have almost the same stability as  $2^\circ$ -alkyl carbocations.

69. (b) Sodium cyanide ( $\text{Na} + \text{C} + \text{N} \rightarrow \text{NaCN}$ ). (Lassaigne's test)
70. (a) Kjeldahl's method is suitable for estimating nitrogen in those compounds in which nitrogen is linked to carbon and hydrogen. This method



is basically used for estimating nitrogen in food fertilizers and agricultural products.

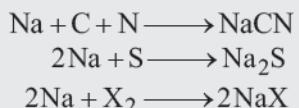


Kjeldahl's method is not used in case of nitro, azo and azoxy compound.

71. (d) Nitrogen, sulphur and halogens are tested in an organic compound by Lassaigne's test.



The organic compound is fused with sodium metal as to convert these elements into ionisable inorganic substances,



The cyanide, sulphide or halide ions can be confirmed in aqueous solution by usual test.

# 13

## Hydrocarbons



### Trend Analysis with Important Topics & Sub-Topics



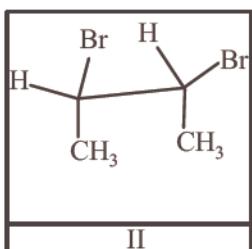
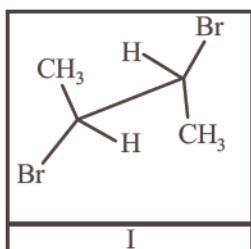
		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Alkanes	conversion (substitution/ wurtz reaction)					1	E				
	conformations of ethane							1	A	1	E
Alkenes	ozonolysis	1	A	1	A						
Alkyne	reduction of alkyne			1	E						
	order of acidity/acidic character							1	E	1	A
	hydration reaction							1	A		
LOD - Level of Difficulty	E - Easy	A - Average		D - Difficult		Qns - No. of Questions					

#### Topic 1: Alkanes

- The alkane that gives only one mono-chloro product on chlorination with  $\text{Cl}_2$  in presence of diffused sunlight is **[NEET Odisha 2019]**
  - Isopentane
  - 2, 2-dimethylbutane
  - neopentane
  - n-pentane
- Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. (A) is **[2018]**
  - $\text{CH} \equiv \text{CH}$
  - $\text{CH}_2 = \text{CH}_2$
  - $\text{CH}_4$
  - $\text{CH}_3 - \text{CH}_3$
- With respect to the conformers of ethane, which of the following statements is true ? **[2017]**
  - Bond angle changes but bond length remains same
  - Both bond angle and bond length change

- Both bond angles and bond length remains same
- Bond angle remains same but bond length changes
- The correct statement regarding the comparison of staggered and eclipsed conformation of ethane, is **[2016]**
  - The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
  - The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
  - The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
  - The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

5. Given



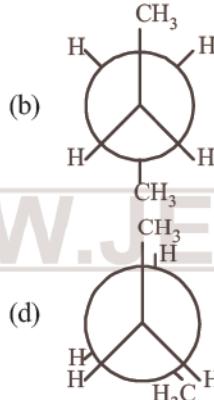
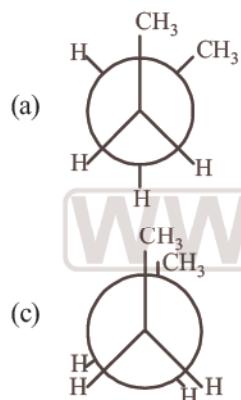
I and II are

[NEET Kar. 2013]

- (a) A pair of optical isomers
- (b) Identical
- (c) A pair of conformers
- (d) A pair of geometrical isomers

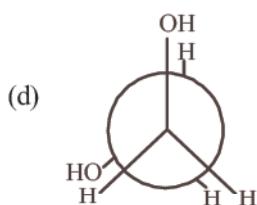
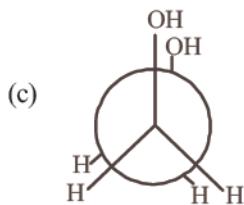
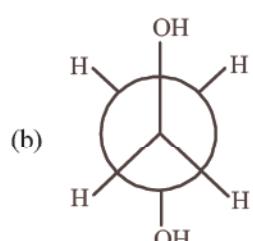
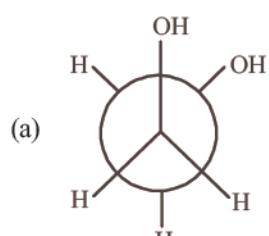
6. In the following the most stable conformation of *n*-butane is:

[2010]



7. Which of the following conformers for ethylene glycol is most stable?

[2010]



8. Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by : [2010]

- (a) Oxidation
- (b) Cracking
- (c) Distillation under reduced pressure
- (d) Hydrolysis

9. A compound of molecular formula of  $C_7H_{16}$  shows optical isomerism, compound will be

- (a) 2,3-Dimethylpentane [2001]
- (b) 2,2-Dimethylbutane
- (c) 2-Methylhexane
- (d) None of the above

10. The reaction of ethyl magnesium bromide with water would give [1999]

- (a) Ethane (b) Ethyl alcohol
- (c) Ethyl bromide (d) Ethyl ether

11. In commercial gasolines the type of hydrocarbons which are more desirable, is

- (a) branched hydrocarbons [1997]
- (b) straight-chain hydrocarbons
- (c) aromatic hydrocarbons such as toluene
- (d) linear unsaturated hydrocarbons

12. The most stable conformation of *n*-butane is [1997]

- (a) skew boat (b) gauche
- (c) staggered-anti (d) eclipsed

13. Which one of the following reactions is expected to readily give a hydrocarbon product in good yields ? [1997]

- (a)  $RCOOK \xrightarrow[\text{oxidation}]{\text{Electrolytic}}$
- (b)  $RCOO^- Ag^+ Br_2 \rightarrow$
- (c)  $CH_3CH_3 \xrightarrow[\text{hv}]{Cl_2} \rightarrow$
- (d)  $(CH_3)_3CCl \xrightarrow{C_2H_5OH} \rightarrow$

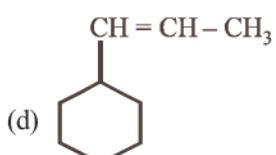
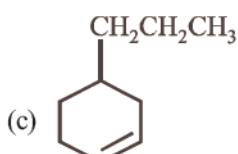
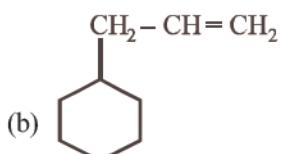
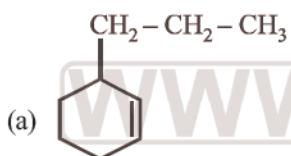
14. In the free radical chlorination of methane, the chain initiating step involves the formation of  
(a) Chlorine free radical [1994]  
(b) Hydrogen chloride  
(c) Methyl radical  
(d) Chloromethyl radical.

15. Reactivity of hydrogen atoms attached to different carbon atoms in alkanes has the order  
**[1993]**

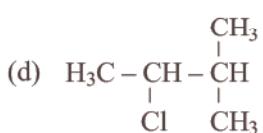
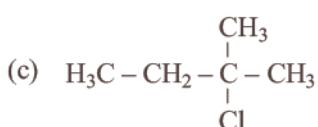
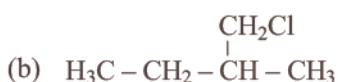
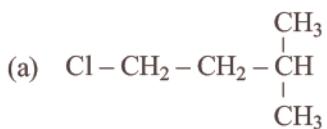
  - (a) Tertiary > Primary > Secondary
  - (b) Primary > Secondary > Tertiary
  - (c) Both (a) and (b)
  - (d) Tertiary > Secondary > Primary

## Topic 2: Alkenes

16. An alkene on ozonolysis gives methanal as one of the product. Its structure is **/2020/**



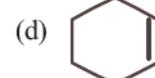
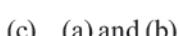
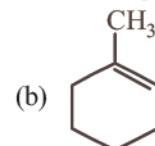
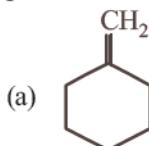
17. An alkene "A" on reaction with  $O_3$  and Zn –  $H_2O$  gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene "A" gives "B" as the major product. The structure of product "B" is: [2019]



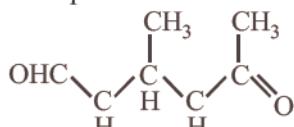
18. 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? **[2015 RS]**



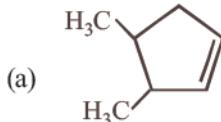
19. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is : /2015 RS/

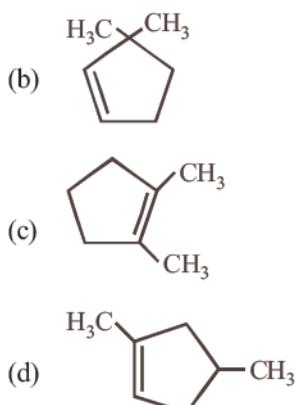


20. A single compound of the structure : [2015]

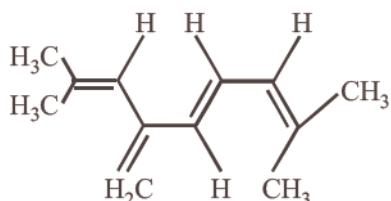


is obtainable from ozonolysis of which of the following cyclic compounds?



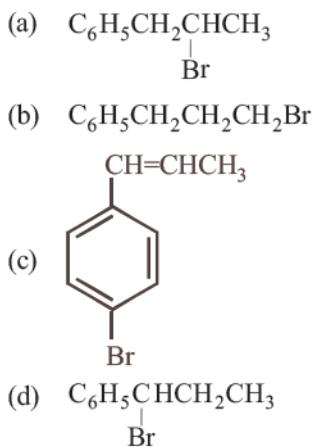


21. The total number of  $\pi$ -bond electrons in the following structure is : **[2015]**

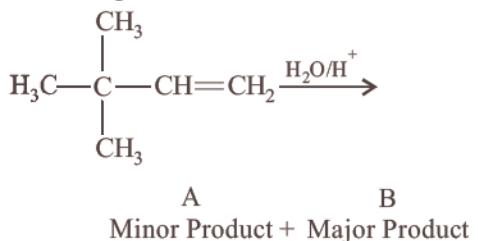




22. The reaction of  $C_6H_5CH = CHCH_3$  with HBr produces: **[2015]**

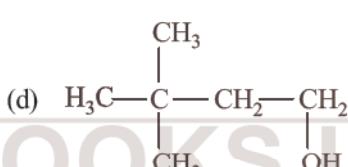
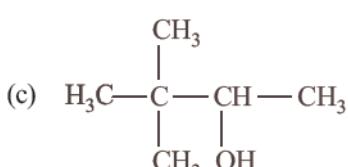
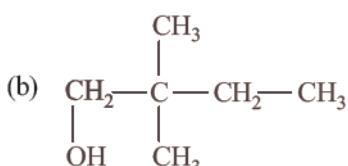
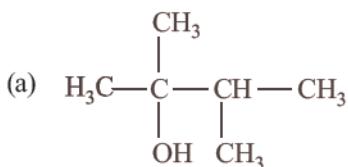


23. In the following reaction :

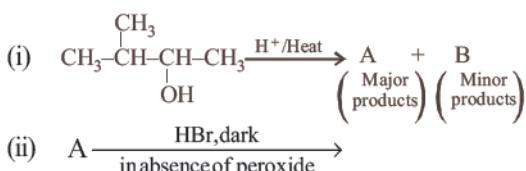


The major product is:

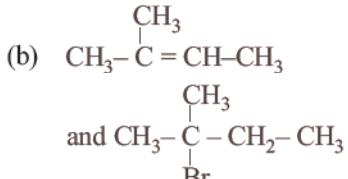
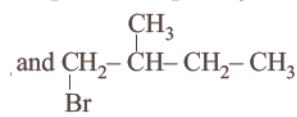
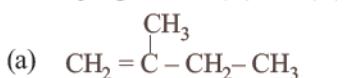
[2012]

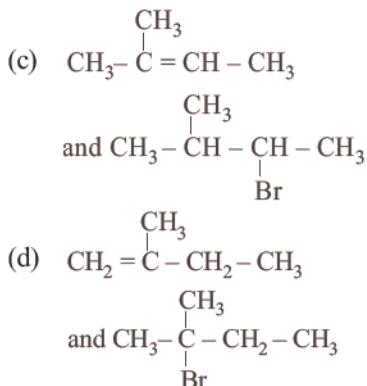


24. In the following reactions, [2011]



the major products (A) and (C) are respectively:





25. The IUPAC name of the compound having the formula  $\text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2$  is : [2009]  
 (a) 1-butyn-3-ene (b) but-1-yne-3-ene  
 (c) 1-butene-3-yne (d) 3-butene-1-yne
26. Which of the following compounds will exhibit cis-trans (geometrical) isomerism? [2009]  
 (a) Butanol (b) 2-Butyne  
 (c) 2-Butenol (d) 2-Butene
27.  $\text{H}_3\text{C} - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \text{CH} = \text{CH}_2 + \text{HBr} \rightarrow A$   
 A (predominantly) is : [2008]  
 (a)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \text{CH}_2 - \text{CH}_2\text{Br}$   
 (b)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{C}} - \text{CH}_2 - \text{CH}_3$   
 (c)  $\text{CH}_3 - \underset{\substack{| \\ \text{Br}}}{\text{CH}} - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \text{CH}_3$   
 (d)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}} - \underset{\substack{| \\ \text{Br}}}{\text{CH}} - \text{CH}_3$
28. Which of the compounds with molecular formula  $\text{C}_5\text{H}_{10}$  yields acetone on ozonolysis? [2007]  
 (a) 3-methyl-1-butene (b) cyclopentane  
 (c) 2-methyl-1-butene (d) 2-methyl-2-butene.
29. Which one of the following alkenes will react faster with  $\text{H}_2$  under catalytic hydrogenation conditions? [2005]  
 (R = Alkyl Substituent)

30. Reaction of HBr with propene in the presence of peroxide gives [2004]  
 (a) isopropyl bromide (b) 3-bromo propane  
 (c) allyl bromide (d) n-propyl bromide
31. The compound  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{C}} = \text{CH} - \text{CH}_3$  on reaction with  $\text{NaIO}_4$  in the presence of  $\text{KMnO}_4$  gives [2003]  
 (a)  $\text{CH}_3\text{CHO} + \text{CO}_2$   
 (b)  $\text{CH}_3\text{COCH}_3$   
 (c)  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COOH}$   
 (d)  $\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CHO}$
32. Geometrical isomers differ in [2002]  
 (a) position of functional group  
 (b) position of atoms  
 (c) spatial arrangement of atoms  
 (d) length of carbon chain
33. Which alkene on ozonolysis gives  $\text{CH}_3\text{CH}_2\text{CHO}$  and  $\text{CH}_3\overset{\substack{| \\ \text{O}}}{\text{C}}\text{CH}_3$  [2001]  
 (a)  $\text{CH}_3\text{CH}_2\text{CH} = \underset{\substack{| \\ \text{CH}_3}}{\text{C}}\text{CH}_3$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_2\text{CH}_3$   
 (c)  $\text{CH}_3\overset{\substack{| \\ \text{CH}_2}}{\text{CH}}\text{CH} = \text{CHCH}_3$   
 (d)  $\text{CH}_3 - \underset{\substack{| \\ \text{CH}_3}}{\text{C}} = \text{CHCH}_3$
34. In preparation of alkene from alcohol using  $\text{Al}_2\text{O}_3$  which is effective factor? [2001]  
 (a) Temperature  
 (b) Concentration  
 (c) Surface area of  $\text{Al}_2\text{O}_3$   
 (d) Porosity of  $\text{Al}_2\text{O}_3$
35. Which of the following reagents convert propene to 1-propanol? [2000]  
 (a)  $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$   
 (b) aqueous KOH  
 (c)  $\text{MgSO}_4, \text{NaBH}_4/\text{H}_2\text{O}$   
 (d)  $\text{B}_2\text{H}_6, \text{H}_2\text{O}_2, \text{OH}^-$

36. Correct order of stability is : **[2000]**

  - cis* -2- butene > 1-butene > *trans* -2-butene
  - trans*-2-butene > *cis*-2-butene > 1-butene
  - 1-butene > *cis*-2-butene > *trans*-2- butene
  - cis*-2-butene > *trans*-2-butene > 1-butene

37. The correct structure of trans-2 hexenal is **[1999]**

(a) 

(b) 

(c) 

(d) 

38. A hydrocarbon 'A' on chlorination gives 'B' which on heating with alcoholic potassium hydroxide changes into another hydrocarbon 'C'. The latter decolourises Baeyer's reagent and on ozonolysis forms formaldehyde only. 'A' is

  - Ethane
  - Butane **[1998]**
  - Methane
  - Ethene

39. In reaction sequence **[1997]**

$$\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{acid}]{\text{Hypochlorous}} \text{M} \xrightarrow{\text{R}} \begin{matrix} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{matrix}$$

molecule 'M' and reagent 'R' respectively are

  - $\text{CH}_3\text{CH}_2\text{Cl}$  and  $\text{NaOH}$
  - $\text{Cl}_2\text{CH}_2\text{OII}$  and  $\text{H}_2\text{SO}_4$
  - $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$  and aqueous  $\text{NaHCO}_3$
  - $\text{CH}_2-\text{CH}_2$  and heat

40. In the presence of platinum catalyst, hydrocarbon *A* adds hydrogen to form *n*-hexane. When hydrogen bromide is added to *A* instead of hydrogen, only a single bromo compound is formed. Which of the following is *A*? **[1996]**

  - $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
  - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$
  - $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
  - $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

41. Which of the following will not show cis-trans isomerism? **[1996]**

  - $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
  - $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$
  - $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$
  - $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$

42. When 3, 3-dimethyl -2-butanol is heated with  $\text{H}_2\text{SO}_4$ , the major product obtained is **[1995]**

  - 2, 3-dimethyl -2-butene
  - 3, 3-dimethyl -1- butene
  - 2, 3-dimethyl -1- butene
  - cis & trans isomers of 2, 3-dimethyl -2-butene

43. The alkene  $\text{R}-\text{CH}=\text{CH}_2$  reacts readily with  $\text{B}_2\text{H}_6$  and formed the product *B* which on oxidation with alkaline hydrogen peroxides produces **[1995]**

  - $\text{R}-\text{CH}_2-\text{CHO}$
  - $\text{R}-\text{CH}_2-\text{CH}_2-\text{OH}$
  - $\text{R}-\text{C}(\text{CH}_3)=\text{O}$
  - $\text{R}-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$

44. Which of the following compounds has the lowest boiling point ? **[1994]**

  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
  - $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
  - $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

45. When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives **[1993]**

  - 2-Chloropropane
  - Allyl chloride
  - No reaction
  - n*-Propyl chloride.

46. The restricted rotation about carbon carbon double bond in 2-butene is due to **[1993]**

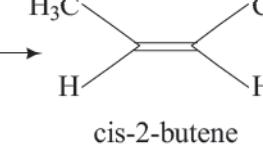
  - Overlap of one *s*- and  $sp^2$  - hybridized orbitals
  - Overlap of two  $sp^2$  - hybridized orbitals
  - Overlap of one *p*- and one  $sp^2$  - hybridized orbitals
  - Sideways overlap of two *p*- orbitals.

47. Which one of the following can exhibit cis-trans isomerism ? **[1989]**

  - $\text{CH}_3-\text{CHCl}-\text{COOH}$
  - $\text{H}-\text{C}\equiv\text{C}-\text{Cl}$
  - $\text{ClCH}=\text{CHCl}$
  - $\text{ClCH}_2-\text{CH}_2\text{Cl}$

## Topic 3: Alkynes

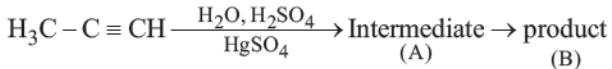
48. In the following reaction, [NEET Odisha 2019]  
 $\text{H}_3\text{C}-\text{C}\equiv\text{CH} \xrightarrow[\text{873 K}]{\substack{\text{Red hot} \\ \text{iron tube}}} \text{A}$ , the  
 number of sigma ( $\sigma$ ) bonds present in the product A, is  
 (a) 18 (b) 21  
 (c) 9 (d) 24

49. The most suitable reagent for the following conversion, is: [2019]  
 $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{CH}_3 \longrightarrow$  

(a) Na/liquid NH<sub>3</sub> (b) H<sub>2</sub>, Pd/C, quinoline  
 (c) Zn/HCl (d) Hg<sup>2+</sup>/H<sup>+</sup>, H<sub>2</sub>O

50. Which one is the correct order of acidity? [2017]  
 (a) CH≡CH > CH<sub>3</sub>-C≡CH > CH<sub>2</sub>=CH<sub>2</sub> > CH<sub>3</sub>-CH<sub>3</sub>  
 (b) CH≡CH > CH<sub>2</sub>=CH<sub>2</sub> = CH<sub>3</sub>-C≡CH > CH<sub>3</sub>-CH<sub>3</sub>  
 (c) CH<sub>3</sub>-CH<sub>3</sub> > CH<sub>2</sub>=CH<sub>2</sub> > CH<sub>3</sub>-C≡CH > CH≡CH  
 (d) CH<sub>2</sub>=CH<sub>2</sub> > CH<sub>3</sub>-CH=CH<sub>2</sub> > CH<sub>3</sub>-C≡CH > CH≡CH

51. Predict the correct intermediate and product in the following reaction : [2017]



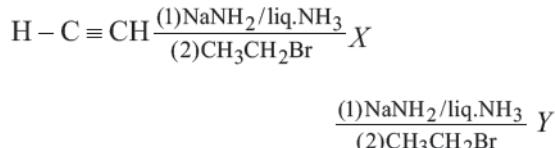
- (a) A :  $\text{H}_3\text{C}-\underset{\text{OH}}{\overset{|}{\text{C}}}=\text{CH}$ , B :  $\text{H}_3\text{C}-\underset{\text{SO}_4}{\overset{|}{\text{C}}}=\text{CH}_2$

(b) A :  $\text{H}_3\text{C}-\underset{\text{O}}{\overset{||}{\text{C}}}=\text{CH}_3$ , B :  $\text{H}_3\text{C}-\text{C}\equiv\text{CH}$

(c) A :  $\text{H}_3\text{C}-\underset{\text{OH}}{\overset{|}{\text{C}}}=\text{CH}_2$ , B :  $\text{H}_3\text{C}-\underset{\text{O}}{\overset{||}{\text{C}}}=\text{CH}_3$

(d) A :  $\text{H}_3\text{C}-\underset{\text{SO}_4}{\overset{|}{\text{C}}}=\text{CH}_2$ , B :  $\text{H}_3\text{C}-\underset{\text{O}}{\overset{||}{\text{C}}}-\text{CH}_3$

52. In the reaction



$X$  and  $Y$  are

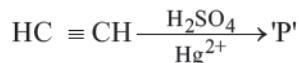
[2016]

- (a)  $X = 1\text{-Butyne}$ ;  $Y = 3\text{-Hexyne}$
  - (b)  $X = 2\text{-Butyne}$ ;  $Y = 3\text{-Hexyne}$
  - (c)  $X = 2\text{-Butyne}$ ;  $Y = 2\text{-Hexyne}$
  - (d)  $X = 1\text{-Butyne}$ ;  $Y = 2\text{-Hexyne}$

53. Which of the following organic compounds has same hybridization as its combustion product ( $\text{CO}_2$ )? [2014]



54. In the following reaction :



Product 'P' will not give [NEET Kar. 2013]

- (a) Iodoform test
  - (b) Tollen's reagent test
  - (c) Brady's reagent test
  - (d) Victor Meyer test

55. Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne?

- (a)  $\text{NaNH}_2$       (b)  $\text{HCl}$       [2012 M]  
 (c)  $\text{O}_2$       (d)  $\text{Br}_2$

- ### 56 The IUPAC name of the compound

$\text{CH}_2\text{CH}=\text{CHC}\equiv\text{CH}$  is [2010]

- (a) Pent-1-yn-3-ene      (b) Pent-4-yn-2-ene  
 (c) Pent-3-en-1-yne      (d) Pent-2-en-4-yne

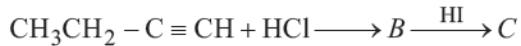
57. Base strength of : [2008]

- (A)  $\text{H}_3\text{C}-\overset{\text{--}}{\underset{\text{--}}{\text{C}}}\text{H}_2$       (B)  $\text{H}_2\text{C}=\overset{\text{--}}{\underset{\text{--}}{\text{C}}}\text{H}$  and

(C)  $\text{H}-\text{C}\equiv\text{C}$

- (a) (B) > (A) > (C)      (b) (C) > (B) > (A)

58. Predict the product C obtained in the following reaction of butyne-1. [2007]



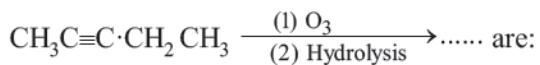
- (a)  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\substack{| \\ \text{Cl}}}{\text{C}} - \text{H}$

(b)  $\text{CH}_3 - \underset{\substack{| \\ \text{I}}}{\text{CH}_2} - \underset{\substack{| \\ \text{I}}}{\text{CH}} - \text{CH}_2\text{Cl}$

(c)  $\text{CH}_3\text{CH}_2 - \underset{\substack{| \\ \text{Cl}}}{\text{C}} - \text{CH}_3$

(d)  $\text{CH}_3 - \underset{\substack{| \\ \text{Cl}}}{\text{CH}} - \text{CH}_2\text{CH}_2\text{I}$

59. Products of the following reaction: [2005]



- (a)  $\text{CH}_3\text{COOH} + \text{CO}_2$   
 (b)  $\text{CH}_3\text{COOH} + \text{HOOC}\cdot\text{CH}_2\text{CH}_3$   
 (c)  $\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO}$   
 (d)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COCH}_3$

60. A compound is treated with  $\text{NaNH}_2$  to give sodium salt. Identify the compound [1993]

- (a)  $\text{C}_2\text{H}_2$       (b)  $\text{C}_6\text{H}_6$   
 (c)  $\text{C}_2\text{H}_6$       (d)  $\text{C}_2\text{H}_4$

61. Reduction of 2-butyne with sodium in liquid ammonia gives predominantly [1993]

- (a) cis-2-butene      (b) No reaction  
 (c) trans-2-butene    (d) n-butane.

62.  $R - CH_2 - CCl_2 - R \xrightarrow{\text{Reagent}} R - C \equiv C - R$   
The reagent is **[1003]**



63. Which is the most suitable reagent among the following to distinguish compound (3) from rest of the compounds ? [1989]

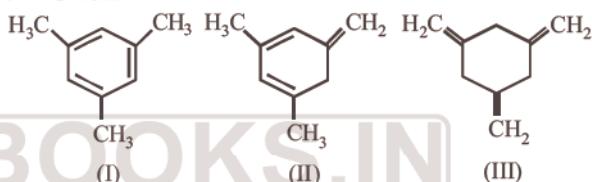
1.  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$
  2.  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
  3.  $\text{CH}_3 - \text{CH}_2 \text{C} \equiv \text{CH}$
  4.  $\text{CH}_3 - \text{CH} = \text{CH}_2$

- (a) Bromine in carbon tetrachloride  
(b) Bromine in acetic acid  
(c) Alk.  $\text{KMnO}_4$   
(d) Ammoniacal silver nitrate.

64. Acetylenic hydrogens are acidic because [1989]  
(a) Sigma electron density of C – H bond in acetylene is nearer to carbon, which has 50% *s*-character  
(b) Acetylene has only open hydrogen in each carbon  
(c) Acetylene contains least number of hydrogens among the possible hydrocarbons having two carbons  
(d) Acetylene belongs to the class of alkynes with molecular formula,  $\text{C}_n\text{H}_{2n-2}$ .

## Topic 4: Aromatic Hydrocarbons

65. Given:



The enthalpy of the hydrogenation of these compounds will be in the order as : [2015]

- (a) III > II > I      (b) II > III > I  
 (c) II > I > III      (d) I > II > III

66. The oxidation of benzene by  $V_2O_5$  in presence of air produces : [2015 RSJ]

- (a) benzoic anhydride (b) maleic anhydride  
 (c) benzoic acid (d) benzaldehyde

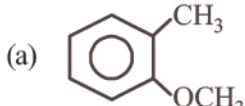
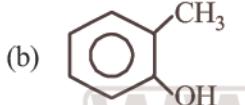
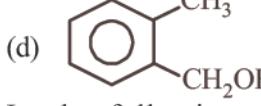
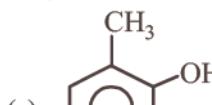
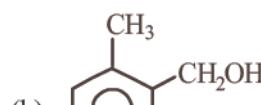
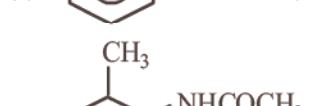
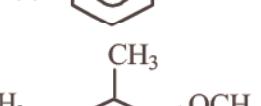
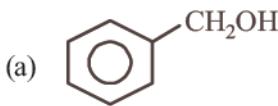
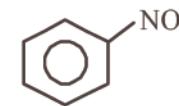
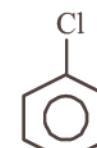
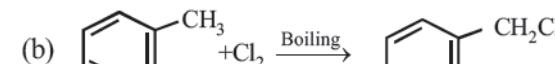
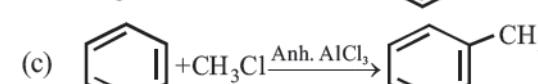
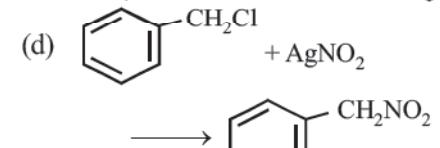
67. The radical,  is aromatic because it has : [NEET 2013]

- (a) 7 p-orbitals and 6 unpaired electrons
  - (b) 7 p-orbitals and 7 unpaired electrons

- (c) 6 p-orbitals and 7 unpaired electrons  
 (d) 6 p-orbitals and 6 unpaired electrons

68. Which of the following chemical system is non aromatic? [NEET Kar. 2013]

- |     |  |     |  |
|-----|--|-----|--|
| (a) |  | (b) |  |
| (c) |  | (d) |  |

69. Some *meta*-directing substituents in aromatic substitution are given. Which one is most deactivating? [NEET 2013]
- (a)  $-\text{SO}_3\text{H}$       (b)  $-\text{COOH}$   
 (c)  $-\text{NO}_2$       (d)  $-\text{C}\equiv\text{N}$
70. Which of the following compounds will not undergo Friedal-Craft's reaction easily? [NEET 2013]
- (a) Xylene      (b) Nitrobenzene  
 (c) Toluene      (d) Cumene
71. Among the following compounds the one that is most reactive towards electrophilic nitration is: [2012]
- (a) Benzoic acid      (b) Nitrobenzene  
 (c) Toluene      (d) Benzene
72. Which one of the following is most reactive towards electrophilic reagent? [2011]
- (a)   
 (b)   
 (c)   
 (d) 
73. In the following reaction,  $\text{C}_6\text{H}_5\text{CH}_2\text{Br} \xrightarrow[2.\text{H}_3\text{O}^+]{1.\text{Mg, Ether}} \text{X}$ , the product 'X' is [2010]
- (a)  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$   
 (b)  $\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$   
 (d)  $\text{C}_6\text{H}_5\text{CH}_3$
74. Which one is most reactive towards electrophilic reagent? [2010]
- (a)   
 (b)   
 (c)   
 (d) 
75. Which of the following species is not electrophilic in nature? [2010]
- (a)  $\overset{\oplus}{\text{NO}_2}$       (b)  $\overset{\oplus}{\text{Cl}}$   
 (c)  $\text{BH}_3$       (d)  $\overset{\oplus}{\text{H}_3\text{O}}$
76. Which one of the following is most reactive towards electrophilic attack? [2008]
- (a)   
 (b)   
 (c)   
 (d) 
77. The order of decreasing reactivity towards an electrophilic reagent, for the following would be [2007]
- (i) benzene      (ii) toluene  
 (iii) chlorobenzene      (iv) phenol  
 (a) (ii)>(iv)>(i)>(iii) (b) (iv)>(iii)>(ii)>(i)  
 (c) (iv)>(ii)>(i)>(iii) (d) (i)>(ii)>(iii)>(iv)
78. Using anhydrous  $\text{AlCl}_3$  as catalyst, which one of the following reactions produces ethylbenzene ( $\text{PhEt}$ )? [2004]
- (a)  $\text{H}_3\text{C}-\text{CH}_2\text{OH} + \text{C}_6\text{H}_6$   
 (b)  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{C}_6\text{H}_6$   
 (c)  $\text{H}_2\text{C}=\text{CH}_2 + \text{C}_6\text{H}_6$   
 (d)  $\text{H}_3\text{C}-\text{CH}_3 + \text{C}_6\text{H}_6$
79. Which one of the following is a free-radical substitution reaction? [2003]
- (a)  $\text{CH}_3\text{CHO} + \text{HCN} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CN}$   
 (b)   
 (c)   
 (d) 

80. The correct order of reactivity towards the electrophilic substitution of the compounds aniline (I), benzene (II) and nitrobenzene (III) is [2003]

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

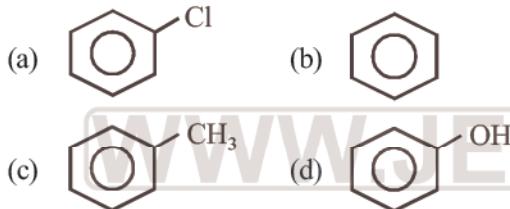
81. For the formation of toluene by Friedal Craft reaction, reactants used in presence of anhydrous  $\text{AlCl}_3$  are [2000]

(a)  $\text{C}_2\text{H}_2$  and  $\text{CCl}_4$       (b)  $\text{CH}_4$  and  $\text{CaCN}_2$   
 (c)  $\text{C}_6\text{H}_6$  and  $\text{CH}_3\text{Cl}$       (d)  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{Zn}$

82. Which of the following compounds reacts slower in electrophilic substitution? [2000]

(a)  $\text{C}_6\text{H}_5\text{NO}_2$       (b)  $\text{C}_6\text{H}_5\text{OH}$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_3$       (d)  $\text{C}_6\text{H}_5\text{NH}_2$

83. Which one of the following compounds will be most easily attacked by an electrophile? [1998]

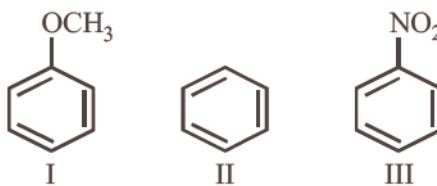


84. Which one of these is not compatible with arenes? [1997]

(a) Greater stability  
 (b) Delocalisation of  $\pi$ -electrons  
 (c) Electrophilic additions  
 (d) Resonance

85. Among the following compounds (I-III), the ease of their reaction with electrophiles is,

[1997]



- (a) II > III > I      (b) III > II > I  
 (c) II > I > III      (d) I > II > III

86. When  $\text{CH}_3\text{Cl}$  and  $\text{AlCl}_3$  are used in Friedel-Crafts reaction, the electrophile is [1994]

(a)  $\text{Cl}^+$       (b)  $\text{AlCl}_4^-$   
 (c)  $\text{CH}_3^+$       (d)  $\text{AlCl}_2^+$

87. An example of electrophilic substitution reaction is [1994]

(a) Chlorination of methane  
 (b) Conversion of methyl chloride to methyl alcohol  
 (c) Nitration of benzene  
 (d) Formation of ethylene from ethyl alcohol.

88. Select the true statement about benzene amongst the following [1992]

(a) Because of unsaturation benzene easily undergoes addition  
 (b) There are two types of C – C bonds in benzene molecule  
 (c) There is cyclic delocalisation of pi-electrons in benzene  
 (d) Monosubstitution of benzene gives three isomeric products.

89. The most reactive compound for electrophilic nitration is [1992]

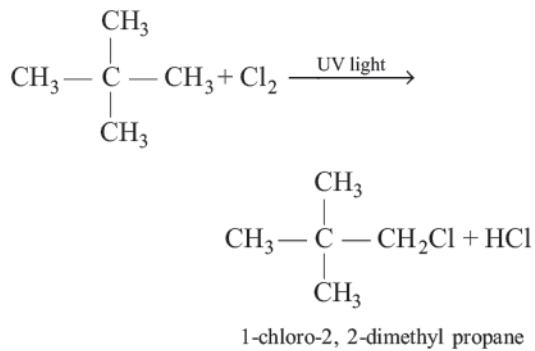
(a) Benzene      (b) Nitrobenzene  
 (c) Benzoic acid      (d) Toluene.

#### ANSWER KEY

1	(c)	10	(a)	19	(c)	28	(d)	37	(a)	46	(d)	55	(a)	64	(a)	73	(d)	82	(a)
2	(c)	11	(a)	20	(d)	29	(a)	38	(a)	47	(c)	56	(c)	65	(a)	74	(d)	83	(d)
3	(c)	12	(c)	21	(a)	30	(d)	39	(c)	48	(b)	57	(d)	66	(b)	75	(d)	84	(c)
4	(d)	13	(a)	22	(d)	31	(c)	40	(a)	49	(b)	58	(c)	67	(d)	76	(c)	85	(d)
5	(c)	14	(a)	23	(a)	32	(c)	41	(c)	50	(a)	59	(b)	68	(a)	77	(c)	86	(c)
6	(b)	15	(d)	24	(b)	33	(a)	42	(a)	51	(c)	60	(a)	69	(c)	78	(c)	87	(c)
7	(a)	16	(b)	25	(c)	34	(a)	43	(b)	52	(a)	61	(c)	70	(b)	79	(b)	88	(c)
8	(b)	17	(c)	26	(d)	35	(d)	44	(d)	53	(b)	62	(c)	71	(c)	80	(a)	89	(d)
9	(a)	18	(b)	27	(b)	36	(b)	45	(a)	54	(d)	63	(d)	72	(b)	81	(c)		

# Hints & Solutions

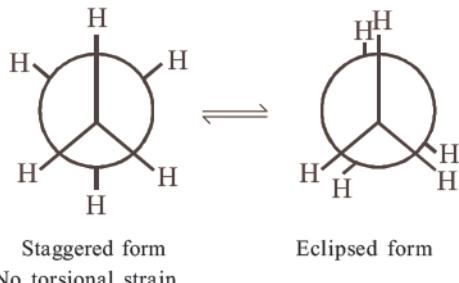
1. (c) Chlorination of neopentane with  $\text{Cl}_2$  in the presence of diffused sunlight gives only one mono-chloro compound



**NOTES** All the hydrogen atoms are similar hence only one mono-chloro compound is formed.

2. (c)  $\text{CH}_4 \xrightarrow[\text{hv}]{\text{Br}_2} \text{CH}_3\text{-Br} \xrightarrow[\text{ether}]{\text{Na}}$
- $$\text{CH}_3 - \text{CH}_3$$
- (less than four 'C')

3. (c) There is no change in bond angles and bond lengths in the conformations of ethane.
4. (d) In staggered conformation any two hydrogen atoms on adjacent carbon atoms are as far apart as possible, thereby minimising repulsion between the electron clouds of  $\sigma$ -bonds of two non-bonded H-atoms (torsional strain)



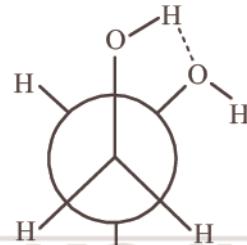
5. (c) Conformers are form of stereoisomers in which isomers can be interconverted by rotation about single bonds. I and II are staggered and eclipsed conformers respectively.

6. (b) The bulky methyl groups are maximum away from each other.



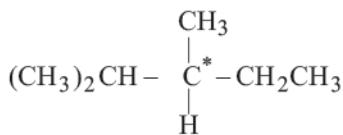
Eclipsed conformation is the highest energy conformation because of unfavorable interactions between the electrons in the front and back C – H bonds. The energy of eclipsed conformation is approx. 3 kcal/mol higher than staggered conformation.

7. (a) Due to hydrogen bonding between the two OH groups, gauche conformation of ethylene glycol (a) is the most stable conformation.



8. (b) During cracking, higher hydrocarbons (liquid) are converted to lower gaseous hydrocarbons.

9. (a) A compound is said to exhibit optical isomerism if it atleast contains one chiral carbon atom, which is an atom bonded to 4 different atoms or groups.

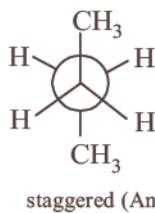


10. (a)  $\text{C}_2\text{H}_5\text{MgBr} + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_6 + \text{Mg}(\text{OH})\text{Br}$

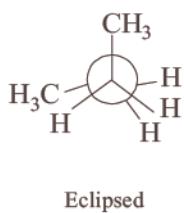
11. (a) Gasoline (petrol) is a mixture of alkanes, alkenes and aromatic hydrocarbons. The quality of a gasoline is determined by the amount of branched chain hydrocarbons (2,2,4-trimethylpentane, commonly known as iso-octane) present in it.

12. (c) Order of stability : staggered (anti) > gauche > skew boat > eclipsed.

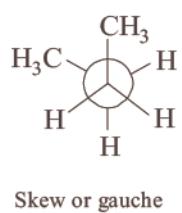
Newman projection of n-butane is given as



staggered (Anti)



# Eclipsed

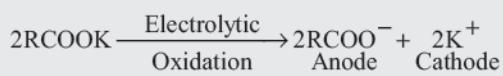


Skew or gauche



## NOTES

## Kolbe's Method



At anode  $2\text{RCOO}^- \rightarrow 2\text{RCOO} + 2\text{e}^- \longrightarrow$

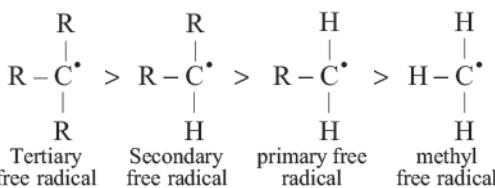


At Cathode  $2\text{K}^+ + 2\text{e}^- \rightarrow 2\text{K}$

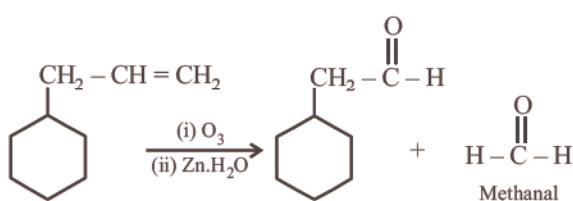


14. (a)  $\text{Cl}_2 \xrightarrow[\text{Chain initiation step}]{h\nu} 2\text{Cl}^\bullet$

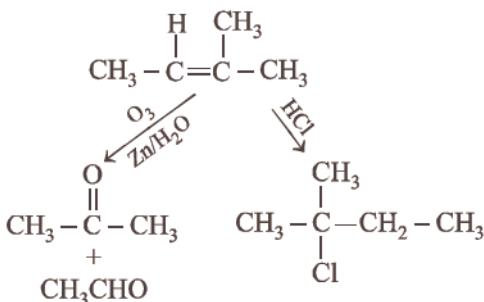
15. (d) The reactivity of H-atoms depends upon the stability of free radicals, follows the order Tertiary > secondary > primary.  
Therefore, reactivity of H-atoms follows the same order, i.e., tertiary > secondary > primary.



16. (b)



17. (c)

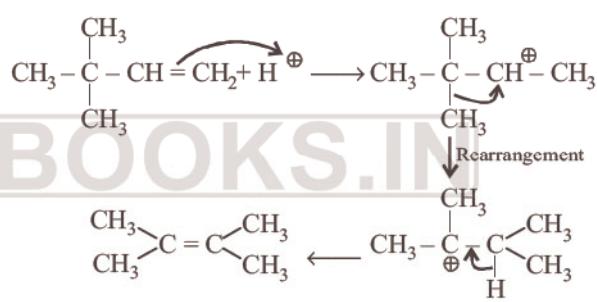


18. (b)  $\begin{array}{c} \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

### 2,3-Dimethyl-2-butene

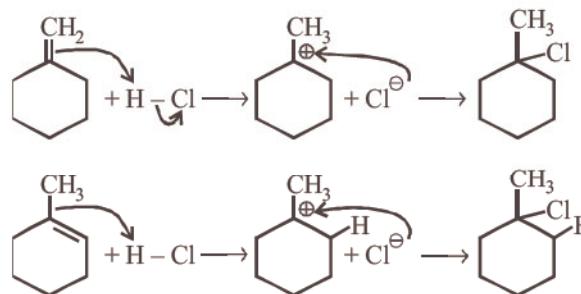
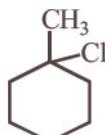
- (a)  $(CH_3)_2CH - CH - CH = CH_2$  contain 7 carbon atoms

- (b)

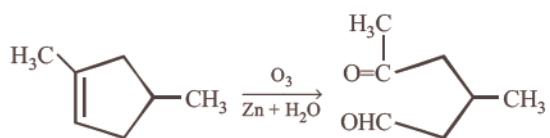


The driving force of the reaction is the stability of the carbocation. Tertiary carbocation is more stable than secondary carbocation which is achieved by 1,2-rearrangement.

19. (c) 1-chloro-1-methylcyclohexane.



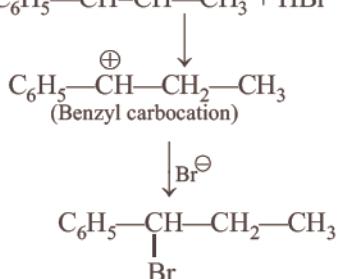
20. (d)



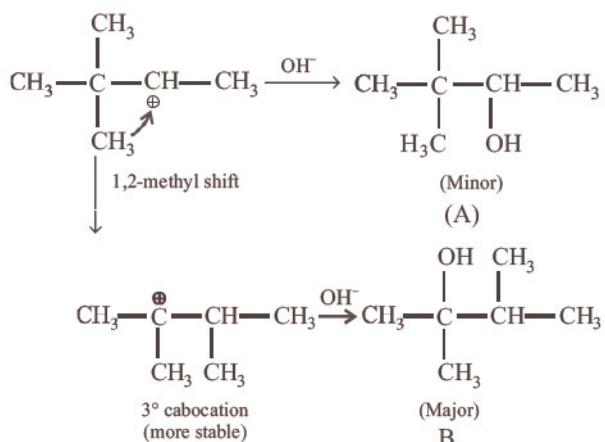
21. (a) No. of double bonds = 4

$$\begin{aligned}\text{No. of } \pi \text{ bond electrons} \\ = 2 \times \text{no. of double bond} \\ = 2 \times 4 = 8\end{aligned}$$

22. (d)  $\text{C}_2\text{H}_5\text{CH}=\text{CH}-\text{CH}_2 + \text{HBr}$

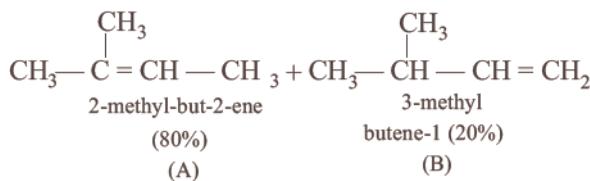


23. (a) 

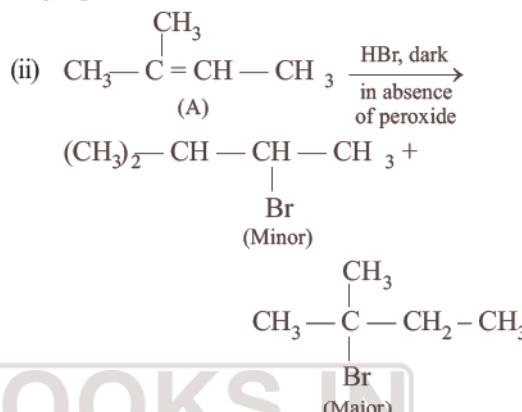


Tertiary carbocation is more stable hence gives major product.

24. (b) (i)  $\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{OH}}{\text{CH}}} - \text{CH}_3 \xrightarrow{\text{H}^+ \text{Heat}}$



In this case, dehydration is governed by Saytzeff's rule, according to which hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms *i.e.*, poor becomes poorer. Thus, 2-methyl but-2-ene is the major product.



This reaction is governed by Markownikoff's rule according to which when an unsymmetrical reagent e.g. HBr adds to an unsymmetrical alkene, then the negative part of the reagent is added to that carbon atom of the double bond which bears the least number of hydrogen atom. Thus, in above case 2-methyl-2-bromobutane will be the major product.

Peroxide effect is shown by HBr only because H-Cl bond is stronger than H-Br and is not cleaved by the free radicals, whereas H-I bond is weaker and Iodine free radical combine to form iodine molecule.

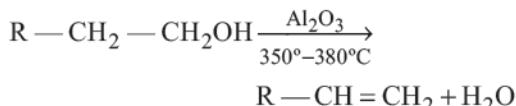
25. (c) So the IUPAC name of the compound is 1-butene-3-yne.

If both the double and triple bonds are present in the compound, it is regarded as derivative of alkyne. Further if double and triple bonds are at equidistance from either side, the preference is given to double bond.

26. (d) Alkenes with double bonds cannot undergo free rotation and can have different geometrical shapes with two different groups on each end of the double bond.

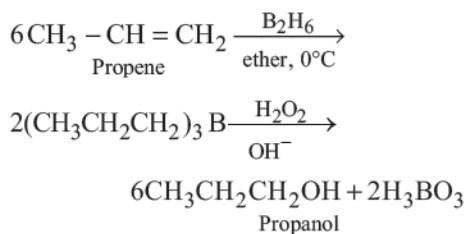


34. (a) Reaction conditions for alcohol in preparation of alkenes are :

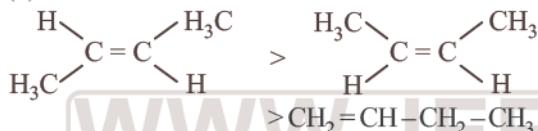


At  $220^\circ - 250^\circ \text{C}$  it forms ether.

35. (d) We know that



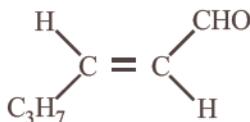
36. (b)



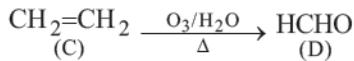
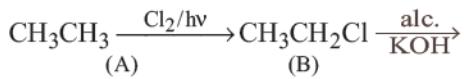
Due to more hyper-conjugation in cis-2-butene ( $6\alpha$ -H atoms) than in 1-butene ( $2\alpha$ -H atoms), the former is more stable.

In trans-2-butene, the two methyl groups are far apart. Hence, it is most stable.

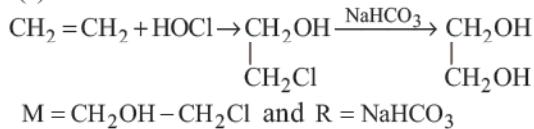
37. (a) When similar atoms are on the opposite side, the compound is in *trans*-form.



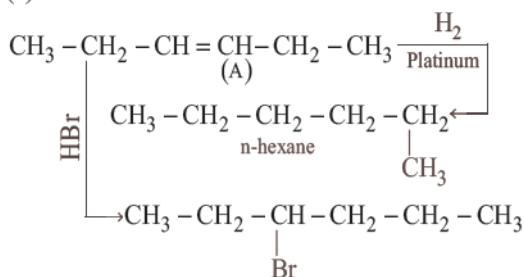
38. (a) Since hydrocarbon C gives only  $\text{CH}_2\text{O}$ , on ozonolysis, C should be  $\text{CH}_2 = \text{CH}_2$ . Hence going backward, A should be ethane. Thus, the reactions are



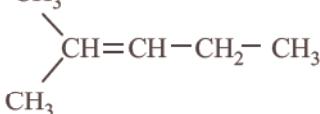
39. (c) We know that



40. (a)

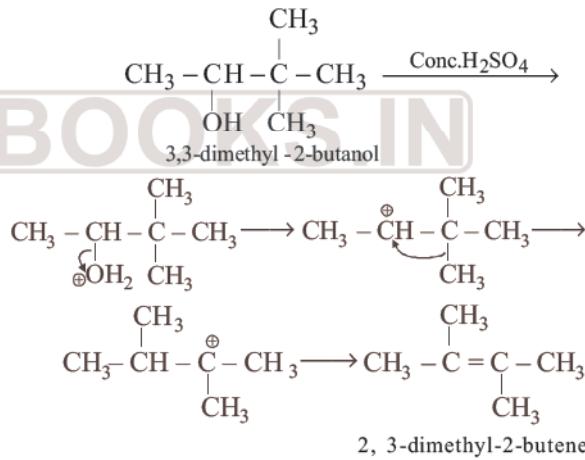


41. (c)



Due to presence of two similar methyl groups at same carbon atom, above compound doesn't show geometrical isomerism.

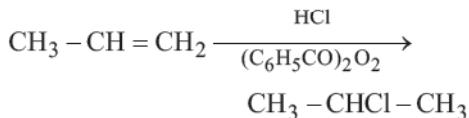
42. (a) When 3, 3 dimethyl - 2-butanol is heated with  $\text{H}_2\text{SO}_4$  the major product obtained is 2, 3-dimethyl - 2-butene.



43. (b)  $6\text{R} - \text{CH} = \text{CH}_2 \xrightarrow[\text{Ether, } 0^\circ \text{C}]{\text{B}_2\text{H}_6} 2(\text{RCH}_2\text{CH}_2)_3\text{B}$
- $$\xrightarrow[\text{NaOH}]{\text{H}_2\text{O}_2} 6\text{RCH}_2\text{CH}_2\text{OH} + 2\text{H}_3\text{BO}_3$$

44. (d) Of all the options listed  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  has the least number of C-atoms and hence has the lowest b.p.

45. (a) Addition of  $\text{HCl}$  to propene even in the presence of benzoyl peroxide occurs according to Markovnikov's rule :





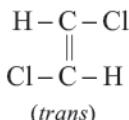
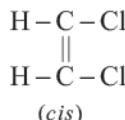
**NOTE** Peroxide effect is observed only in case of HBr.

46. (d) Restricted rotation about carbon carbon double bond in 2-butene is due to sideways overlap of two  $p$ -orbital.

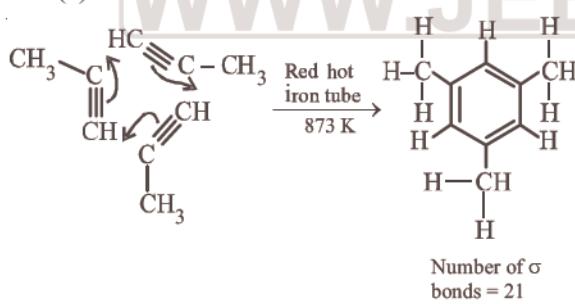


**NOTE** Rotation around  $\pi$  bond is not possible. If any attempt is made to rotate one of the carbon atoms, the lobes of  $\pi$ -orbital will no longer remain coplanar i.e. no parallel overlap will be possible and thus  $\pi$ -bond will break. This is known as concept of restricted rotation. In other words the presence of  $\pi$ -bonds fix the position of two carbon atoms.

47. (c) Such isomers, which possess the same molecular and structural formula but differ in the arrangement of atoms around the double bonded carbon atoms are known as geometrical isomers.

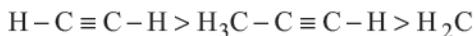


48. (b)

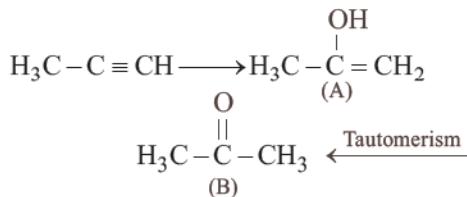


49. (b) Alkynes can be reduced to cis-alkenes with the use of Lindlar's catalyst

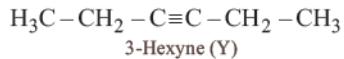
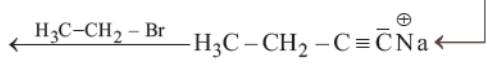
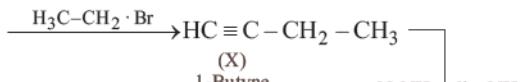
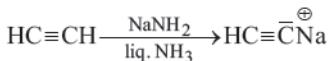
50. (a) Correct order is



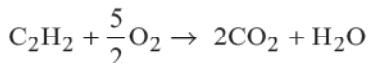
51. (c) Hydration of alkynes give ketones.



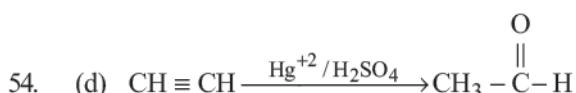
52. (a)



53. (b) The combustion reaction of ethylene is



Both  $\text{HC} \equiv \text{CH}$  and  $\text{CO}_2$  have  $sp$  hybridization.

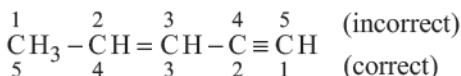


$\text{CH}_3\text{CHO}$  does not give Victor Meyer test.

55. (a) 1-Butyne and 2-butyne are distinguished by  $\text{NaNH}_2$  because 1-Butyne react with  $\text{NaNH}_2$  due to presence of terminal hydrogen.



56. (c) When double and triple, both bonds are present, then 'lowest set of locants' rule will decide the IUPAC name.

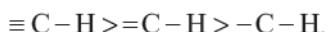


Hence, the correct name will be pent-3-en-1-yne.

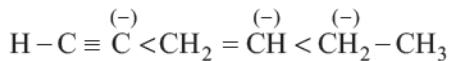
57. (d) The amount of  $s$ -character in various hybrid orbitals is as follows.

$$sp = 50\%, sp^2 = 33\% \text{ and } sp^3 = 25\%$$

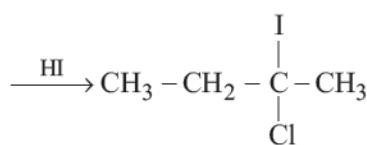
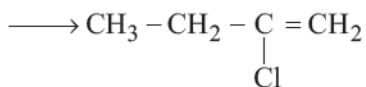
Therefore  $s$ -character of the C – H bond in acetylene ( $sp$ ) is greater than that of the C – H bond in alkene ( $sp^2$  hybridized) which in turn has greater  $s$ -character of the C – H bond in alkanes. Thus, owing to a high  $s$ -character of the C – H bond in alkynes, the electrons constituting this bond are more strongly held by the carbon nucleus with the result the hydrogen present on such a carbon atom can be easily removed as proton. The acidic nature of three types of C – H bonds follows the following order



Further, as we know that conjugate base of a strong acid is a weak base, hence the correct order of basicity is

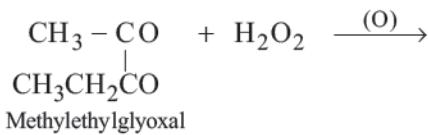


58. (c)  $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{CH} + \text{HCl}$



According to Markownikoff's rule which states that when an unsymmetrical alkene undergo hydrohalogenation, the negative part goes to the C-atom which contain lesser no. of H-atom.

59. (b)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_2 - \text{CH}_3 \xrightarrow{\text{O}_3}$

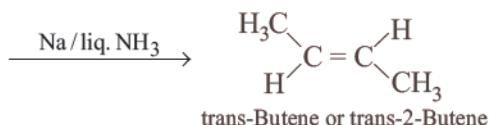


The glyoxal formed as an intermediate is oxidised by  $\text{H}_2\text{O}_2$  to give the acids.'

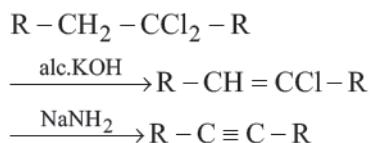
60. (a) Only  $\text{C}_2\text{H}_2$  (acetylene) has acidic H-atoms and hence reacts with  $\text{NaNH}_2$  to form sodium salt, i.e.,



61. (c) Reduction of alkynes with Na/liq.  $\text{NH}_3$  gives trans-alkenes. This reaction is called Birch reduction.



62. (c) On heating ethylene chloride (1, 1 dichloro ethane) with alcoholic KOH followed by sodamide, alkyne is obtained



63. (d)  $\text{Br}_2$  in  $\text{CCl}_4$  (a),  $\text{Br}_2$  in  $\text{CH}_3\text{COOH}$  (b) and alk.  $\text{KMnO}_4$  (c) will react with all unsaturated compounds, i.e., 1, 3 and 4 while ammoniacal  $\text{AgNO}_3$  (d) reacts only with terminal alkynes, i.e., 3 and hence compound 3 can be distinguished from 1, 2 and 4 by ammoniacal  $\text{AgNO}_3$  (d).

64. (a) The acidity of acetylene or 1-alkynes can be explained on the basis of molecular orbital concept according to which formation of C-H bond in acetylene involves  $sp$ -hybridised carbon atom.



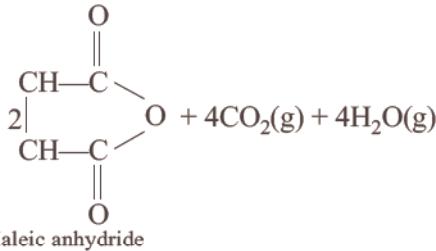
*s* electrons are closer to the nucleus than *p* electrons, the electrons present in a bond having more *s*-character will be correspondingly more closer to the nucleus. Thus, owing to high *s* character of the C—H bond in alkynes (*s* = 50%), the electrons constituting this bond are more strongly held by the carbon nucleus (*i.e.*, the acetylenic carbon atom) or the *sp* orbital acts as more electronegative species than the *sp*<sup>2</sup> and *sp*<sup>3</sup> with the result the hydrogen present on such a carbon atom ( $\equiv \text{C}—\text{H}$ ) can be easily removed as a proton.

65. (a) Enthalpy of hydrogenation

$$\infty \frac{1}{\text{stability of alkene}}$$

∴ III > II > I

66. (b)  $2C_6H_6(g) + 9O_2(g) \xrightarrow[410^\circ C]{V_2O_5}$



67. (d) Presence of 6  $p$  orbitals, each containing one unpaired electron, in a six membered cyclic structure is in accordance with Huckel rule of aromaticity.

68. (a) Huckel rule is not obeyed. It has only four electrons. Further it does not have continuous conjugation.

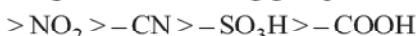


In thiophene, one lone pair of electrons are involved in delocalisation.



Thus, the effective number of p-electrons become 6 which is of the form  $(4n + 2)$ . Also the ring is planar, hence this is an aromatic compound.

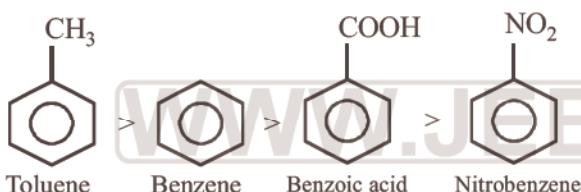
69. (c) Decreasing order of deactivating effect of the given *m*-directing group is



$-\text{NO}_2$  group is most deactivating group due to strong  $-E$ ,  $-I$  and  $-M$  effects.

70. (b)  $-\text{NO}_2$  is a powerful electron withdrawing group. Its presence on ring makes the ring less active.

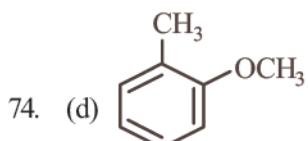
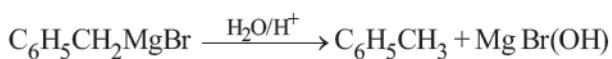
71. (c) Electrophilic rate order



Since nitration is an electrophilic substitution hence presence of electron releasing group like  $\text{CH}_3$  in the nucleus facilitates nitration.

72. (b) Due to  $+ M$  effect of  $-\text{OH}$  group and hyperconjugation of  $-\text{CH}_3$  group.

73. (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br} + \text{Mg} \xrightarrow{\text{ether}}$



Among  $-\text{OH}$ ,  $-\text{CH}_2\text{OH}$ ,  $-\text{NHCOCH}_3$  and  $-\text{OCH}_3$ , methoxy group has the highest  $+M$  effect.

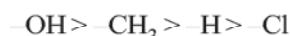
75. (d)  $\text{H}_3\ddot{\text{O}}^+ \left( \text{H}-\ddot{\text{O}}^+-\text{H} \right)$  has a lone pair of electrons on oxygen atom, thus it is not an electrophile. Also the octet is complete.

76. (c) Out of the given compounds the most reactive towards nucleophilic attack is



Phenoxide ion is stable due to resonance.

77. (c) Electrophiles have high affinity for electrons. They attack at the site where electron-density is highest. Electron donating groups increases the electron density. The electron donating tendency decreases in the order :

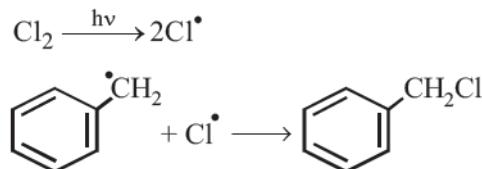
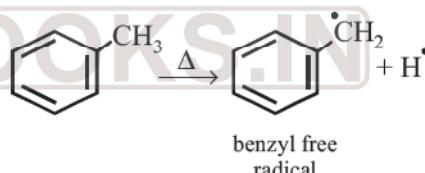


Therefore, the correct order of reactivity towards electrophile is

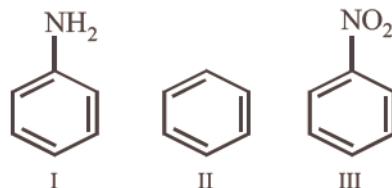


78. (c)  $\text{C}_6\text{H}_6 + \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$

79. (b) In the presence of UV rays or energy  $\text{O}_2$  by boiling, free radical is generated which attack the methyl carbon atom of toluene.

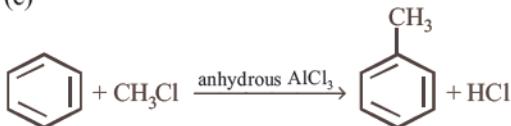


80. (a) Amino group is ring activating while nitro group is deactivating. Hence, correct order is aniline > benzene > nitrobenzene.



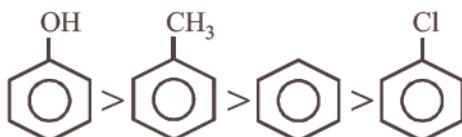
$-\text{NO}_2$  is an electron attracting group hence decrease the electron density on ring, whereas  $-\text{NH}_2$  group is electron releasing group hence increase electron density on ring. Benzene is also  $e^-$  rich due to delocalization of electrons.

81. (c)



82. (a)  $\text{CH}_3$  and  $\text{NH}_2$  and  $\text{OH}$  are electron donating groups, whereas  $\text{NO}_2$  is an electron withdrawing group and leaves the benzene ring deactivated. Due to stronger electron attracting ( $-I$  effect) effect of  $\text{NO}_2$  group,  $\text{C}_6\text{H}_5\text{NO}_2$  shows least reactivity towards electrophilic substitution.
83. (d)  $-\text{Cl}$  atom shows *o/p*-directive influence but deactivate the benzene ring, while  $[-\text{OH}/-\text{CH}_3]$  groups show *o/p* influence and activate the benzene ring but  $-\text{OH}$  group is more activating than  $-\text{CH}_3$ .

Hence order of electrophilic substitution



84. (c) In arenes,  $\pi$  electrons are delocalised, hence arenes do not undergo addition reactions easily. Aromatic compounds (Arenes) are highly stable and show resonance eg. Benzene is the simplest example.

85. (d)  $-\text{OCH}_3$  activates the benzene ring.  $-\text{NO}_2$  deactivates the ring. Hence, the reaction of the given compounds with electrophiles is in the order, I > II > III.



Electrophile

87. (c) Chlorination of methane proceeds via free radical mechanism. Conversion of methyl chloride to methyl alcohol proceeds via nucleophilic substitution. Formation of ethylene from ethyl alcohol proceeds via dehydration reaction. Nitration of benzene is electrophilic substitution reaction.

88. (c) Benzene do not show addition reaction like other unsaturated hydrocarbons. Due to resonance all the C – C bonds have the same nature, which is possible because of the cyclic delocalisation of  $\pi$ -electrons in benzene. Monosubstitution will give only a single product.

89. (d) Due to  $+I$ -effect of the  $\text{CH}_3$ -group, toluene has much higher electron density in the ring than benzene, Nitrobenzene and benzoic acid.

**NOTES**

Nitro and carboxylic group show-  $I$ -effect and hence deactivate the ring towards electrophilic substitution.

# 14

# Environmental Chemistry

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Air pollution	green house effect			1	E						
	air pollution					1	E				
Water and soil pollution	soil pollution							1	E		

LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

### Topic 1: Air Pollution

- Among the following, the one that is not a green house gas is: [2019]  
(a) nitrous oxide      (b) methane  
(c) ozone      (d) sulphur dioxide
- Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity? [2018]  
(a)  $N_2O_5$       (b)  $NO_2$   
(c) NO      (d)  $N_2O$
- Which of the following is not a common component of Photochemical Smog? [2014]  
(a) Ozone  
(b) Acrolein  
(c) Peroxyacetyl nitrate  
(d) Chlorofluorocarbons
- Which one of the following statements regarding photochemical smog is not correct? [2012]  
(a) Carbon monoxide does not play any role in photochemical smog formation.  
(b) Photochemical smog is an oxidising agent in character.  
(c) Photochemical smog is formed through photochemical reaction involving solar energy.  
(d) Photochemical smog does not cause irritation in eyes and throat.

- The greenhouse effect is because of the  
(a) presence of gases, which in general are strong infrared absorbers, in the atmosphere  
(b) presence of  $CO_2$  only in the atmosphere  
(c) pressure of  $O_3$  and  $CH_4$  in the atmosphere  
(d)  $N_2O$  and chlorofluorohydrocarbons in the atmosphere [1996]

- Which of the following is/are the hazardous pollutant(s) present in automobile exhaust gases?  
(i)  $N_2$       (ii) CO  
(iii)  $CH_4$       (iv) Oxides of nitrogen  
(a) (ii) and (iii)      (b) (i) and (ii) [1996]  
(c) (ii) and (iv)      (d) (i) and (iii)

### Topic 2: Water and Soil Pollution

- The liquified gas that is used in dry cleaning along with a suitable detergent is [NEET Odisha 2019]  
(a)  $CO_2$       (b) Water gas  
(c) Petroleum gas      (d)  $NO_2$
- Which of the following is a sink for CO? [2017]  
(a) Microorganism present in the soil  
(b) Oceans  
(c) Plants  
(d) Haemoglobin

8. Which of the following is a sink for CO? [2017]

  - (a) Microorganism present in the soil
  - (b) Oceans
  - (c) Plants
  - (d) Haemoglobin

9. Roasting of sulphides give the gas X as a by product. This is colorless gas with choking smell of burnt sulphur and caused great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas X is : [NEET 2013]

  - (a)  $\text{SO}_2$
  - (b)  $\text{CO}_2$
  - (c)  $\text{SO}_3$
  - (d)  $\text{H}_2\text{S}$

10. Which one of the following statements is not true? [NEET Kar. 2013]

  - (a) Dissolved oxygen (DO) in cold water can reach a concentration upto 10 ppm.
  - (b) Clean water would have a BOD value of 5 ppm.

(c) Fluoride deficiency in drinking water is harmful. Soluble fluoride is often used to bring its concentration upto 1 ppm.

(d) When the pH of rain water is higher than 6.5, it is called acid rain.

11. Which one of the following statement is not true ? [2011]

  - (a) pH of drinking water should be between 5.5 – 9.5.
  - (b) Concentration of DO below 6 ppm is good for the growth of fish.
  - (c) Clean water would have a BOD value of less than 5 ppm.
  - (d) Oxides of sulphur, nitrogen and carbon are the most widespread air pollutant.

12. Green chemistry means such reactions which

  - (a) produce colour during reactions [2008]
  - (b) reduce the use and production of hazardous chemicals
  - (c) are related to the depletion of ozone layer
  - (d) study the reactions in plants

ANSWER KEY

# Hints & Solutions

1. (d) Sulphur dioxide is not a green house gas.

2. (a) Nitrous oxide ( $N_2O$ ) occurs naturally in environment.

In automobile engine, when fuel is burnt dinitrogen and dioxygen combine to yield NO and  $NO_2$ .

Thus,  $N_2O_5$  is the answer.

3. (d) The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.

In automobile engine, when fuel is burnt dinitrogen and dioxygen combine to yield NO and  $\text{NO}_2$ .

Thus,  $\text{N}_2\text{O}_5$  is the answer.

- Hydrocarbons + O<sub>2</sub>, NO<sub>2</sub>, NO, O, O<sub>3</sub> → Peroxides, formaldehyde, peroxyacetyl-nitrate (PAN), acrolein etc. Hence, chlorofluoro carbons are not common component of photochemical smog.

4. (d) The oxidised hydrocarbons and ozone in presence of humidity cause photochemical smog.

Hydrocarbons + O<sub>2</sub>, NO<sub>2</sub>, NO, O, O<sub>3</sub> → Peroxides, formaldehyde, peroxyacetyl nitrate (PAN), acrolein etc.

Hydrocarbons + O<sub>2</sub>, NO<sub>2</sub>, NO, O, O<sub>3</sub>  
 → Peroxides, formaldehyde, peroxyacetyl nitrate (PAN), acrolein etc.

It is oxidising in nature and causes irritation to eyes, lungs, nose, asthamatic attack and damage plants.

5. (a) Green house gases such as  $\text{CO}_2$ , ozone, methane, the chlorofluoro carbon compounds and water vapour form a thick cover around the earth which prevents the IR rays emitted by the earth to escape. It gradually leads to increase in temperature of atmosphere.



Water vapour is the largest contributor to the earth's greenhouse effect. However water vapour does not control the Earth's temperature.

6. (c) CO and oxides of Nitrogen are poisonous gases present in automobile exhaust gases.
7. (a) Liquified  $\text{CO}_2$  (carbon dioxide) with a suitable detergent is used in dry cleaning.
8. (a) Microorganisms present in the soil is a sink for CO.



Microorganism present in soil convert CO to  $\text{CO}_2$ , thus it's sink.

9. (a) Based on the features given, gas must be  $\text{SO}_2$ .
10. (d) Acid rain is the rain water containing sulphuric acid and nitric acid which are formed from the oxides of sulphur and nitrogen present in the air as pollutants. Rain water has a pH below 5.6.
11. (b) The growth of fishes get hindered if the concentration of D.O. is below 6 ppm.
12. (b) Green chemistry are the reaction, which reduces the use of hazardous chemicals.



Green chemistry is the programme of developing new chemical products and chemical processes or making improvements in the already existing compounds and processes so as to make them less harmful to human health and environment. This means the same as to reduce the use and production of hazardous chemicals.

# 15

## The Solid State

### Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Cubic system and Bragg's equation	relation between r and a	1	A								
	formula of compound and voids			1	A						
	density ratio and structure					1	D				

LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

#### Topic 1: Properties and Types of Solids

- A solid with high electrical and thermal conductivity from the following is [1994]
  - Si
  - Li
  - NaCl
  - Ice
- The pure crystalline substance on being heated gradually first forms a turbid liquid at constant temperature and still at higher temperature turbidity completely disappears. The behaviour is a characteristic of substance forming [1993]
  - Allotropic crystals
  - Liquid crystals
  - Isomeric crystals
  - Isomorphous crystals.
- Most crystals show good cleavage because their atoms, ions or molecules are [1991]
  - weakly bonded together
  - strongly bonded together
  - spherically symmetrical
  - arranged in planes.
- The ability of a substances to assume two or more crystalline structures is called [1990]
  - Isomerism
  - Polymorphism
  - Isomorphism
  - Amorphism

#### Topic 2: Crystal Structure of Solids

- A solid compound XY has NaCl structure. If the radius of the cation is 100 pm, the radius of the anion ( $Y^-$ ) will be : [2011 MJ]
  - 275.1 pm
  - 322.5 pm
  - 241.5 pm
  - 165.7 pm
- The pyknometric density of sodium chloride crystal is  $2.165 \times 10^3 \text{ kg m}^{-3}$  while its X-ray density is  $2.178 \times 10^3 \text{ kg m}^{-3}$ . The fraction of unoccupied sites in sodium chloride crystal is [2003]
  - $5.96 \times 10^{-3}$
  - 5.96
  - $5.96 \times 10^{-2}$
  - $5.96 \times 10^{-1}$
- When molten zinc is converted into solid state, it acquires hcp structure. The number of nearest neighbours will be [2001]
  - 6
  - 12
  - 8
  - 4
- In the solid state, MgO has the same structure as that of sodium chloride. The number of oxygens surrounding each magnesium in MgO is [1999]
  - 6
  - 1
  - 2
  - 4

9. For orthorhombic system, axial ratios are  $a \neq b \neq c$  and the axial angles are [1991]  
 (a)  $\alpha = \beta = \gamma \neq 90^\circ$   
 (b)  $\alpha = \beta = \gamma = 90^\circ$   
 (c)  $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$   
 (d)  $\alpha \neq \beta \neq \gamma = 90^\circ$

### Topic 3: Cubic System and Bragg's Equation

10. An element has a body centered cubic (bcc) structure with a cell edge of 288 pm. The atomic radius is: [2020]

- (a)  $\frac{\sqrt{2}}{4} \times 288 \text{ pm}$       (b)  $\frac{4}{\sqrt{3}} \times 288 \text{ pm}$   
 (c)  $\frac{4}{\sqrt{2}} \times 288 \text{ pm}$       (d)  $\frac{\sqrt{3}}{4} \times 288 \text{ pm}$

11. A compound is formed by cation C and anion A. The anions form hexagonal close packed (hcp) lattice and the cations occupy 75% of octahedral voids. The formula of the compound is: [2019]

- (a)  $C_2A_3$       (b)  $C_3A_2$   
 (c)  $C_3A_4$       (d)  $C_4A_3$

12. Iron exhibits bcc structure at room temperature. Above  $900^\circ\text{C}$ , it transforms to fcc structure. The ratio of density of iron at room temperature to that at  $900^\circ\text{C}$  (assuming molar mass and atomic radii of iron remains constant with temperature) is [2018]

- (a)  $\frac{\sqrt{3}}{\sqrt{2}}$       (b)  $\frac{4\sqrt{3}}{3\sqrt{2}}$   
 (c)  $\frac{1}{2}$       (d)  $\frac{3\sqrt{3}}{4\sqrt{2}}$

13. Which of the following statements about the interstitial compounds is incorrect? [NEET 2013]

- (a) They are chemically reactive.  
 (b) They are much harder than the pure metal.  
 (c) They have higher melting points than the pure metal.  
 (d) They retain metallic conductivity.

14. The number of carbon atoms per unit cell of diamond unit cell is: [NEET 2013]

- (a) 8      (b) 6  
 (c) 1      (d) 4

15. A metal has an fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal

is  $2.72 \text{ g cm}^{-3}$ . The molar mass of the metal is : ( $N_A$ , Avogadro's constant =  $6.02 \times 10^{23} \text{ mol}^{-1}$ ) [NEET 2013]

- (a)  $30 \text{ g mol}^{-1}$       (b)  $27 \text{ g mol}^{-1}$   
 (c)  $20 \text{ g mol}^{-1}$       (d)  $40 \text{ g mol}^{-1}$

16. Structure of a mixed oxide is cubic close-packed (c.c.p). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is : [2012 MJ]

- (a)  $ABO_2$       (b)  $A_2BO_2$   
 (c)  $A_2B_3O_4$       (d)  $AB_2O_2$

17. The number of octahedral void(s) per atom present in a cubic close-packed structure is : [2012]

- (a) 1      (b) 3  
 (c) 2      (d) 4

18. A metal crystallizes with a face-centered cubic lattice. The edge length of the unit cell is 408 pm. The diameter of the metal atom is : [2012]

- (a) 288 pm      (b) 408 pm  
 (c) 144 pm      (d) 204 pm

19. AB crystallizes in a body centred cubic lattice with edge length ' $a$ ' equal to 387 pm. The distance between two oppositely charged ions in the lattice is : [2010]

- (a) 335 pm      (b) 250 pm  
 (c) 200 pm      (d) 300 pm

20. Copper crystallises in a face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm? [2009]

- (a) 157      (b) 181  
 (c) 108      (d) 128

21. Lithium metal crystallises in a body centred cubic crystal. If the length of the side of the unit cell of lithium is 351 pm, the atomic radius of the lithium will be: [2009]

- (a) 151.8 pm      (b) 75.5 pm  
 (c) 300.5 pm      (d) 240.8 pm

22. Percentage of free space in a body centred cubic unit cell is : [2008]

- (a) 30%      (b) 32%  
 (c) 34%      (d) 28%

23. If ' $a$ ' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively,

[2008]

- (a)  $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$  (b)  $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
- (c)  $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{3}}{2}a$  (d)  $a : \sqrt{3}a : \sqrt{2}a$
24. The fraction of total volume occupied by the atoms present in a simple cube is [2007]
- (a)  $\frac{\pi}{3\sqrt{2}}$  (b)  $\frac{\pi}{4\sqrt{2}}$   
 (c)  $\frac{\pi}{4}$  (d)  $\frac{\pi}{6}$
25. CsBr crystallises in a body centered cubic lattice. The unit cell length is 436.6 pm. Given that the atomic mass of Cs = 133 and that of Br = 80 amu and Avogadro number being  $6.02 \times 10^{23} \text{ mol}^{-1}$  the density of CsBr is [2006]
- (a)  $0.425 \text{ g/cm}^3$  (b)  $8.25 \text{ g/cm}^3$   
 (c)  $4.25 \text{ g/cm}^3$  (d)  $42.5 \text{ g/cm}^3$
26. In face-centred cubic lattice, a unit cell is shared equally by how many unit cells? [2005]
- (a) 2 (b) 4  
 (c) 6 (d) 8
27. A compound formed by elements *X* and *Y* crystallizes in a cubic structure in which the *X* atoms are at the corners of a cube and the *Y* atoms are at the face-centres. The formula of the compound is [2004]
- (a)  $XY_3$  (b)  $X_3Y$   
 (c)  $XY$  (d)  $XY_2$
28. A compound is formed by elements *A* and *B*. The crystalline cubic structure has the *A* atoms at the corners of the cube and *B* atoms at the body centre. The simplest formula of the compound is [2000]
- (a)  $AB$  (b)  $A_6B$   
 (c)  $AB_6$  (d)  $A_8B_4$
29. The second order Bragg diffraction of X-rays with  $\lambda = 1.00 \text{ \AA}$  from a set of parallel planes in a metal occurs at an angle  $60^\circ$ . The distance between the scattering planes in the crystal is [1998]
- (a)  $0.575 \text{ \AA}$  (b)  $1.00 \text{ \AA}$   
 (c)  $2.00 \text{ \AA}$  (d)  $1.15 \text{ \AA}$
30. The intermetallic compound LiAg crystallizes in a cubic lattice in which both lithium and silver atoms have coordination number of eight. To what crystal class does the unit cell belong?
- (a) Simple cubic  
 (b) Face-centred cubic  
 (c) Body-centred cubic  
 (d) None
31. The edge length of a face centred unit cubic cell is 508 pm. If the radius of the cation is 100 pm, the radius of the anion is [1996]
- (a) 288 pm (b) 398 pm  
 (c) 154 pm (d) 618 pm
32. In the fluorite structure, the coordination number of  $\text{Ca}^{2+}$  ion is: [1993]
- (a) 4 (b) 6  
 (c) 8 (d) 3
33. The number of atoms contained in an *fcc* unit cell of a monoatomic substance is [1993]
- (a) 1 (b) 2  
 (c) 4 (d) 6
- Topic 4: Imperfection in Solids**
34. Formula of nickel oxide with metal deficiency defect in its crystal is  $\text{Ni}_{0.98}\text{O}$ . The crystal contains  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  ions. The fraction of nickel existing as  $\text{Ni}^{2+}$  ions in the crystal is [NEET Odisha 2019]
- (a) 0.31 (b) 0.96  
 (c) 0.04 (d) 0.50
35. With which one of the following elements silicon should be doped so as to give *p*-type semiconductor? [2008]
- (a) Germanium (b) Arsenic  
 (c) Selenium (d) Boron
36. If  $\text{NaCl}$  is doped with  $10^{-4}$  mol % of  $\text{SrCl}_2$ , the concentration of cation vacancies will be ( $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ ) [2007]
- (a)  $6.02 \times 10^{16} \text{ mol}^{-1}$  (b)  $6.02 \times 10^{17} \text{ mol}^{-1}$   
 (c)  $6.02 \times 10^{14} \text{ mol}^{-1}$  (d)  $6.02 \times 10^{15} \text{ mol}^{-1}$
37. The appearance of colour in solid alkali metal halides is generally due to [2006]
- (a) Schottky defect (b) Frenkel defect  
 (c) Interstitial positions (d) F-centres
38. Schottky defect in crystals is observed when [1998]
- (a) an ion leaves its normal site and occupies an interstitial site  
 (b) unequal number of cations and anions are missing from the lattice  
 (c) density of the crystal is increased  
 (d) equal number of cations and anions are missing from the lattice

39. When electrons are trapped into the crystal in anion vacancy, the defect is known as [1994]
- Schottky defect
  - Frenkel defect
  - Stoichiometric defect
  - F-centres
40. On doping Ge metal with a little of In or Ga, one gets [1993]
- p-type semi conductor
  - n-type semi conductor
  - insulator
  - rectifier

## ANSWER KEY

1	(b)	5	(c)	9	(b)	13	(a)	17	(a)	21	(a)	25	(c)	29	(d)	33	(c)	37	(d)
2	(b)	6	(a)	10	(d)	14	(a)	18	(a)	22	(b)	26	(c)	30	(c)	34	(b)	38	(d)
3	(d)	7	(b)	11	(c)	15	(b)	19	(a)	23	(a)	27	(a)	31	(c)	35	(d)	39	(d)
4	(b)	8	(a)	12	(d)	16	(d)	20	(d)	24	(d)	28	(a)	32	(c)	36	(b)	40	(a)

## Hints &amp; Solutions

1. (b) Out of the given substances, only Li has high electrical and thermal conductivity.
2. (b) Liquid crystals on heating first become turbid and on further heating they become clear.
3. (d) Crystals show good cleavage because their constituent particles are arranged in planes.
4. (b) The phenomenon of occurrence of a substance in two or more crystalline structures is called polymorphism.
5. (c) Radius ratio of NaCl like crystal  

$$= \frac{r^+}{r^-} = 0.414$$
  

$$r^- = \frac{100}{0.414} = 241.5 \text{ pm } (r^+ = 100)$$
6. (a) Fraction of unoccupied sites in NaCl crystal  

$$= \frac{\text{x-ray density} - \text{pyknometric density}}{\text{x-ray density}}$$
  

$$= \frac{2.178 \times 10^3 - 2.165 \times 10^3}{2.178 \times 10^3} = \frac{0.013 \times 10^3}{2.178 \times 10^3}$$
  

$$= 5.96 \times 10^{-3}$$

## NOTES

Pyknometric density is nearest to true density calculated from the molecular mass and crystalline lattice of the product.

7. (b) hcp is a closed packed arrangement in which the unit cell is hexagonal and coordination number is 12.
8. (a) Since MgO has a rock salt structure. In this structure each cation is surrounded by six anions and vice versa.

9. (b) For orthorhombic system  $\alpha = \beta = \gamma = 90^\circ$

10. (d) For bcc,  $\sqrt{3}a = 4r \Rightarrow r = \frac{\sqrt{3}a}{4}$

Given,  $a = 288 \text{ pm}$

$$r = \frac{\sqrt{3}}{4} \times 288 \text{ pm}$$

11. (c) Oh void (C) : HCP (A)

No. of ions  $\Rightarrow 6 \times \frac{75}{100} : 6$

$$\frac{3}{4} : 1$$

$$3 : 4 \quad C_3A_4$$

12. (d) For bcc lattice :  $Z = 2, a = \frac{4r}{\sqrt{3}}$

For fcc lattice :  $Z = 4, a = 2\sqrt{2}r$

$$\therefore \frac{d_{25^\circ C}}{d_{900^\circ C}} = \frac{\left( \frac{ZM}{N_A a^3} \right)_{bcc}}{\left( \frac{ZM}{N_A a^3} \right)_{fcc}}$$

$$= \frac{2}{4} \left( \frac{2\sqrt{2}r}{\frac{4r}{\sqrt{3}}} \right)^3 = \frac{3\sqrt{3}}{4\sqrt{2}}$$

13. (a) Interstitial compounds are chemically inert.



In interstitial compounds small atoms like H, B & C enter into the void sites between the packed atoms of crystalline metal. They retain metallic conductivity and are chemically inert.

14. (a) Diamond is like ZnS. In diamond cubic unit cell, there are eight corner atoms, six face centered atoms and four more atoms inside the structure (tetrahedral voids).

Total no. of atoms present per unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 8$$

(corners) (face centered) (inside body)

15. (b) Density is given by

$$d = \frac{Z \times M}{N_A a^3}; \text{ where } Z = \text{number of formula units}$$

present in unit cell, which is 4 for fcc

$a$  = edge length of unit cell.  $M$  = Molecular mass

$$2.72 = \frac{4 \times M}{6.02 \times 10^{23} \times (404 \times 10^{-10})^3}$$

( $\because 1\text{pm} = 10^{-10}\text{cm}$ )

$$M = \frac{2.72 \times 6.02 \times (404)^3}{4 \times 10^7} = 26.99 = 27 \text{ g mol}^{-1}$$

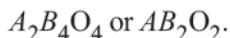
16. (d) No. of  $A^{2+}$  ions =  $\frac{1}{4} \times 8 = 2$

No. of  $B^+$  ions =  $4 \times 1 = 4$

No. of atoms in CCP,

$$O^{2-} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Hence the formula of the oxide will be



17. (a) Number of octahedral voids in CCP is equal to effective number of atoms.

In CCP, effective number of atoms are 4 so, 4 octahedral voids.

So, 1 octahedral voids per atom.

18. (a) For fcc structure,  $\sqrt{2}a = 4r$

$$\frac{\sqrt{2} \times 408}{2} = 2r \quad (2r = \text{Diameter})$$

Diameter =  $288.5 \approx 288 \text{ pm}$

19. (a) For bcc lattice, diagonal =  $a\sqrt{3}$ .

The distance between the two oppositely

$$\text{charged ions} = \frac{a}{2}\sqrt{3}$$

$$= \frac{387 \times 1.732}{2} \approx 335 \text{ pm}$$

20. (d) Since Cu metal crystallises in a face centred cubic lattice

$$\therefore r = \frac{a}{2\sqrt{2}}$$

$$r = \frac{361}{2\sqrt{2}} = 127.6 \approx 128 \text{ pm}$$

21. (a) Since lithium metal crystallises in a body centred cubic crystal

$$\therefore r = \frac{a\sqrt{3}}{4} = \frac{351 \times 1.732}{4} = 151.98 \text{ pm}$$

22. (b) Percentage of occupied space in a bcc is 68%.

$\therefore$  Percentage of free space in a bcc is  $(100 - 68) = 32\%$

23. (a) Following generalization can be easily derived for various types of lattice arrangements in cubic cells between the edge length ( $a$ ) of the cell and  $r$  the radius of the sphere.

For simple cubic :  $a = 2r$  or  $r = \frac{a}{2}$

For body centred cubic :

$$a = \frac{4}{\sqrt{3}}r \text{ or } r = \frac{\sqrt{3}}{4}a$$

For face centred cubic :

$$a = 2\sqrt{2}r \text{ or } r = \frac{1}{2\sqrt{2}}a$$

Thus the ratio of radii of spheres will be simple : bcc : fcc

$$= \frac{a}{2} : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$$

24. (d) Number of atoms per unit cell = 1  
Atoms touch each other along edges. Hence

$$r = \frac{a}{2}$$

( $r$  = radius of atom and  $a$  = edge length)

$$\text{Therefore \% fraction} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6} = 0.52$$

25. (c) In body centred cubic lattice one molecule of CsBr is within one unit cell.

Atomic mass of unit cell =  $133 + 80 = 213 \text{ a.m.u}$

Volume of cell =  $(436.6 \times 10^{-10})^3 \text{ cm}^3$

$$\text{Density} = \frac{Z \times \text{at.wt.}}{\text{Av.no.} \times \text{vol.of unit cell}}$$

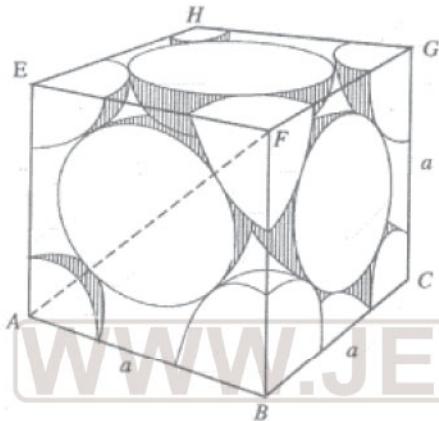
$$\text{Density} = \frac{1 \times 213}{6.02 \times 10^{23} \times (436.6)^3 \times 10^{-30}}$$

$$= \frac{213 \times 10^7}{6.02 \times (436.6)^3} = 4.25 \text{ g/cm}^3$$



In the density formula, Z is number of particles present in a unit cell and M is molar mass of that particle. For any diatomic molecule like CsBr, Z = 2 but for any mono atomic molecule like Li, Z = 1 for bcc lattice.

26. (c)



An isolated fcc cell is shown here. Each face of the cell is common to two adjacent cells. Therefore, each face centre atom contributes only half of its volume and mass to one cell. Arranging six cells each sharing the remaining half of the face centred atoms, constitutes fcc cubic lattice. e.g., Cu and Al.

27. (a) For the given cubic structure,

$$\text{No. of } X \text{ atoms at the corners} = 8 \times \frac{1}{8} = 1$$

$$\text{No. of } Y \text{ atoms at the face-centres} = 6 \times \frac{1}{2} = 3$$

$$\therefore \text{Formula of the compound} = XY_3$$

28. (a) Given: Atoms are present at the corners of the cube = A and atoms present at body centre = B. We know that a cubic unit cell has 8 corners. Therefore contribution of each atom at the corner =  $\frac{1}{8}$ . Since number of atoms per unit cell is 8, therefore total contribution =  $8 \times \frac{1}{8} = 1$ . We also know the one atom is in the body centre,

therefore number of atoms per unit cell = 1. Thus formula of the compound is AB.

29. (d) Given : Order of Bragg diffraction ( $n$ ) = 2; Wavelength ( $\lambda$ ) = 1 Å and angle ( $\theta$ ) = 60°. We know from the Bragg's equation  $n\lambda = 2d \sin \theta$  or  $2 \times 1 = 2d \sin 60^\circ$

$$\Rightarrow 2 \times 1 = 2.d \cdot \frac{\sqrt{3}}{2} \Rightarrow d = \frac{2}{\sqrt{3}} = 1.15 \text{ \AA}$$

(where  $d$  = difference between the scattering planes)

30. (c) A body-centred cubic system consists of eight atoms at the corners plus one atom at the centre of cube.
31. (c) For fcc, the edge length of the unit cell,  $a = r + 2R + r$   
where,  $R$  = Radius of anion &  $r$  = radius of cation  
 $\therefore 508 = 2 \times 100 + 2R \Rightarrow R = 154 \text{ pm}$
32. (c) In fluorite structure, each  $F^-$  ion is surrounded by four  $Ca^{2+}$  ions whereas, each  $Ca^{2+}$  is surrounded by eight  $F^-$  ions, giving a body centred cubic arrangement. Thus the co-ordination number of  $Ca^{2+} = 8$ .
33. (c) The no. of atoms in a unit cell may be calculated by the formula

$$Z = \frac{n_c}{8} + \frac{n_b}{1} + \frac{n_f}{2} + \frac{n_e}{4}$$

where  $n_c$  = no. of atom at the corner  $n_b$  = no. of atoms at body centre  $n_f$  = no. of atoms at face centre,  $n_e$  = no. of atoms at edge centre.

An fcc crystal contains

$$= \frac{8}{8} + \frac{6}{2} = 4 \text{ atoms in a unit cell.}$$

34. (b)  $Ni_{0.98}O = (Ni^{2+})_x(Ni^{3+})_{0.98-x}(O^{2-})_1$

Net charge = 0

$$[x \times 2] + [(0.98 - x) \times 3] + [-2 \times 1] = 0$$

$$x = 0.94$$

Fraction of nickel existing as

$$Ni^{2+} = \frac{0.94}{0.98} = 0.959 \approx 0.96$$

35. (d) The semiconductors formed by the introduction of impurity atoms containing one electron less than the parent atoms of insulators are termed as *p*-type semiconductors. Therefore, silicon containing 14 electrons has to be doped with boron containing 13 electrons to give a *p*-type semi-conductor.

36. (b) For each  $\text{Sr}^{2+}$  ion added, one  $\text{Na}^+$  ion is removed to maintain the electrical neutrality.

Hence concentration of cation vacancies

$$= \text{mole \% of } \text{SrCl}_2 \text{ added} = 10^{-4} \text{ mole \%}$$

$$= \frac{10^{-4}}{100} \times 6.023 \times 10^{23} = 6.023 \times 10^{17}$$

37. (d) When the crystal is irradiated with white light, the trapped electrons in a hole absorbs photon for excitation from ground state to excited state. This gives colour to the compound.

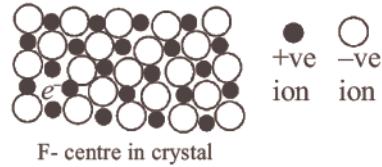


**SEILO**  
Alkali metal halide may have excess metal ion if a negative ion is absent from its lattice site, leaving a hole, which is occupied by electron to maintain electrical neutrality. The 'holes' occupied by electrons are called F-centres or colour centres.

38. (d) If in an ionic crystal of the type  $A^+, B^-$ , equal number of cations and anions are missing

from their lattice sites so that the electrical neutrality is maintained. The defect is called Schottky defect.

39. (d) When electrons are trapped in anion vacancies, these are called F-centres.



F- centre in crystal

40. (a) p-type of semiconductors are produced by adding impurity containing less electrons (i.e. atoms of group 13). Ge belongs to Group 14 and In to Group 13. Hence, on doping, p-type semiconductor is obtained.

16

# Solutions



## Trend Analysis with Important Topics & Sub-Topics



# Topic 1: Solubility and Concentration of Solutions

6. 25.3 g of sodium carbonate,  $\text{Na}_2\text{CO}_3$  is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ions,  $\text{Na}^+$  and carbonate ions,  $\text{CO}_3^{2-}$  are respectively (Molar mass of  $\text{Na}_2\text{CO}_3 = 106 \text{ g mol}^{-1}$ ) [2010]
- 0.955 M and 1.910 M
  - 1.910 M and 0.955 M
  - 1.90 M and 1.910 M
  - 0.477 M and 0.477 M
7. The mole fraction of the solute in one molal aqueous solution is: [2005]
- 0.009
  - 0.018
  - 0.027
  - 0.036
8. 1 M, 2.5 litre NaOH solution is mixed with another 0.5 M, 3 litre NaOH solution. Then find out the molarity of resultant solution [2002]
- 0.80 M
  - 1.0 M
  - 0.73 M
  - 0.50 M
9. Molarity of liquid HCl will be, if density of solution is 1.17 g/cc [2001]
- 36.5
  - 32.05
  - 18.25
  - 42.10
10. Which of the following statements, regarding the mole fraction ( $x$ ) of a component in solution, is incorrect? [1999]
- $0 \leq x \leq 1$
  - $x \leq 1$
  - $x$  is always non-negative
  - $-2 \leq x \leq 2$
11. A 5% solution of cane sugar (mol. wt. = 342) is isotonic with 1% solution of a substance  $X$ . The molecular weight of  $X$  is [1998]
- 34.2
  - 171.2
  - 68.4
  - 136.8
12. The number of moles of oxygen in one litre of air containing 21% oxygen by volume, in standard conditions, is [1995]
- 0.186
  - 0.21
  - 0.0093
  - 2.10
13. Which of the following modes of expressing concentration is independent of temperature? [1992, 1995]

- Molarity
- Molality
- Formality
- Normality

### Topic 2: Vapour Pressure, Laws of Solutions and Ideal, Non-ideal Solutions

14. The mixture which shows positive deviation from Raoult's law is [2020]
- Benzene + Toluene
  - Acetone + Chloroform
  - Chloroethane + Bromoethane
  - Ethanol + Acetone
15. Which of the following statements is correct regarding a solution of two components A and B exhibiting positive deviation from ideal behaviour? [NEET Odisha 2019]
- Intermolecular attractive forces between A-A and B-B are equal to those between A-B.
  - Intermolecular attractive forces between A-A and B-B are stronger than those between A-B.
  - $\Delta_{\text{mix}}H = 0$  at constant T and P.
  - $\Delta_{\text{mix}}V = 0$  at constant T and P.
16. In water saturated air, the mole fraction of water vapour is 0.02. If the total pressure of the saturated air is 1.2 atm, the partial pressure of dry air is [NEET Odisha 2019]
- 0.98 atm
  - 1.18 atm
  - 1.76 atm
  - 1.176 atm
17. The mixture that forms maximum boiling azeotrope is: [2019]
- Water + Nitric acid
  - Ethanol + Water
  - Acetone + Carbon disulphide
  - Heptane + Octane
18. Which of the following statement about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. (Given : Vapour pressure data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa) [2016]
- The vapour will contain a higher percentage of benzene
  - The vapour will contain a higher percentage of toluene
  - The vapour will contain equal amounts of benzene and toluene
  - Not enough information is given to make a predication

19. At 100 °C the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If  $K_b = 0.52$ , the boiling point of this solution will be [2016]
- 101 °C
  - 100 °C
  - 102 °C
  - 103 °C
20. Which one is not equal to zero for an ideal solution: [2015]
- $\Delta S_{mix}$
  - $\Delta V_{mix}$
  - $\Delta P = P_{observed} - P_{Raoult}$
  - $\Delta H_{mix}$
21.  $P_A$  and  $P_B$  are the vapour pressure of pure liquid components, A and B, respectively of an ideal binary solution. If  $X_A$  represents the mole fraction of component A, the total pressure of the solution will be [2012]
- $p_a + x_a(p_b - p_a)$
  - $p_a + x_a(p_a - p_b)$
  - $p_b + x_a(p_b - p_a)$
  - $p_b + x_a(p_a - p_b)$
22. Vapour pressure of chloroform ( $\text{CHCl}_3$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) at 25 °C are 200 mm Hg and 41.5 mm Hg respectively. Vapour pressure of the solution obtained by mixing 25.5 g of  $\text{CHCl}_3$  and 40 g of  $\text{CH}_2\text{Cl}_2$  at the same temperature will be : (Molecular mass of  $\text{CHCl}_3$  = 119.5 u and molecular mass of  $\text{CH}_2\text{Cl}_2$  = 85 u). [2012 M]
- 173.9 mm Hg
  - 615.0 mm Hg
  - 347.9 mm Hg
  - 285.5 mm Hg
23. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase? [2010]
- Addition of NaCl
  - Addition of  $\text{Na}_2\text{SO}_4$
  - Addition of 1.00 molal KI
  - Addition of water
24. A solution of acetone in ethanol [2006]
- shows a positive deviation from Raoult's law
  - behaves like a non ideal solution
  - obeys Raoult's law
  - shows a negative deviation from Raoult's law
25. The vapour pressure of two liquids 'P' and 'Q' are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 mole of 'P' and 2 mole of 'Q' would be [2005]
- 72 torr
  - 140 torr
  - 68 torr
  - 20 torr
26. Formation of a solution from two components can be considered as [2003]
- Pure solvent → separated solvent molecules,  $\Delta H_1$
  - Pure solute → separated solute molecules,  $\Delta H_2$
  - Separated solvent → Solution,  $\Delta H_3$  & solute molecules
- Solution so formed will be ideal if
- $\Delta H_{soln} = \Delta H_3 - \Delta H_1 - \Delta H_2$
  - $\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$
  - $\Delta H_{soln} = \Delta H_1 + \Delta H_2 - \Delta H_3$
  - $\Delta H_{soln} = \Delta H_1 - \Delta H_2 - \Delta H_3$
27. A solution containing components A and B follows Raoult's law when [2002]
- A–B attraction force is greater than A–A and B–B
  - A–B attraction force is less than A–A and B–B
  - A–B attraction force remains same as A–A and B–B
  - Volume of solution is different from sum of volume of solute and solvent
28. The beans are cooked earlier in pressure cooker, because [2001]
- Boiling point increases with increasing pressure
  - Boiling point decreases with increasing pressure
  - Internal energy is not lost while cooking in pressure cooker
  - Extra pressure of pressure cooker, softens the beans
29. The vapour pressure of a solvent decreased by 10 mm of mercury 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 mercury? [1998]
- 0.8
  - 0.6
  - 0.4
  - 0.2
30. The vapour pressure at a given temperature of an ideal solution containing 0.2 mol of a non-volatile solute and 0.8 mol of solvent is 60 mm of Hg. The vapour pressure of the pure solvent at the same temperature is [1996]

**Solutions**

- (a) 150 mm ofHg      (b) 60 mm ofHg  
 (c) 75 mm ofHg      (d) 120 mm ofHg
31. Vapour pressure of benzene at 30 °C is 121.8 mm. When 15 g of a non volatile solute is dissolved in 250 g of benzene, its vapour pressure decreased to 120.2 mm. The molecular weight of the solute (Mo. wt. of solvent = 78) **[1995]**  
 (a) 356.2      (b) 456.8  
 (c) 530.1      (d) 656.7
32. According to Raoult's law, relative lowering of vapour pressure for a solution is equal to  
**[1995]**  
 (a) moles of solute  
 (b) moles of solvent  
 (c) mole fraction of solute  
 (d) mole fraction of solvent
33. The relative lowering of the vapour pressure is equal to the ratio between the number of  
**[1991]**  
 (a) solute molecules to the solvent molecules  
 (b) solute molecules to the total molecules in the solution  
 (c) solvent molecules to the total molecules in the solution  
 (d) solvent molecules to the total number of ions of the solute.
34. An ideal solution is formed when its components  
**[1988]**  
 (a) have no volume change on mixing  
 (b) have no enthalpy change on mixing  
 (c) have both the above characteristics  
 (d) have high solubility.
35. All form ideal solution except **[1988]**  
 (a)  $C_6H_6$  and  $C_6H_5CH_3$   
 (b)  $C_2H_6$  and  $C_2H_5I$   
 (c)  $C_6H_5Cl$  and  $C_6H_5Br$   
 (d)  $C_2H_5I$  and  $C_2H_5OH$ .
- Topic 3: Colligative Properties and Abnormal Molecular Masses**
36. The freezing point depression constant ( $K_f$ ) of benzene is  $5.12 \text{ K kg mol}^{-1}$ . The freezing point depression for the solution of molality 0.078 m containing a non-electrolyte solute in benzene is (rounded off upto two decimal places) :
- (a) 0.80K      (b) 0.40K **[2020]**  
 (c) 0.60K      (d) 0.20K
37. Which one of the following electrolytes has the same value of van't Hoff's factor (*i*) as that of the  $Al_2(SO_4)_3$  (if all are 100% ionised) ? **[2015]**  
 (a)  $K_3[Fe(CN)_6]$       (b)  $Al(NO_3)_3$   
 (c)  $K_4[Fe(CN)_6]$       (d)  $K_2SO_4$
38. The boiling point of  $0.2 \text{ mol kg}^{-1}$  solution of *X* in water is greater than equimolar solution of *Y* in water. Which one of the following statements is true in this case ? **[2015]**  
 (a) Molecular mass of *X* is greater than the molecular mass of *Y*.  
 (b) Molecular mass of *X* is less than the molecular mass of *Y*.  
 (c) *Y* is undergoing dissociation in water while *X* undergoes no change.  
 (d) *X* is undergoing dissociation in water.
39. Of the following  $0.10 \text{ m}$  aqueous solutions, which one will exhibit the largest freezing point depression? **[2014]**  
 (a)  $KCl$       (b)  $C_6H_{12}O_6$   
 (c)  $Al_2(SO_4)_3$       (d)  $K_2SO_4$
40. The freezing point depression constant for water is  $-1.86 \text{ }^{\circ}\text{C m}^{-1}$ . If  $5.00 \text{ g}$   $Na_2SO_4$  is dissolved in  $45.0 \text{ g}$   $H_2O$ , the freezing point is changed by  $-3.82 \text{ }^{\circ}\text{C}$ . Calculate the van't Hoff factor for  $Na_2SO_4$ . **[2011]**  
 (a) 2.05      (b) 2.63  
 (c) 3.11      (d) 0.381
41. The van't Hoff factor *i* for a compound which undergoes dissociation in one solvent and association in other solvent is respectively : **[2011]**  
 (a) less than one and greater than one.  
 (b) less than one and less than one.  
 (c) greater than one and less than one.  
 (d) greater than one and greater than one.
42. A  $0.1 \text{ molal}$  aqueous solution of a weak acid is  $30\%$  ionized. If  $\kappa_f$  for water is  $1.86 \text{ }^{\circ}\text{C/m}$ , the freezing point of the solution will be : **[2011 MJ]**  
 (a)  $-0.18 \text{ }^{\circ}\text{C}$       (b)  $-0.54 \text{ }^{\circ}\text{C}$   
 (c)  $-0.36 \text{ }^{\circ}\text{C}$       (d)  $-0.24 \text{ }^{\circ}\text{C}$

43. 200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be  $2.57 \times 10^{-3}$  bar. The molar mass of protein will be ( $R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$ ) **[2011 MJ]**
- (a) 51022 g mol<sup>-1</sup> (b) 122044 g mol<sup>-1</sup>  
 (c) 31011 g mol<sup>-1</sup> (d) 61038 g mol<sup>-1</sup>
44. A solution of sucrose (molar mass = 342 g mol<sup>-1</sup>) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup>). **[2010]**
- (a) -0.372 °C (b) -0.520 °C  
 (d) +0.372 °C (d) -0.570 °C
45. A 0.0020 m aqueous solution of an ionic compound  $\text{Co}(\text{NH}_3)_5(\text{NO}_2)\text{Cl}$  freezes at -0.00732 °C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be ( $K_f = -1.86 \text{ }^{\circ}\text{C}/\text{m}$ ) **[2009]**
- (a) 3 (b) 4  
 (c) 1 (d) 2
46. 0.5 molal aqueous solution of a weak acid ( $\text{HX}$ ) is 20% ionised. If  $K_f$  for water is 1.86 K kg mol<sup>-1</sup>, the lowering in freezing point of the solution is **[2007]**
- (a) 0.56K (b) 1.12K  
 (c) -0.56K (d) -1.12K
47. During osmosis, flow of water through a semipermeable membrane is **[2006]**
- (a) from both sides of semipermeable membrane with equal flow rates  
 (b) from both sides of semipermeable membrane with unequal flow rates  
 (c) from solution having lower concentration only  
 (d) from solution having higher concentration only
48. A solution containing 10 g dm<sup>-3</sup> of urea (molecular mass = 60 g mol<sup>-1</sup>) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is **[2006]**
- (a) 300 g mol<sup>-1</sup> (b) 350 g mol<sup>-1</sup>  
 (c) 200 g mol<sup>-1</sup> (d) 250 g mol<sup>-1</sup>
49. 1.00 g of a non-electrolyte solute (molar mass 250 g mol<sup>-1</sup>) was dissolved in 51.2 g of benzene. If the freezing point depression constant,  $K_f$  of benzene is 5.12 K kg mol<sup>-1</sup>, the freezing point of benzene will be lowered by **[2006]**
- (a) 0.3 K (b) 0.5 K  
 (c) 0.4 K (d) 0.2
50. A solution of urea (mol. mass 56 g mol<sup>-1</sup>) 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<sup>-1</sup> respectively, the above solution will freeze at **[2005]**
- (a) 0.654 °C (b) -0.654 °C  
 (c) 6.54 °C (d) -6.54 °C
51. Camphor is often used in molecular mass determination because **[2004]**
- (a) it is readily available  
 (b) it has a very high cryoscopic constant  
 (c) it is volatile  
 (d) it is solvent for organic substances
52. A solution contains non-volatile solute of molecular mass  $M_2$ . Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure ? **[2002]**
- (a)  $M_2 = \left( \frac{m_2}{\pi} \right) VRT$  (b)  $M_2 = \left( \frac{m_2}{V} \right) \frac{RT}{\pi}$   
 (c)  $M_2 = \left( \frac{m_2}{V} \right) \pi RT$  (d)  $M_2 = \left( \frac{m_2}{V} \right) \frac{\pi}{RT}$
53. Which of the following colligative property can provide molar mass of proteins (or polymers or colloids) with greatest precision ? **[2000]**
- (a) Osmotic pressure  
 (b) Elevation of boiling point  
 (c) Depression of freezing point  
 (d) Relative lowering of vapour pressure
54. Which of the following 0.10 m aqueous solutions will have the lowest freezing point ? **[1997]**
- (a)  $\text{Al}_2(\text{SO}_4)_3$  (b)  $\text{C}_6\text{H}_{12}\text{O}_6$   
 (c)  $\text{KCl}$  (d)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
55. At 25 °C, the highest osmotic pressure is exhibited by 0.1 M solution of **[1994]**
- (a)  $\text{CaCl}_2$  (b)  $\text{KCl}$   
 (c) Glucose (d) Urea.

56. Which one of the following salts will have the same value of van't Hoff factor ( $i$ ) as that of  $K_4[Fe(CN)_6]$ . [1994]  
 (a)  $Al_2(SO_4)_3$       (b)  $NaCl$   
 (c)  $Al(NO_3)_3$       (d)  $Na_2SO_4$ .
57. Which one is a colligative property? [1992]  
 (a) boiling point      (b) vapour pressure  
 (c) osmotic pressure      (d) freezing point
58. If 0.1 M solution of glucose and 0.1 M solution of urea are placed on two sides of the semi-permeable membrane to equal heights, then it will be correct to say that [1992]  
 (a) There will be no net movement across the membrane
59. Which of the following aqueous solution has minimum freezing point? [1991]  
 (a) 0.01 m  $NaCl$       (b) 0.005 m  $C_2H_5OH$   
 (c) 0.005 m  $MgI_2$       (d) 0.005 m  $MgSO_4$ .
60. Blood cells retain their normal shape in solution which are [1991]  
 (a) hypotonic to blood  
 (b) isotonic to blood  
 (c) hypertonic to blood  
 (d) equinormal to blood.

## ANSWER KEY

1	(d)	7	(b)	13	(b)	19	(a)	25	(a)	31	(a)	37	(c)	43	(d)	49	(c)	55	(a)
2	(c)	8	(c)	14	(d)	20	(a)	26	(b)	32	(c)	38	(d)	44	(a)	50	(b)	56	(a)
3	(a)	9	(b)	15	(b)	21	(d)	27	(c)	33	(b)	39	(c)	45	(d)	51	(b)	57	(c)
4	(d)	10	(d)	16	(d)	22	(N)	28	(a)	34	(c)	40	(b)	46	(b)	52	(b)	58	(a)
5	(d)	11	(c)	17	(a)	23	(d)	29	(b)	35	(d)	41	(c)	47	(c)	53	(a)	59	(a)
6	(b)	12	(c)	18	(a)	24	(a)	30	(c)	36	(b)	42	(d)	48	(a)	54	(a)	60	(b)

## Hints &amp; Solutions

1. (d) Let, volume of solution = 1 L  
 Mole of  $NaOH = 2$   
 Mass of  $NaOH$  solution = volume  $\times$  density  
 $= 1000 \times 1.28 = 1280$  g  
 Mass of  $H_2O = (1280 - 2 \times 40) = 1200$  g = 1.2 kg  
 $Molality (m) = \frac{\text{Mole of } NaOH}{\text{Mass of solvent (kg)}} = \frac{2}{1.2} = 1.67m$
2. (c)  $K_f$  (molal depression constant) only depends on the nature of the solvent and is independent of the concentration of the solution.
3. (a) Molarity depends on the volume of a solution which can be changed with change in temperature.

4. (d) Molality =  $\frac{W}{M} \times \frac{1}{V(kg)}$   
 $= \frac{n}{V(kg)}$       (where  $n_{\text{solute}} = W/M$ )  
 $1.00 m = \frac{n}{V(kg)}$  i.e., 1 mole in 1 kg of water  
 Moles of 1 kg  $H_2O$   
 $= \frac{1000 g}{18 g / mol} = 55.55$  mole  
 Moles of solute = 1  
 Mole fraction  
 $= \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{water}}} = \frac{1}{(1 + 55.55)}$   
 $= 0.01768 = 0.0177$

5. (d) Molarity (M) =  $\frac{\text{wt} \times 1000}{\text{mol. wt.} \times \text{vol (mL)}}$

$$2 = \frac{\text{wt.}}{63} \times \frac{1000}{250}$$

$$\text{wt.} = \frac{63}{2} \text{ g}$$

$$\text{wt. of 70% acid} = \frac{100}{70} \times 31.5 = 45 \text{ g}$$

6. (b) Concentration of

$$\text{Na}_2\text{CO}_3 = \frac{25.3}{106} \times \frac{1000}{250} = 0.955 \text{ M}$$

$$[\text{Na}^+] = 2 \times 0.955 = 1.91 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.955 \text{ M}$$

7. (b) One molal solution means one mole solute present in 1 kg (1000 g) solvent  
i.e., mole of solute = 1

$$\text{Mole of solvent (H}_2\text{O}) = \frac{1000 \text{ g}}{18 \text{ g}} = \frac{1000}{18}$$

$$\text{Mole fraction of solute} = \frac{1}{\left(1 + \frac{1000}{18}\right)}$$

$$= \frac{18}{1018} = 0.01768 \approx 0.018.$$

8. (c) From molarity equation

$$M_1 V_1 + M_2 V_2 = MV$$

$$1 \times 2.5 + 0.5 \times 3 = M \times 5.5$$

$$M = \frac{4}{5.5} = 0.727 \approx 0.73 \text{ M}$$

9. (b) Density = 1.17 g/cc

$$\text{As } d = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{volume} = 1 \text{ cc} \therefore \text{mass} = 1.17 \text{ g}$$

$$\text{Now molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{1.17 \times 1000}{36.5 \times 1} = \frac{1170}{36.5} = 32.05 \text{ M}$$

10. (d) The mole fraction can never be equal to -2 or 2. It is always between 0 and 1 i.e.,  $0 < x < 1$ .

11. (c) 5% cane sugar solution means 100ml of solution contain cane sugar = 5g

$\therefore 1000 \text{ mL of solution contain cane sugar}$

$$= \frac{5}{100} \times 1000 = 50 \text{ g/L}$$

Similarly 1% solution contains  $= \frac{1 \times 1000}{100}$

$$= 10 \text{ g/L of } X.$$

$$(\pi_1) = C \times R \times T = \frac{50 \text{ g/L}}{342} \times R \times T$$

Osmotic pressure of 1% solution of substance

$$(\pi_2) = \frac{10 \text{ g/L}}{M} \times R \times T$$

As both are isotonic,

$$\text{So } \pi_1 = \pi_2$$

$$\text{or } \frac{50}{342} \times R \times T = \frac{10}{M} \times R \times T$$

$$\therefore M (\text{mol. wt. of } X) = \frac{342}{5} = 68.4$$

12. (c) Percentage volume of oxygen = 21%.

So, 100 mL of air contains = 21 mL of O<sub>2</sub>

$\therefore$  Volume of oxygen in one litre of air

$$= \frac{21}{100} \times 1000 = 210 \text{ mL.}$$

$$\text{Therefore, no. of moles} = \frac{210}{22400} = 0.0093$$

( $\because$  volume of 1 mole of gas at S.T.P. is 22400 mL)

13. (b) The molality involves weights of the solute and the solvent. Since weight does not change with the temperature, therefore molality does not depend upon the temperature.

14. (d) Hydrogen bond of ethanol gets weakened by addition of acetone. Thus the mixture of ethanol and acetone show positive deviation from Raoult's law.

15. (b) In case of positive deviation from ideal behaviour A-B interactions are weaker than A-A and B-B interactions.

16. (d) Mole fraction of water vapour = 0.02  
 $\therefore$  Mole fraction of dry air =  $1 - 0.02 = 0.98$

Total pressure of saturated air = 1.2 atm

Acc. to Dalton's law of partial pressure,

$$P_{\text{Dry air}} = P_{\text{Total}} x_{\text{Dry air}} = 1.2 \times 0.98 = 1.176 \text{ atm}$$

17. (a) The solutions which show a large negative deviation from Raoult's law form maximum

**Solutions**

boiling azeotrope. Nitric acid and water forms a maximum boiling azeotrope with a boiling point of 393.5 K.

18. (a) Let us consider that A is benzene and B is toluene

1 : 1 molar mixture of A and B

$$\therefore x_A = \frac{1}{2} \text{ and } x_B = \frac{1}{2}$$

Total pressure of solution ( $P$ ) =  $P_A^0 x_A + P_B^0 x_B$

$$P = 12.8 \times \frac{1}{2} + 3.85 \times \frac{1}{2} = 8.325 \text{ kPa}$$

$$y_A = \frac{P_A^0 x_A}{P} = \frac{12.8 \times \frac{1}{2}}{8.325} = 0.768$$

$$\therefore y_B = 1 - y_A = 1 - 0.768 = 0.232$$

so, the vapour will contain higher percentage of benzene.



As the molar composition is same and benzene has higher vapour pressure, the vapour will contain higher percentage of benzene.

19. (a)  $\left( \frac{P^\circ - P_s}{P^\circ} \right) = \frac{n}{N} - \frac{W_1}{M_1} \times \frac{M_2}{W_2}$

Where,  $W_1$  = wt of solute

$W_2$  = wt of solvent

$M_1$  = Mass of solute

$M_2$  = Mass of solvent

at 100 °C,  $P^\circ = 760 \text{ mm}$

$$\frac{760 - 732}{760} = \frac{6.5 \times 18}{M_1 \times 100}$$

$$M_1 = 31.75 \text{ g mol}^{-1}$$

$$\Delta T_b = m \times K_b = \frac{W_1 \times 1000}{M_1 \times W_2} \times K_b$$

$$\Delta T_b = \frac{0.52 \times 6.5 \times 1000}{31.75 \times 100} = 1.06 \text{ }^\circ\text{C}$$

∴ boiling point of solution

$$= 100 \text{ }^\circ\text{C} + 1.06 \text{ }^\circ\text{C} = 101 \text{ }^\circ\text{C}$$

20. (a) For an ideal solution  $\Delta S_{\text{mix}} > 0$



Entropy will always increase upon mixing two compounds as disorder increases.

21. (d)  $P = P_A X_A + P_B X_B = P_A X_A + P_B (1 - X_A)$   
(for binary sol.  $X_A + X_B = 1$ )

$$\Rightarrow P_A X_A + P_B - P_B X_A$$

$$\Rightarrow P_B + X_A (P_A - P_B)$$

22. (N)  $n_{\text{CHCl}_3} = \frac{25.5}{119.5} = 0.213$

$$n_{\text{CH}_2\text{Cl}_2} = \frac{40}{85} = 0.47$$

$$\begin{aligned} P_T &= P_A^\circ X_A + P_B^\circ X_B \\ &= 200 \times \frac{0.213}{0.683} + 41.5 \times \frac{0.47}{0.683} \\ &= 62.37 + 28.55 = 90.92 \end{aligned}$$

23. (d) When the aqueous solution of one molal KI is diluted with water, concentration decreases, therefore the vapour pressure of the resulting solution increases.

24. (a) A solution of acetone in ethanol shows positive deviation from Raoult's law. It is because ethanol molecules are strongly hydrogen bonded. When acetone is added, these molecules break the hydrogen bonds and ethanol becomes more volatile. Therefore, its vapour pressure is increased.

25. (a) Given  $V.P_p = 80 \text{ torr}$

$$V.P_Q = 60 \text{ torr}$$

$$P_{\text{total}} = V.P_p \times X_p + V.P_Q \times X_Q$$

$$= \left[ 80 \times \frac{3}{5} + 60 \times \frac{2}{5} \right] = 16 \times 3 + 12 \times 2$$

$$P_{\text{total}} = 48 + 24 = 72 \text{ torr}$$

26. (b) For an ideal solution,  $\Delta H_{\text{mixing}} = 0$   
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$  (According to Hess's law)



for ideal solutions there is no change in magnitude of the attractive forces in the two components present.

27. (c) These two components  $A$  and  $B$  follows the condition of Raoult's law if the force of attraction between  $A$  and  $B$  is equal to the force of attraction between  $A$  and  $A$  or  $B$  and  $B$ .

28. (a) The beans are cooked earlier in pressure cooker because boiling point increases with increasing pressure.

29. (b) According to Raoult's law

$$\frac{P^o - p}{P^o} = \frac{n}{n+N} \text{ (mole fraction of solute)}$$

$$\frac{10}{P^o} = 0.2 \quad \therefore P^o = 50 \text{ mm}$$

For other solution of same solvent

$$\frac{20}{P^o} = \frac{n}{n+N} \text{ (mole fraction of solute)}$$

$$\Rightarrow \frac{20}{50} = \text{mole fraction of solute}$$

$$\Rightarrow \text{Mole fraction of solute} = 0.4$$

$$\text{Hence, mole fraction of solvent} = 1 - 0.4 = 0.6$$



Decrease in vapour pressure  $\mu$  Mole fraction of solute.  
Thus, depression of  $2 \times 0.2$  mm Hg vapour pressure requires  $= 2 \times 0.2$  mole fraction of solute.

30. (c) According to Raoult's law

$$\frac{P^o - P}{P^o} = x_B$$

$$\left[ x_B = \text{Mole fraction of solute} = \frac{.2}{.2 + .8} = \frac{1}{5} \right]$$

$$P = 60 \text{ mm of Hg}$$

$$\frac{P^o - P}{P^o} = \frac{1}{5} \text{ or } 4P^o = (P) \times 5$$

$$\Rightarrow P^o = \frac{60 \times 5}{4} = 75 \text{ mm of Hg}$$

31. (a) Given vapour pressure ( $P^o$ ) = 121.8 mm; Weight of solute ( $w$ ) = 15 g

Weight of solvent ( $W$ ) = 250 g

From Raoult's law,

$$= \frac{P^o - P}{P^o} = \frac{w}{m} \times \frac{M}{W} = \frac{121.8 - 120.2}{121.8} = \frac{15}{m} \times \frac{78}{250}$$

$$\text{or } m = \frac{15 \times 78}{250} \times \frac{121.8}{1.6} = 356.2$$

32. (c) Relative lowering of vapour pressure depends upon the mole fraction of solute.

$$\text{i.e., } \frac{P^o - P}{P^o} = \text{mole fraction of solute}$$

33. (b) According to Raoult's law, the relative lowering in vapour pressure of a dilute solution is equal to the mole fraction of the solute present in the solution.

$$\frac{P^o - P}{P^o} = \text{mole fraction of solute} = \frac{n}{n+N}$$

34. (c) For ideal solution,

$$\Delta V_{\text{mixing}} = 0 \text{ and } \Delta H_{\text{mixing}} = 0.$$

35. (d) Ethyl alcohol forms hydrogen bonding with itself, hence it will not form ideal solution with  $C_2H_5I$ .

$$36. (b) \Delta T_f = K_f m = 5.12 \times 0.078 = 0.399 \text{ K} = 0.40 \text{ K}$$

$$37. (c) K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$



$\therefore$  van't Hoff factor is 5 for both  $Al_2(SO_4)_3$  and  $K_4[Fe(CN)_6]$

$$38. (d) \Delta T_b = iK_b m$$

$$\text{Given, } (\Delta T_b)_x > (\Delta T_b)_y$$

$\therefore i_x K_b m > i_y K_b m$   
( $K_b$  is same for same solvent)

$$i_x > i_y$$

So,  $x$  is undergoing dissociation in water.

39. (c) Colligative properties  $\propto$  no. of particles. Since  $Al_2(SO_4)_3$  contains maximum number of particles, hence will have the largest value of freezing point depression.

40. (b) Given  $K_f = -1.86^\circ \text{ cm}^{-1}$ , mass of solute = 5.00 g, mass of solvent = 45.0 g

$$\Delta T_f = i \times K_f \cdot m$$

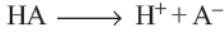
$$3.82 = i \times 1.86 \times \frac{5 \times 1000}{142 \times 45}$$

(Molecular mass of  $Na_2SO_4 = 142$ )

$$\therefore i = 2.63$$

41. (c) If compound dissociates in solvent  $i > 1$  and on association  $i < 1$ .

42. (d) Given  $\alpha = 30\%$  i.e., 0.3



$$1 - \alpha \quad \alpha \quad \alpha$$

$$1 - 0.3 \quad 0.3 \quad 0.3$$

$$i = 1 - 0.3 + 0.3 + 0.3$$

$$i = 1.3$$

$$\Delta T_f = 1.3 \times 1.86 \times 0.1 = 0.2418$$

$$T_f = 0 - 0.2418 = -0.2418^\circ\text{C}$$

43. (d)  $\pi = CRT$  (Osmotic pressure)

$$\begin{aligned}\pi &= \frac{\text{wt} \times 1000}{\text{Molecular mass} \times V} RT = 2.57 \times 10^{-3} \\ &= \frac{1.26 \times 1000}{\text{Mol. mass} \times 200} \times 0.083 \times 300\end{aligned}$$

$$\begin{aligned}\text{Molecular mass} &= \frac{1.26 \times 0.083 \times 300 \times 1000}{200 \times 2.57 \times 10^{-3}} \\ &= 61038 \text{ g mol}^{-1}\end{aligned}$$

$$\begin{aligned}44. (a) \quad \Delta T_f &= K_f \frac{1000 W_2}{M_2 W_1} \\ &= \frac{1.86 \times 1000 \times 68.5}{342 \times 1000} = 0.372^\circ\text{C}\end{aligned}$$

$$T_f = -0.372^\circ\text{C} \quad \because (0 - \Delta T_f)$$

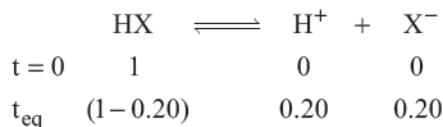
45. (d)  $\Delta T_f = 0 - (-0.00732^\circ) = 0.00732$

$$\Delta T_f = i \times K_f \times m$$

$$i = \frac{\Delta T_f}{K_f \times m} = \frac{0.00732}{1.86 \times 0.002} = 2$$

46. (b) As  $\Delta T_f = i K_f m$

For



$$\begin{aligned}\text{Total no. of moles} &= 1 - 0.20 + 0.20 + 0.20 \\ &= 1 + 0.20 = 1.2\end{aligned}$$

$$\therefore \Delta T_f = 1.2 \times 1.86 \times 0.5 = 1.1160 \approx 1.12 \text{ K}$$

47. (c) During osmosis, water flows through semipermeable membrane from lower concentration to higher concentration.

48. (a) Osmotic pressure of urea from the formula

$$\pi V = nRT \Rightarrow \pi = \frac{nRT}{V}$$

$$\Rightarrow \frac{10}{60} \times 0.0821 \times T \quad [1 \text{ dm}^3 = 1 \text{ litre}]$$

5% solution means

100 ml  $\equiv$  5 g

1000 ml  $=$  50 g/L

Osmotic pressure of solution having non-

$$\text{volatile solute } \pi_2 = \frac{50}{M} \times 0.0821 \times T$$

For isotonic solution,  $\pi_1 = \pi_2$

$$\frac{10}{60} \times 0.0821 \times T = \frac{50}{M} \times 0.0821 \times T$$

$$M = 300 \text{ gm mol}^{-1}$$

$$49. (c) \quad \Delta T = K_f m = 5.12 \times \frac{1}{250} \times \frac{1000}{51.2} = 0.4 \text{ K}$$

50. (b) As  $\Delta T_f = K_f \cdot m$

$$\Delta T_b = K_b \cdot m$$

$$\text{Hence, we have } m = \frac{\Delta T_f}{K_f} = \frac{\Delta T_b}{K_b}$$

$$\text{or } \Delta T_f = \Delta T_b \frac{K_f}{K_b}$$

$$\Rightarrow [\Delta T_b = 100.18 - 100 = 0.18^\circ\text{C}]$$

$$= 0.18 \times \frac{1.86}{0.512} = 0.654^\circ\text{C}$$

As the Freezing Point of pure water is  $0^\circ\text{C}$ ,

$$\Delta T_f = 0 - T_f$$

$$0.654 = 0 - T_f$$

$$\therefore T_f = -0.654$$

Thus the freezing point of solution will be  $-0.654^\circ\text{C}$ .

51. (b) Solvent having high cryoscopic constant can be used in determination of molecular mass by cryoscopic method.

$$52. (b) \quad \pi V = nRT = \frac{m}{M} RT \text{ or } M_2 = \left( \frac{m_2}{V} \right) \frac{RT}{\pi}$$

Where  $M_2$  = molecular mass of solute  
and  $m_2$  = mass of solute

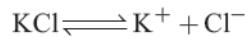
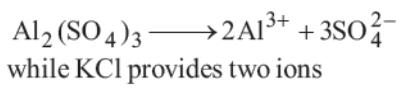
53. (a) Molecular masses of polymers are best determined by osmotic pressure method. Because other colligative properties give so low values that they cannot be measured accurately.



Osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.

54. (a) Depression in F.P.  $\propto$  No. of particles.

$\text{Al}_2(\text{SO}_4)_3$  provides five ions on ionisation



$C_6H_{12}O_6$  and  $C_{12}H_{22}O_{11}$  are not ionised so they have single particle.

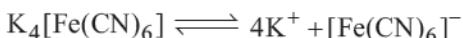
Hence,  $Al_2(SO_4)_3$  have maximum value of depression in *F.P.* or lowest *F.P.*

55. (a) Conc. of particles in  $CaCl_2$  sol. will be max. as  $i = 3$  is max. So it exhibits highest osmotic pressure.

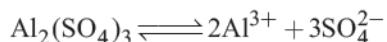


Glucose and urea do not dissociate into ions, as they are non-electrolytes.

56. (a)  $K_4[Fe(CN)_6]$  and  $Al_2(SO_4)_3$  both dissociates to give 5 ions or  $i = 5$



and



57. (c) Osmotic pressure, **elevation** in boiling point, **lowering** of vapour pressure and **depression** in freezing point are colligative properties.

58. (a) As both the solutions are isotonic hence there will be no net movement of the solvent through the semipermeable membrane between two solutions.

59. (a)  $\Delta T_f = i \times K_f \times m$   
Van't Hoff factor,  $i = 2$  for  $NaCl$ ,  
hence  $\Delta T_f = 0.02 K_f$  which is maximum in the present case.  
Hence  $\Delta T_f$  is maximum or freezing point is minimum.

60. (b) Blood cells neither swell nor shrink in isotonic solution. As isotonic solution have equal concentration therefore, there is no flow of solvent.



Blood cell shrink when placed in hypertonic solution and swells when placed in hypotonic solution.

# 17

# Electrochemistry

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Conductance and conductivity	ionic mobility							1	E		
Electrolysis and types of electrolysis	electrolysis	1	E								
Cells and electrode potential, Nernst equation	Faraday's law	1	A								
	relation between equilibrium constant and $E_{cell}$			1	A						
	relation between equilibrium constant and Gibbs energy			1	E						
	Nernst equation							1	D		
LOD - Level of Difficulty		E - Easy		A - Average		D - Difficult		Qns - No. of Questions			

### Topic 1: Conductance and Conductivity

1. Following limiting molar conductivities are given as *[NEET Odisha 2019]*

$$\lambda_m^\circ(H_2SO_4) = x \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(K_2SO_4) = y \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\circ(CH_3COOK) = z \text{ S cm}^2 \text{ mol}^{-1}$$

$\lambda_m^\circ$  (in  $\text{S cm}^2 \text{ mol}^{-1}$ ) for  $CH_3COOH$  will be

- (a)  $\frac{(x-y)}{2} + z$       (b)  $x-y+2z$   
 (c)  $x+y+z$       (d)  $x-y+z$

2. Ionic mobility of which of the following alkali metal ions is lowest when aqueous solution of their salts are put under an electric field? *[2017]*

- (a) K      (b) Rb  
 (c) Li      (d) Na

3. Aqueous solution of which of the following compounds is the best conductor of electric current? *[2015 RS]*

- (a) Acetic acid,  $C_2H_4O_2$   
 (b) Hydrochloric acid, HCl  
 (c) Ammonia,  $NH_3$   
 (d) Fructose,  $C_6H_{12}O_6$

4. At  $25^\circ\text{C}$  molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is  $9.54 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and at infinite dilution its molar conductance is  $238 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . The degree of ionisation of ammonium hydroxide at the same concentration and temperature is: *[NEET 2013]*

- (a) 20.800%      (b) 4.008%  
 (c) 40.800%      (d) 2.080%

5. Limiting molar conductivity of  $NH_4OH$  (*i.e.*,  $\Lambda_m^\circ(NH_4OH)$ ) is equal to: *[2012]*

- (a)  $\Lambda_m^\circ(NH_4Cl) + \Lambda_m^\circ(NaCl) - \Lambda_m^\circ(NaOH)$   
 (b)  $\Lambda_m^\circ(NaOH) + \Lambda_m^\circ(NaCl) - \Lambda_m^\circ(NH_4Cl)$   
 (c)  $\Lambda_m^\circ(NH_4OH) + \Lambda_m^\circ(NH_4Cl) - \Lambda_m^\circ(HCl)$   
 (d)  $\Lambda_m^\circ(NH_4Cl) + \Lambda_m^\circ(NaOH) - \Lambda_m^\circ(NaCl)$

6. Molar conductivities ( $\Lambda_m^\circ$ ) at infinite dilution of NaCl, HCl and  $\text{CH}_3\text{COONa}$  are 126.4, 425.9 and 91.0  $\text{S cm}^2 \text{ mol}^{-1}$  respectively.  $\Lambda_m^\circ$  for  $\text{CH}_3\text{COOH}$  will be : **[2012 MJ]**
- 425.5  $\text{S cm}^2 \text{ mol}^{-1}$
  - 180.5  $\text{S cm}^2 \text{ mol}^{-1}$
  - 290.8  $\text{S cm}^2 \text{ mol}^{-1}$
  - 390.5  $\text{S cm}^2 \text{ mol}^{-1}$
7. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to: **[2010]**
- increase in ionic mobility of ions
  - 100% ionisation of electrolyte at normal dilution
  - increase in both i.e. number of ions and ionic mobility of ions
  - increase in number of ions
8. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of  $\text{Al}_2(\text{SO}_4)_3$ ? Given that  $\Lambda_{\text{Al}^{3+}}^\circ$  and  $\Lambda_{\text{SO}_4^{2-}}^\circ$  are the equivalent conductances at infinite dilution of the respective ions. **[2010]**
- $\frac{1}{3}\Lambda_{\text{Al}^{3+}}^\circ + \frac{1}{2}\Lambda_{\text{SO}_4^{2-}}^\circ$
  - $2\Lambda_{\text{Al}^{3+}}^\circ + 3\Lambda_{\text{SO}_4^{2-}}^\circ$
  - $\Lambda_{\text{Al}^{3+}}^\circ + \Lambda_{\text{SO}_4^{2-}}^\circ$
  - $(\Lambda_{\text{Al}^{3+}}^\circ + \Lambda_{\text{SO}_4^{2-}}^\circ) \times 6$
9. The equivalent conductance of  $\frac{\text{M}}{32}$  solution of a weak monobasic acid is 8.0 mho  $\text{cm}^2$  and at infinite dilution is 400 mho  $\text{cm}^2$ . The dissociation constant of this acid is: **[2009]**
- $1.25 \times 10^{-6}$
  - $6.25 \times 10^{-4}$
  - $1.25 \times 10^{-4}$
  - $1.25 \times 10^{-5}$
10. Kohlrausch's law states that at : **[2008]**
- finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.
  - infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.
11. (c) infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.
- (d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.
12. The ionic conductance of  $\text{Ba}^{2+}$  and  $\text{Cl}^-$  are respectively 127 and 76  $\text{ohm}^{-1} \text{ cm}^2$  at infinite dilution. The equivalent conductance (in  $\text{ohm}^{-1} \text{ cm}^2$ ) of  $\text{BaCl}_2$  at infinite dilution will be : **[2000]**
- 139.5
  - 203
  - 279
  - 101.5
13. Specific conductance of a 0.1 N KCl solution at 23°C is 0.012  $\text{ohm}^{-1} \text{ cm}^{-1}$ . Resistance of cell containing the solution at same temperature was found to be 55 ohm. The cell constant is **[2000]**
- 0.918  $\text{cm}^{-1}$
  - 0.66  $\text{cm}^{-1}$
  - 1.142  $\text{cm}^{-1}$
  - 1.12  $\text{cm}^{-1}$
14. Equivalent conductances of NaCl, HCl and  $\text{CH}_3\text{COONa}$  at infinite dilution are 126.45, 426.16 and 91  $\text{ohm}^{-1} \text{ cm}^2$  respectively. The equivalent conductance of  $\text{CH}_3\text{COOH}$  at infinite dilution would be **[1997]**
- 101.38  $\text{ohm}^{-1} \text{ cm}^2$
  - 253.62  $\text{ohm}^{-1} \text{ cm}^2$
  - 390.71  $\text{ohm}^{-1} \text{ cm}^2$
  - 678.90  $\text{ohm}^{-1} \text{ cm}^2$
15. If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4  $\text{cm}^{-1}$ , then its molar conductance in  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  is **[1997]**
- $10^2$
  - $10^4$
  - 10
  - $10^3$
16. On heating one end of a piece of a metal, the other end becomes hot because of **[1995]**
- resistance of the metal
  - mobility of atoms in the metal
  - energised electrons moving to the other end
  - minor perturbation in the energy of atoms
17. If 0.5 A current is passed through acidified silver nitrate solution for 100 minutes. The mass of silver deposited on cathode, is (eq.wt.of silver nitrate = 108) **[1995]**
- 2.3523 g
  - 3.3575 g
  - 5.3578 g
  - 6.3575 g
17. Which of the following is an insulator ? **[1992]**
- Graphite
  - Aluminium
  - Diamond
  - Silicon.

**Topic 2: Electrolysis and Types of Electrolysis**

18. On electrolysis of dil. sulphuric acid using Platinum (Pt) electrode, the product obtained at anode will be [2020]  
 (a) Oxygen gas      (b)  $\text{H}_2\text{S}$  gas  
 (c)  $\text{SO}_2$  gas      (d) Hydrogen gas
19. The number of Faradays(F) required to produce 20 g of calcium from molten  $\text{CaCl}_2$  (Atomic mass of Ca = 40 g mol<sup>-1</sup>) is: [2020]  
 (a) 2                  (b) 3  
 (c) 4                  (d) 1
20. When 0.1 mol  $\text{MnO}_4^{2-}$  is oxidised, the quantity of electricity required to completely oxidise  $\text{MnO}_4^{2-}$  to  $\text{MnO}_4^-$  is: [2014]  
 (a) 96500 C            (b)  $2 \times 96500$  C  
 (c) 9650 C            (d) 96.50 C
21. The weight of silver (at wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of  $\text{O}_2$  at STP will be :- [2014]  
 (a) 5.4 g            (b) 10.8 g  
 (c) 54.9 g            (d) 108.0 g
22. How many grams of cobalt metal will be deposited when a solution of cobalt (II) chloride is electrolyzed with a current of 10 amperes for 109 minutes (1 Faraday = 96,500 C; Atomic mass of Co = 59 u) [NEET Kar. 2013]  
 (a) 0.66            (b) 4.0  
 (c) 20.0            (d) 40.0
23.  $\text{Al}_2\text{O}_3$  is reduced by electrolysis at low potentials and high currents. If  $4.0 \times 10^4$  amperes of current is passed through molten  $\text{Al}_2\text{O}_3$  for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency and At. mass of Al = 27 g mol<sup>-1</sup>) [2009]  
 (a)  $8.1 \times 10^4$  g    (b)  $2.4 \times 10^5$  g  
 (c)  $1.3 \times 10^4$  g    (d)  $9.0 \times 10^3$  g
24. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from  $\text{Al}^{3+}$  solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from  $\text{H}^+$  ions in solution by the same quantity of electric charge will be [2005]  
 (a) 44.8 L            (b) 22.4 L  
 (c) 11.2 L            (d) 5.6 L
25. In electrolysis of  $\text{NaCl}$ , when Pt electrode is taken, then  $\text{H}_2$  is liberated at cathode while with Hg cathode, it forms sodium amalgam. This is because [2002]

- (a) Hg is more inert than Pt  
 (b) More voltage is required to reduce  $\text{H}^+$  at Hg than at Pt  
 (c) Na is dissolved in Hg while it does not dissolve in Pt  
 (d) Conc. of  $\text{H}^+$  ions is larger when Pt electrode is taken
26. Standard electrode potentials are :  $\text{Fe}^{+2}/\text{Fe}$  [ $E^\circ = -0.44$ ];  $\text{Fe}^{+3}/\text{Fe}^{+2}$  [ $E^\circ = +0.77$ ] ; If  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$  and Fe blocks are kept together, then [2001]  
 (a)  $\text{Fe}^{+2}$  increases  
 (b)  $\text{Fe}^{+3}$  decreases  
 (c)  $\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}}$  remains unchanged  
 (d)  $\text{Fe}^{+2}$  decreases
27. On passing a current of 1.0 ampere for 16 min and 5 sec through one litre solution of  $\text{CuCl}_2$ , all copper of the solution was deposited at cathode. The strength of  $\text{CuCl}_2$  solution was (Molar mass of Cu = 63.5; Faraday constant = 96,500 C mol<sup>-1</sup>) [1996]  
 (a) 0.01 N            (b) 0.01 M  
 (c) 0.02 M            (d) 0.2 N
28. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be [1992]  
 (a) hydrogen            (b) oxygen  
 (c) hydrogen sulphide    (d) sulphur dioxide.

**Topic 3: Cells and Electrode Potential, Nernst Equation**

29. For a cell involving one electron  $E_{\text{cell}}^! = 0.59$  V at 298 K, the equilibrium constant for the cell reaction is : [2019]  
 Given that  $\frac{2.303RT}{F} = 0.059$  V at T = 298 K  
 (a)  $1.0 \times 10^2$             (b)  $1.0 \times 10^5$   
 (c)  $1.0 \times 10^{10}$             (d)  $1.0 \times 10^{30}$
30. For the cell reaction [2019]  
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$   
 0.24 V at 298 K. The standard Gibbs energy ( $\Delta G^\circ$ ) of the cell reaction is:  
 [Given that Faraday constant F = 96500 C mol<sup>-1</sup>]  
 (a)  $-46.32 \text{ kJ mol}^{-1}$     (b)  $-23.16 \text{ kJ mol}^{-1}$   
 (c)  $46.32 \text{ kJ mol}^{-1}$     (d)  $23.16 \text{ kJ mol}^{-1}$

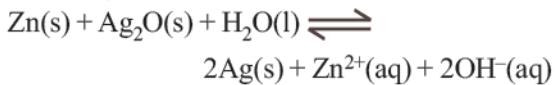
31. In the electrochemical cell :- [2003, 2017]  
 $Zn|ZnSO_4(0.01M)||CuSO_4(1.0\text{ M})|Cu$ , the emf of this Daniel cell is  $E_1$ . When the concentration of  $ZnSO_4$  is changed to 1.0M and that of  $CuSO_4$  changed to 0.01M, the emf changes to  $E_2$ . From the followings, which one is the relationship between  $E_1$  and  $E_2$ ? (Given,  $\frac{RT}{F} = 0.059$ )  
 (a)  $E_1 < E_2$       (b)  $E_1 > E_2$   
 (c)  $E_2 = 0 \neq E_1$       (d)  $E_1 = E_2$
32. The pressure of  $H_2$  required to make the potential of  $H_2$ -electrode zero in pure water at 298 K is : [2016]  
 (a)  $10^{-14}$  atm      (b)  $10^{-12}$  atm  
 (c)  $10^{-10}$  atm      (d)  $10^{-4}$  atm
33. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as : [2015]  
 (a) Electrolytic cell      (b) Dynamo  
 (c) Ni-Cd cell      (d) Fuel Cell
34. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be ? [NEET 2013]  
 (a) 0.59 V      (b) 0.118 V  
 (c) 1.18 V      (d) 0.059 V
35. Consider the half-cell reduction reaction :  
 $Mn^{2+} + 2e^- \rightarrow Mn, E^\circ = -1.18\text{ V}$   
 $Mn^{2+} \rightarrow Mn^{3+} + e^-, E^\circ = -1.51\text{ V}$   
 The  $E^\circ$  for the reaction  $3Mn^{2+} \rightarrow Mn^0 + 2Mn^{3+}$ , and possibility of the forward reaction are, respectively [NEET Kar. 2013]  
 (a) -2.69 V and no      (b) -4.18 V and yes  
 (c) +0.33 V and yes      (d) +2.69 V and no
36. Standard electrode potential of three metals  $X$ ,  $Y$  and  $Z$  are -1.2 V, +0.5 V and -3.0 V, respectively. The reducing power of these metals will be : [2011]  
 (a)  $Y > Z > X$       (b)  $X > Y > Z$   
 (c)  $Z > X > Y$       (d)  $X > Y > Z$
37. The electrode potentials for  
 $Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$   
 and  $Cu^+(aq) + e^- \longrightarrow Cu(s)$   
 are +0.15 V and +0.50V, respectively. The value of  $E^\circ_{Cu^{2+}/Cu}$  will be :
38. (a) 0.500 V      (b) 0.325 V  
 (c) 0.650 V      (d) 0.150 V
39. Standard electrode potential for  $Sn^{4+} / Sn^{2+}$  couple is + 0.15 V and that for the  $Cr^{3+} / Cr$  couple is -0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be : [2011]  
 (a) +1.19 V      (b) +0.89 V  
 (c) +0.18 V      (d) +1.83 V
40. If the  $E^\circ_{cell}$  for a given reaction has a negative value, then which of the following gives the correct relationships for the values of  $\Delta G^\circ$  and  $K_{eq}$ ? [2011]  
 (a)  $\Delta G^\circ > 0 ; K_{eq} > 1$       (b)  $\Delta G^\circ < 0 ; K_{eq} > 1$   
 (c)  $\Delta G^\circ < 0 ; K_{eq} < 1$       (d)  $\Delta G^\circ > 0 ; K_{eq} < 1$
41. A solution contains  $Fe^{2+}$ ,  $Fe^{3+}$  and  $I^-$  ions. This solution was treated with iodine at 35°C.  $E^\circ$  for  $Fe^{3+} / Fe^{2+}$  is + 0.77 V and  $E^\circ$  for  $I_2/2I^- = 0.536$  V. The favourable redox reaction is : [2011 MJ]  
 (a)  $I_2$  will be reduced to  $I^-$   
 (b) There will be no redox reaction  
 (c)  $I^-$  will be oxidised to  $I_2$   
 (d)  $Fe^{2+}$  will be oxidised to  $Fe^{3+}$
42. For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46 V at 25°C. The value of standard Gibbs energy,  $\Delta G^\circ$  will be ( $F = 96500\text{ C mol}^{-1}$ )  
 (a) -89.0 kJ      (b) -89.0 J [2010]  
 (c) -44.5 kJ      (d) -98.0 kJ
43. Consider the following relations for emf of a electrochemical cell: [2010]  
 (i) emf of cell = (Oxidation potential of anode) - (Reduction potential of cathode)  
 (ii) emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)  
 (iii) emf of cell = (Reduction potential of anode) + (Reduction potential of cathode)  
 (iv) emf of cell = (Oxidation potential of anode) - (Oxidation potential of cathode)  
 Which of the above relations are correct?  
 (a) (ii) and (iv)      (b) (iii) and (i)  
 (c) (i) and (ii)      (d) (iii) and (iv)
- Given: [2009]  
 (i)  $Cu^{2+} + 2e^- \rightarrow Cu, E^\circ = 0.337\text{ V}$   
 (ii)  $Cu^{2+} + e^- \rightarrow Cu^+, E^\circ = 0.153\text{ V}$   
 Electrode potential,  $E^\circ$  for the reaction,  $Cu^+ + e^- \rightarrow Cu$ , will be :  
 (a) 0.90 V      (b) 0.30 V  
 (c) 0.38 V      (d) 0.52 V

44. On the basis of the following  $E^\circ$  values, the strongest oxidizing agent is : **[2008]**
- $$[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-} + \text{e}^-; E^\circ = -0.35 \text{ V}$$
- $$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^- \quad E^\circ = -0.77 \text{ V}$$
- (a)  $[\text{Fe}(\text{CN})_6]^{4-}$       (b)  $\text{Fe}^{2+}$   
 (c)  $\text{Fe}^{3+}$       (d)  $[\text{Fe}(\text{CN})_6]^{3-}$
45. The equilibrium constant of the reaction:
- $$\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}; E^\circ = 0.46 \text{ V at } 298 \text{ K} \quad \text{[2007]}$$
- (a)  $2.0 \times 10^{10}$       (b)  $4.0 \times 10^{10}$   
 (c)  $4.0 \times 10^{15}$       (d)  $2.4 \times 10^{10}$
46. If  $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.441 \text{ V}$  and  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.771 \text{ V}$ , the standard EMF of the reaction  $\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$  will be **[2006]**
- (a) 1.653 V      (b) 1.212 V  
 (c) 0.111 V      (d) 0.330 V
47. A hypothetical electrochemical cell is shown below
- $$\text{A}|\text{A}^+(\text{xM})||\text{B}^+(\text{yM})|\text{B} \quad \text{[2006]}$$
- The emf measured is +0.20 V. The cell reaction is
- (a)  $\text{A}^+ + \text{e}^- \rightarrow \text{A}; \text{B}^+ + \text{e}^- \rightarrow \text{B}$   
 (b) The cell reaction cannot be predicted  
 (c)  $\text{A} + \text{B}^+ \rightarrow \text{A}^+ + \text{B}$   
 (d)  $\text{A}^+ + \text{B} \rightarrow \text{A} + \text{B}^+$
48. The standard e.m.f. of a galvanic cell involving cell reaction with  $n = 2$  is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be  
 (Given  $F = 96500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ) **[2004]**
- (a)  $2.0 \times 10^{11}$       (b)  $4.0 \times 10^{12}$   
 (c)  $1.0 \times 10^2$       (d)  $1.0 \times 10^{10}$
49. On the basis of the information available from the reaction
- $$\frac{4}{3}\text{Al} + \text{O}_2 \rightarrow \frac{2}{3}\text{Al}_2\text{O}_3, \Delta G = -827 \text{ kJ mol}^{-1} \text{ of O}_2.$$
- The minimum e.m.f required to carry out an electrolysis of  $\text{Al}_2\text{O}_3$  is ( $F = 96500 \text{ C mol}^{-1}$ )
- (a) 8.56 V      (b) 2.14 V **[2003]**  
 (c) 4.28 V      (d) 6.42 V
50. Which reaction is not feasible? **[2002]**
- (a)  $2\text{KI} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$   
 (b)  $2\text{KBr} + \text{I}_2 \rightarrow 2\text{KI} + \text{Br}_2$   
 (c)  $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$   
 (d)  $2\text{H}_2\text{O} + 2\text{F}_2 \rightarrow 4\text{HF} + \text{O}_2$
51. Cu(aq) is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction : **[2000]**
- $$2\text{Cu}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$$
- choose correct  $E^\circ$  for above reaction if  $E^\circ \text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$  and  $E^\circ \text{Cu}^{2+}/\text{Cu}^+ = 0.15 \text{ V}$
- (a) -0.38 V      (b) +0.49 V  
 (c) +0.38 V      (d) -0.19 V
52. What is the  $E^\circ_{\text{cell}}$  for the reaction
- $$\text{Cu}^{2+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons \text{Cu}(\text{s}) + \text{Sn}^{4+}(\text{aq})$$
- at 25°C if the equilibrium constant for the reaction is  $1 \times 10^6$ ? **[1999]**
- (a) 0.5328 V      (b) 0.3552 V  
 (c) 0.1773 V      (d) 0.7104 V
53. For the cell reaction, **[1998]**
- $$\text{Cu}^{2+}(\text{C}_1, \text{aq}) + \text{Zn}(\text{s}) = \text{Zn}^{2+}(\text{C}_2, \text{aq}) + \text{Cu}(\text{s})$$
- of an electrochemical cell, the change in free energy,  $\Delta G$ , at a given temperature is a function of
- (a)  $\ln(C_1)$       (b)  $\ln(C_2/C_1)$   
 (c)  $\ln(C_2)$       (d)  $\ln(C_1 + C_2)$
54. Without losing its concentration  $\text{ZnCl}_2$  solution cannot be kept in contact with **[1998]**
- (a) Au      (b) Al  
 (c) Pb      (d) Ag
55.  $E^\circ$  for the cell,  $\text{Zn}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}$  is 1.10 V at 25°C. The equilibrium constant for the cell reaction:
- $$\text{Zn} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Cu} + \text{Zn}^{2+}(\text{aq}),$$
- is of the order of **[1997]**
- (a)  $10^{-18}$       (b)  $10^{-37}$   
 (c)  $10^{18}$       (d)  $10^{37}$
56. Standard potentials ( $E^\circ$ ) for some half-reactions are given below : **[1997]**
- (1)  $\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}; E^\circ = +0.15 \text{ V}$   
 (2)  $2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}; E^\circ = +0.92 \text{ V}$   
 (3)  $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}; E^\circ = +1.45 \text{ V}$
- Based on the above, which one of the following statements is correct ?
- (a)  $\text{Sn}^{4+}$  is a stronger oxidising agent than  $\text{Pb}^{4+}$   
 (b)  $\text{Sn}^{2+}$  is a stronger reducing agent than  $\text{Hg}_2^{2+}$   
 (c)  $\text{Hg}^{2+}$  is a stronger oxidising agent than  $\text{Pb}^{4+}$   
 (d)  $\text{Pb}^{2+}$  is a stronger reducing agent than  $\text{Sn}^{2+}$

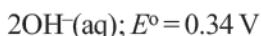
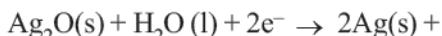
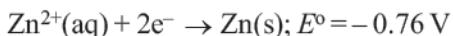
57. The correct relationship between free energy and equilibrium constant  $K$  of a reaction is [1996]  
 (a)  $\Delta G^\circ = -RT \ln K$  (b)  $\Delta G = RT \ln K$   
 (c)  $\Delta G^\circ = RT \ln K$  (d)  $\Delta G = -RT \ln K$
58. An electrochemical cell is set up as: Pt; H<sub>2</sub> (1atm) | HCl(0.1 M) || CH<sub>3</sub>COOH (0.1 M) | H<sub>2</sub> (1atm); Pt. The e.m.f of this cell will not be zero, because [1995]  
 (a) the temperature is constant  
 (b) e.m.f depends on molarities of acids used  
 (c) acids used in two compartments are different  
 (d) pH of 0.1 M HCl and 0.1 M CH<sub>3</sub>COOH is not same
59. The standard reduction potentials at 25°C of Li<sup>+</sup> / Li, Ba<sup>2+</sup> / Ba, Na<sup>+</sup> / Na and Mg<sup>2+</sup> / Mg are – 3.03, – 2.73, – 2.71 and – 2.37 respectively. Which one of the following is the strongest oxidising agent? [1994]  
 (a) Na<sup>+</sup> (b) Li<sup>+</sup>  
 (c) Ba<sup>2+</sup> (d) Mg<sup>2+</sup>

#### Topic 4: Commercial Cells and Corrosion

60. A button cell used in watches functions as following



If half cell potentials are :



- The cell potential will be : [NEET 2013]  
 (a) 0.42V (b) 0.84V  
 (c) 1.34V (d) 1.10V
61. Standard free energies of formation (in kJ/mol) at 298 K are – 237.2, – 394.4 and – 8.2 for H<sub>2</sub>O(l), CO<sub>2</sub>(g) and pentane (g), respectively. The value of  $E^\circ_{\text{cell}}$  for the pentane-oxygen fuel cell is :  
 (a) 1.968V (b) 2.0968V [2008]  
 (c) 1.0968V (d) 0.0968V
62. The efficiency of a fuel cell is given by [2007]  
 (a)  $\frac{\Delta G}{\Delta S}$  (b)  $\frac{\Delta G}{\Delta H}$   
 (c)  $\frac{\Delta S}{\Delta G}$  (d)  $\frac{\Delta H}{\Delta G}$
63. In the silver plating of copper, K[Ag(CN)<sub>2</sub>] is used instead of AgNO<sub>3</sub>. The reason is [2002]  
 (a) A thin layer of Ag is formed on Cu  
 (b) More voltage is required  
 (c) Ag<sup>+</sup> ions are completely removed from solution  
 (d) Less availability of Ag<sup>+</sup> ions, as Cu cannot displace Ag from [Ag(CN)<sub>2</sub>]<sup>-</sup> ion
64. The most convenient method to protect the bottom of ship made of iron is [2001]  
 (a) Coating it with red lead oxide  
 (b) White tin plating  
 (c) Connecting it with Mg block  
 (d) Connecting it with Pb block
65. The most durable metal plating on iron to protect against corrosion is [1994]  
 (a) nickel plating (b) copper plating  
 (c) tin plating (d) zinc plating.

#### ANSWER KEY

1	(a)	8	(c)	15	(c)	22	(c)	29	(c)	36	(c)	43	(d)	50	(b)	57	(a)	64	(c)
2	(c)	9	(d)	16	(b)	23	(a)	30	(a)	37	(b)	44	(c)	51	(c)	58	(d)	65	(d)
3	(b)	10	(d)	17	(c)	24	(d)	31	(b)	38	(b)	45	(c)	52	(c)	59	(d)		
4	(b)	11	(b)	18	(a)	25	(b)	32	(a)	39	(d)	46	(b)	53	(b)	60	(d)		
5	(d)	12	(b)	19	(d)	26	(b)	33	(d)	40	(c)	47	(c)	54	(b)	61	(c)		
6	(d)	13	(c)	20	(c)	27	(a)	34	(a)	41	(a)	48	(d)	55	(d)	62	(b)		
7	(a)	14	(d)	21	(d)	28	(b)	35	(a)	42	(a)	49	(b)	56	(b)	63	(d)		

# Hints & Solutions

1. (a) According to Kohlrausch's law

$$\lambda_m^{\circ}(AB) = \lambda_m^{\circ}(A^+) + \lambda_m^{\circ}(B^-)$$

$$\text{So, } \lambda_m^{\circ}(\text{CH}_3\text{COOH}) = \lambda_m^{\circ}(\text{CH}_3\text{COO}^-) + \lambda_m^{\circ}(\text{H}^+)$$

$$\text{So } \lambda_m^{\circ}(\text{CH}_3\text{COOH})$$

$$= \lambda_m^{\circ}(\text{CH}_3\text{COOK}) + \frac{1}{2}\lambda_m^{\circ}(\text{H}_2\text{SO}_4) - \frac{1}{2}\lambda_m^{\circ}(\text{K}_2\text{SO}_4)$$

$$= z + \frac{x}{2} - \frac{y}{2} = z + \left( \frac{x-y}{2} \right)$$

2. (c)  $\text{Li}^+$  being smallest, has maximum charge density.

$\therefore \text{Li}^+$  is most heavily hydrated among all alkali metal ions. Effective size of  $\text{Li}^+$  in aqueous solution is therefore, largest. So, moves slowest under electric field.

3. (b) HCl completely dissociates to give  $\text{H}^+$  and  $\text{Cl}^-$  ions, hence act as very good electrolyte. While others are non-electrolytes.

$$4. \text{ (b) } \alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{9.54}{238} = 0.04008 = 4.008\%$$

$$5. \text{ (d) } \begin{aligned} \overset{o}{\Lambda}_m(\text{NH}_4\text{Cl}) &= \overset{o}{\Lambda}_m\text{NH}_4^+ + \overset{o}{\Lambda}_m\text{Cl}^- \\ \overset{o}{\Lambda}_m(\text{NaOH}) &= \overset{o}{\Lambda}_m\text{Na}^+ + \overset{o}{\Lambda}_m\text{OH}^- \\ \overset{o}{\Lambda}_m(\text{NaCl}) &= \overset{o}{\Lambda}_m\text{Na}^+ + \overset{o}{\Lambda}_m\text{Cl}^- \\ \therefore \overset{o}{\Lambda}_m\left(\text{NH}_4^+\right) + \overset{o}{\Lambda}_m\left(\text{OH}^-\right) &= \overset{o}{\Lambda}_m\left(\text{NH}_4^+\right) + \overset{o}{\Lambda}_m\left(\text{Cl}^-\right) + \overset{o}{\Lambda}_m\left(\text{Na}^+\right) \\ &\quad + \overset{o}{\Lambda}_m\left(\text{OH}^-\right) - \left[ \overset{o}{\Lambda}_m\left(\text{Na}^+\right) + \overset{o}{\Lambda}_m\left(\text{Cl}^-\right) \right] \\ \overset{o}{\Lambda}_m(\text{NH}_4\text{OH}) &= \overset{o}{\Lambda}_m(\text{NH}_4\text{Cl}) + \overset{o}{\Lambda}_m(\text{NaOH}) \\ &\quad - \overset{o}{\Lambda}_m(\text{NaCl}) \end{aligned}$$

$$6. \text{ (d) } \overset{o}{\Lambda}_{\text{CH}_3\text{COOH}} = \overset{o}{\Lambda}_{\text{CH}_3\text{COONa}} + \overset{o}{\Lambda}_{\text{HCl}} - \overset{o}{\Lambda}_{\text{NaCl}} \\ = 91 + 425.9 - 126.4 = 390.5$$

7. (a) Strong electrolytes are completely ionised at all concentrations. On increasing dilution, the number of ions remains the same but the ionic mobility increases.



$$\lambda_{eq}^c = \frac{K}{N} = \frac{\text{Conductivity}}{\text{Normality}}$$

On increasing dilution, both conductivity and normality decreases. But the decreases in conductivity is more than compensated by decrease in its normality. Hence, effectively  $\lambda_{eq}^c$  increases on dilution.

8. (c) Equivalent conductance of an electrolyte at infinite dilution is given by the sum of equivalent conductances of the respective ions at infinite dilution.

9. (d) Degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}} = \frac{8.0}{400} = 2 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2 = \frac{1}{32} \times (2 \times 10^{-2})^2 \\ = 1.25 \times 10^{-5}$$

10. (d) Kohlrausch's Law states that at infinite dilution, each ion migrates independently of its co-ion and contributes to the total equivalent conductance of an electrolyte a definite share which depends only on its own nature. From this definition we can see that option (d) is the correct answer.

11. (b) The ionic conductance or equivalent conductance are given as:

$$\overset{\infty}{\Lambda}_{\text{Ba}^{2+}} = 127 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}$$

$$\overset{\infty}{\Lambda}_{\text{Cl}^-} = 76 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}$$

The equivalent conductance of  $\text{BaCl}_2$  at infinite dilution will be given by:

$$\overset{\infty}{\Lambda}_{\text{BaCl}_2} = \overset{\infty}{\Lambda}_{\text{Ba}^{2+}} + \overset{\infty}{\Lambda}_{\text{Cl}^-} = 127 + 76 \\ = 203 \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}$$



If equivalent conductance (conductivity) of cation and anion are  $\overset{\infty}{\lambda}_{+eq}$  and  $\overset{\infty}{\lambda}_{-eq}$  and equivalent conductance of electrolyte is  $\overset{\infty}{\lambda}_{eq}$  in infinite dilution, then,

$$\overset{\infty}{\lambda}_{eq} = \overset{\infty}{\lambda}_{+eq} + \overset{\infty}{\lambda}_{-eq}$$

At infinite dilution, if molar conductances of cation, anion and electrolyte are  $\lambda_{+m}^{\infty}$ ,  $\lambda_{-m}^{\infty}$  and  $\lambda_m^{\infty}$  respectively for the electrolyte  $A_xB_y$ , then

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$\lambda_{eq}^{\circ} = \frac{1}{y}\lambda_{+m}^{\infty} + \frac{1}{x}\lambda_{-m}^{\infty} \text{ and}$$

$$\lambda_m^{\infty} = x\lambda_{+m}^{\infty} + y\lambda_{-m}^{\infty}$$

12. (b) Given specific conductance of the solution ( $\kappa$ ) = 0.012 ohm $^{-1}$  cm $^{-1}$  and resistance (R) = 55 ohm. We know that cell constant = Specific conductance  $\times$  Observed resistance = 0.012  $\times$  55 = 0.66 cm $^{-1}$ .
13. (c) By Kohlraush's law,  $\lambda_{eq}^{\circ}$  NaCl = 126.45

$$\lambda_{Na^+}^{\circ} + \lambda_{Cl^-}^{\circ} = 126.45 \quad \dots(1)$$

$$\lambda_{H^+}^{\circ} + \lambda_{Cl^-}^{\circ} = 426.16 \quad \dots(2)$$

$$\lambda_{CH_3OO^-}^{\circ} + \lambda_{Na^+}^{\circ} = 91 \quad \dots(3)$$

on adding (2) and (3) then subtract (1) from it

$$\lambda_{CH_3COO^-}^{\circ} + \lambda_{H^+}^{\circ} = 517.16 - 126.45$$

$$\lambda_{(CH_3COOH)}^{\circ} = 390.71 \text{ ohm}^{-1} \text{ cm}^2$$

14. (d) Given molarity = 0.01 M  
Resistance = 40 ohm;

$$\text{Cell constant } \frac{1}{A} = 0.4 \text{ cm}^{-1}$$

Specific conductivity ( $\kappa$ )

$$= \frac{\text{cell constant}}{\text{resistance}} = \frac{0.4}{40} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Molar conductance } (\lambda_m) = \frac{1000\kappa}{\text{Molarity}}$$

$$= \frac{1000 \times 0.01}{0.01} = 10^3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

15. (c) When one end of a metal is heated, the free electrons are energised and move to the other end. It heats up the other end of the metal.
16. (b) Given current ( $i$ ) = 0.5 A;  
Time ( $t$ ) = 100 minutes  $\times$  60 = 6000 sec  
Equivalent weight of silver nitrate ( $E$ ) = 108.  
According to Faraday's first law of electrolysis

$$W = \frac{Eit}{96500} = \frac{108 \times 0.5 \times 6000}{96500} = 3.3575 \text{ g.}$$

17. (c) Diamond is an insulator, because of no free electrons.
18. (a) During the electrolysis of dil. sulphuric acid using Pt electrodes following reaction occurs.
- At cathode :**  $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$
- At anode :**  $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
19. (d) 1 equivalent of any substance is deposited by 1 F of charge.

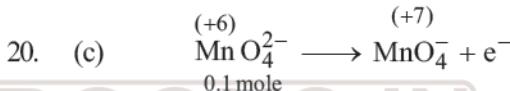
20 g calcium contains,

$$\text{Number of equivalents} = \frac{\text{Given mass}}{\text{Equivalent mass}} \\ (\text{Equivalent mass of Ca})$$

$$= \frac{\text{Atomic mass}}{\text{Valency}} = \frac{40}{2} = 20)$$

$$= \frac{20}{20} = 1$$

So, 1 Faraday of charge is required to deposit 1 equivalent of Ca.



$$\text{Quantity of electricity required} = 0.1F \\ = 0.1 \times 96500 = 9650 \text{ C}$$

21. (d)  $w_{O_2} = n_{O_2} \times 32$   
 $w_{O_2} = \frac{5600}{22400} \times 32 = 8 \text{ g} = 1 \text{ equivalent of O}_2$   
 $= 1 \text{ equivalent of Ag} = 108$
22. (c) Applying,

$$w = Zit = \frac{Eit}{96500}$$

Equivalent weight of cobalt (II) = 59/2  
 $I = 10 \text{ A}$

Time ( $t$ ) = 109 min = 109  $\times$  60 sec  
Substituting these values we get,

$$w = \frac{59 \times 10 \times 109 \times 60}{2 \times 96500} = 20.0$$

23. (a) As  $Q = i \times t$   
 $\therefore Q = 4.0 \times 10^4 \times 6 \times 60 \times 60 \text{ C}$   
 $= 8.64 \times 10^8 \text{ C}$

Now since 96500 C liberates 9 g of Al

$$8.64 \times 10^8 \text{ C liberates } \frac{9}{96500} \times 8.64 \times 10^8 \text{ g Al} \\ = 8.1 \times 10^4 \text{ g of Al}$$

24. (d) No. of gram equivalent of  $H^+$  = No. of eq. of

$$Al^{3+} = \frac{4.5}{9} = 0.5$$

$$Eq. wt of Al^{3+} = \frac{27}{3} = 9$$

No. of gm eq. of  $H^+$  = no. of mole of  $H^+$

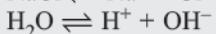
Hence, Mass of  $H^+$  =  $0.5 \times 1$  g = 0.5 g

We know that, 2g  $H_2$  at STP = 22.4 L

$$\therefore 0.5 \text{ g } H_2 \text{ at STP} = \frac{22.4}{2}, 0.5 = 5.6 \text{ L}$$

25. (b) If mercury is used as cathode,  $H^+$  ions are not discharged at mercury cathode because mercury has a high over voltage for hydrogen.

**NOTES** In electrolysis of  $NaCl$ , following ionisations take place:

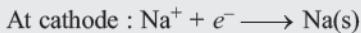


$Na^+$  and  $H^+$  ions move towards cathode.

However, only  $H^+$  ions are discharged more readily than  $Na^+$  ions because in electrochemical series, hydrogen is lower than sodium.



If mercury is used as cathode, then  $Na^+$  ions are discharged at cathode in preference to  $H^+$  ions, yielding sodium, which dissolves in mercury to form sodium amalgam.



26. (b) The reduction potential is higher in case of  $E^\circ(Fe^{3+}/Fe^{2+}) = +0.77V$ . Thus,  $Fe^{3+}$  will readily reduce to  $Fe^{2+}$  and quantity of  $Fe^{3+}$  will decrease.

27. (a) By Faraday's I<sup>st</sup> Law,  $\frac{W}{E} = \frac{q}{96500}$

(where  $q$  = it = total electric charge)  
we know that no. of equivalent

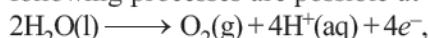
$$= \frac{W}{E} = \frac{it}{96500} = \frac{1 \times 965}{96500} = \frac{1}{100}$$

(where  $i = 1$  A,  $t = 16 \times 60 + 5 = 965$  sec.)

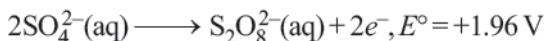
Since, we know that

$$Normality = \frac{\text{no. of equivalent}}{\text{Volume (in litre)}} = \frac{1}{100} = 0.01 \text{ N}$$

28. (b) During electrolysis of sulphuric acid, the following processes are possible at cathode:



$$E^\circ = +1.23 \text{ V}$$



For dilute sulphuric acid, first reaction is preferred but for concentrated acid, second reaction is preferred.

29. (c)  $E_{\text{cell}}^\circ = \frac{2.303RT}{nF} \log K$

Given :  $E_{\text{cell}}^\circ = 0.59 \text{ V}$ ,  $n = 1$

$$0.59 = \frac{0.059}{1} \log K$$

$$\frac{0.59}{0.059} = \log K$$

$$10 = \log K$$

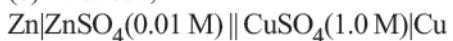
$$K = 10^{10}$$

30. (a)  $\Delta G = -nFE^\circ$

$$= -2 \times 96500 \times 0.24 = -46320 \text{ J/mol}$$

$$= -46.32 \text{ kJ/mol}$$

31. (b) For cell,



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \frac{\log [Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore E_1 = E_{\text{cell}}^\circ - \frac{2.303RT}{2 \times F} \times \log \frac{(0.01)}{1}$$

When concentrations are changed for  $ZnSO_4$  and  $CuSO_4$ , we can write

$$E_2 = E_{\text{cell}}^\circ - \frac{2.303RT}{2F} \times \log \frac{1}{0.01}$$

$$\therefore E_1 > E_2$$

32. (a)  $2H^+(aq) + 2e^- \rightarrow H_2(g)$

$$\therefore E = E^\circ - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

$$0 = 0 - 0.0295 \log \frac{P_{H_2}}{(10^{-7})^2}$$

$$\frac{P_{H_2}}{(10^{-7})^2} = 1$$

$$P_{H_2} = 10^{-14} \text{ atm}$$

33. (d) A device that converts energy of combustion of fuels, directly into electrical energy is known as fuel cell.

34. (a)  $H_2 \xrightarrow[1 \text{ atm}]{10^{-10}} 2H^+ + 2e^-$

$$E_{H_2/H^+} = 0 - \frac{0.059}{2} \log \frac{(10^{-10})^2}{1}$$

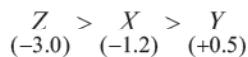
$$E_{H_2/H^+} = +0.59 \text{ V}$$

35. (a)  $\Delta E^\circ = E_{red}^\circ + E_{oxd}^\circ = -1.81 - 1.51 = -2.69$   
 Since  $\Delta E^\circ$  is negative  
 $\therefore \Delta G = -nFE^\circ$ ,  $\Delta G$  will have positive value so, forward reaction is not possible.

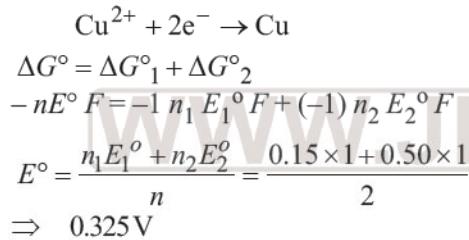


The value of electrode potential of a half-cell reaction does not depend on stoichiometric coefficient. e.g.  
 $Mn^{2+} \rightarrow Mn^{3+} + e^- ; E^\circ = -1.51V$   
 $2Mn^{2+} \rightarrow 2Mn^{3+} + 2e^- ; E^\circ = -1.51V$

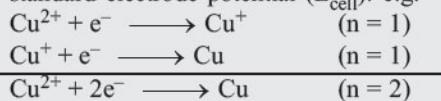
36. (c) As the value of standard reduction potential decreases the reducing power increases i.e.,



37. (b)  $Cu^{2+} + 1e^- \rightarrow Cu^+$   
 $E_1^\circ = 0.15V ; \Delta G_1^\circ = -n_1 E_1^\circ F$   
 $Cu^+ + 1e^- \rightarrow Cu$   
 $E_2^\circ = 0.50V ; \Delta G_2^\circ = -n_2 E_2^\circ F$



When exchange of electrons (n) is different for all three reactions, we can not use the formula for standard electrode potential ( $E_{cell}^\circ$ ). e.g.



$$E_{Cu^{2+}/Cu}^\circ \neq E_{Cu^{2+}/Cu^+}^\circ + E_{Cu^+/Cu}^\circ$$

38. (b) The couple for which SRP value is high, will act as cathode and the other couple will act as an anode.

$$\begin{aligned} E_{cell}^\circ &= E_{cathode}^\circ - E_{anode}^\circ \\ &= 0.15V - (-0.74V) = +0.89V \end{aligned}$$

39. (d) Standard Gibbs free energy is given as  $\Delta G^\circ = -nE^\circ F$

If  $E_{cell}^\circ < 0$  i.e.  $-ve$   
 $\Delta G^\circ > 0$

Further  $\Delta G^\circ = -RT \ln K_{eq}$   
 $\Delta G^\circ > 0$  when  $K_{eq} < 1$

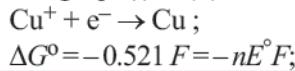
40. (c) Given  $Fe^{+3}/Fe^{2+} = +0.77V$   
 and  $I_2/2I^- = 0.536V$   
 Reduction potential of  $Fe^{3+}/Fe^{2+} > I_2/I^-$ , so  $Fe^{3+}$  will be reduced and  $I^-$  will be oxidised.

41. (a)  $Cu + 2 Ag_{(aq)}^+ \rightarrow Cu^{2+}_{(aq)} + 2 Ag_{(s)}$   
 Here,  $n = 2$ ,  $E_{cell}^\circ = +0.46V$   
 $\Delta G^\circ = -nE^\circ F = \frac{-2 \times 0.46 \times 96500}{1000} kJ \approx -89 kJ$

42. (a)  $E_{cell} = E_{cathode} - E_{anode}$   
 $\Rightarrow E_{cell} = E_{red/cathode} + E_{oxi/anode}$   
 $\Rightarrow E_{cell} = -E_{oxi/cathode} + E_{oxi/anode}$   
 Hence, option (a) is correct.

43. (d)  $Cu^{2+} + 2e^- \rightarrow Cu ; \Delta G^\circ = -nE^\circ F$   
 $= -2 \times F \times 0.337 = -0.674F$  ....(i)  
 $Cu^+ + e^- \rightarrow Cu ; \Delta G^\circ = -nE^\circ F$   
 $= -1 \times F \times -0.153 = 0.153F$  ....(ii)

On adding eqn (i) & (ii)



Here  $n = 1 \therefore E^\circ = +0.52V$

44. (c) From the given data we find  $Fe^{3+}$   
 $(E_{(Fe^{3+}/Fe^{2+})}^\circ = +0.77V)$  is strongest oxidizing agent.

- NOTES** More the positive value of reduction potential, more is the tendency to get reduced (better oxidising agent).

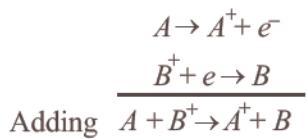
45. (c) As  $E_{cell}^\circ = \frac{0.0591}{n} \log K_c$   
 $\therefore 0.46 = \frac{0.0591}{2} \log K_c$   
 $\therefore \log K_c = \frac{2 \times 0.46}{0.0591} = 15.57$

or  $K_c = \text{Antilog } 15.57 = 3.7 \times 10^{15} \approx 4 \times 10^{15}$

46. (b)  $Fe \rightarrow Fe^{2+} + 2e^-$  [Anode]  $E = -0.441V$   
 $[Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2$  [Cathode]  $E = +0.771V$   
 $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

$$\begin{aligned} E_{cell}^\circ &= E_{cathode}^\circ - E_{Anode}^\circ \\ &= 0.771 - (-0.441) = 0.771 + 0.441 = 1.212V \end{aligned}$$

47. (c) The cell reaction is as follows :



48. (d)  $E^\circ = \frac{0.0591}{n} \log_{10} K$

Here,  $n = 2, E^\circ = 0.295$

$$\therefore \log_{10} K = \frac{2 \times 0.295}{0.0591} = 10 \text{ or } K = 1 \times 10^{10}$$

49. (b)  $\Delta G = -nEF, Al \rightarrow Al^{3+} + 3e^-$

For 1 mol of Al,  $n = 3$

$$\therefore \text{for } \frac{4}{3} \text{ mol of Al, } n = 3 \times \frac{4}{3} = 4$$

According to question,

$$827 \times 1000 = 4 \times E \times 96500$$

$$E = \frac{827 \times 1000}{4 \times 96500} = 2.14V$$

50. (b)  $2KBr + I_2 \longrightarrow 2KI + Br_2$

reaction is not possible because  $Br^-$  ion is not oxidised to  $Br_2$  with  $I_2$  due to higher electrode (oxidation) potential of  $I_2$  than bromine.

51. (c)  $2Cu^+ \longrightarrow Cu^{+2} + Cu$

$$2e^- + Cu^{+2} \longrightarrow Cu; E_1^\circ = 0.34V; \dots (i)$$

$$e^- + Cu^{+2} \longrightarrow Cu^+; E_2^\circ = 0.15V; \dots (ii)$$

$$Cu^+ + e^- \longrightarrow Cu; E_3^\circ = ? \dots (iii)$$

Now,  $\Delta G_1^\circ = -nFE_1^\circ = -2 \times 0.34F$

$$\Delta G_2^\circ = -1 \times 0.15F, \Delta G_3^\circ = -1 \times E_3^\circ F$$

Again,  $\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ$

$$\Rightarrow -0.68F = -0.15F - E_3^\circ F$$

$$\Rightarrow E_3^\circ = 0.68 - 0.15 = 0.53V$$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ (Cu^+ / Cu) - E_{\text{anode}}^\circ (Cu^{+2} / Cu^+) \\ = 0.53 - 0.15 = 0.38 V.$$

52. (c)  $E_{\text{cell}}^\circ = \frac{2.303 RT}{nF} \log K_{eq} = \frac{0.0591}{n} \log K_{eq}$

$$= \frac{0.0591}{2} \log 10^6 = 0.0591 \times 3 = 0.1773V$$

53. (b)  $\Delta G = -nE^\circ F$

For concentration cell,  $E = \frac{RT}{nF} \ln \frac{C_2}{C_1}$

In it  $R, T, n$  and  $F$  are constant

So  $E$  is based upon  $\ln C_2 / C_1$

$$\text{Now } \Delta G = -nEF = -nF \times \frac{RT}{nF} \ln C_2 / C_1 \\ = -RT \ln C_2 / C_1$$

At constant temperature  $\Delta G$  is based upon  $\ln C_2 / C_1$ .

54. (b) Without losing its concentration  $ZnCl_2$  solution cannot be kept in contact with Al because Al is more reactive than Zn due to high electrode (reduction) potential.

55. (d) Given for the reaction



$$E^\circ = +1.10V.$$

At equilibrium

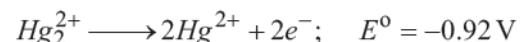
$$\therefore E_{\text{cell}}^\circ = \frac{0.0591}{n} \log_{10} K_{\text{eq}}$$

here ( $n \rightarrow$  number of exchange of electrons)

$$\text{or } 1.10 = \frac{0.0591}{2} \log_{10} K_{\text{eq}} \frac{2.20}{0.059} = \log_{10} K_{\text{eq}}$$

$$= 37.22 \text{ or } K_{\text{eq}} = 1.66 \times 10^{37}$$

56. (b)  $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-; E^\circ = -0.15V$



Thus,  $Sn^{2+}$  can more easily get oxidized than  $Hg_2^{2+}$  or  $Sn^{2+}$  is stronger reducing agent than  $Hg_2^{2+}$ .

57. (a) The relation between free energy change and equilibrium constant is given by Nernst equation

$$E_{\text{cell}} = E^\circ - \frac{RT}{nF} \ln Q$$

At equilibrium,  $E_{\text{cell}} = 0$  and  $Q = K_C$

$$\therefore E^\circ = \frac{RT}{nF} \ln K \dots (i)$$

Again  $\Delta G^\circ = -nFE^\circ$   $\dots (ii)$   
put in (i)

$$\frac{-\Delta G^\circ}{nF} = \frac{RT}{nF} \ln K; \Delta G^\circ = -RT \ln K$$

58. (d) For a concentration cell having different concentrations of ions.

$$E = \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

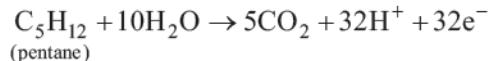
If all the concentrations are identical then obviously the cell voltage is zero. But as the pH of 0.1 M HCl (strong acid) & pH of 0.1M CH<sub>3</sub>COOH(weak acid) is not same, therefore the cell voltage will not be zero.

59. (d) Higher the reduction potential, stronger is the oxidising agent.

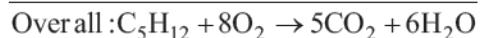
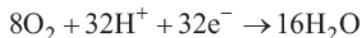
60. (d)  $E^\circ_{\text{Cell}} = E^\circ_{\text{OP}} + E^\circ_{\text{RP}} = 0.76 + 0.34 = 1.10 \text{ V}$

61. (c) Writing the equation for pentane-oxygen fuel cell at respective electrodes and over all reaction, we get

At Anode:



At Cathode:



Calculation of  $\Delta G^\circ$  for the above reaction

$$\begin{aligned}\Delta G^\circ &= [5 \times (-394.4) + 6 \times (-237.2)] - [-8.2] \\ &= -1972.0 - 1423.2 + 8.2 = -3387.0 \text{ kJ} \\ &= -3387000 \text{ Joules.}\end{aligned}$$

From the overall equation we find  $n = 32$

Using the relation,  $\Delta G^\circ = -nFE_{\text{cell}}^0$  and substituting various values, we get

$$-3387000 = -32 \times 96500 \times E_{\text{cell}}^0 \quad (\text{F} = 96500 \text{ C})$$

or  $E_{\text{cell}}^0 = \frac{3387000}{32 \times 96500} = \frac{3387000}{3088000}$

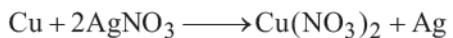
or  $\frac{3387}{3088} \text{ V} = 1.0968 \text{ V}$

62. (b) Efficiency of a fuel cell ( $\eta$ ) =  $\frac{\Delta G}{\Delta H}$



$\Delta H$  is the required energy (input) and  $\Delta G$  is the useful energy obtained (output).

63. (d) In the silver plating of copper, K[Ag(CN)<sub>2</sub>] is used instead of AgNO<sub>3</sub>. Copper being more electropositive readily precipitate silver from their salt solution



whereas in K[Ag(CN)<sub>2</sub>] solution a complex anion [Ag(CN)<sub>2</sub>]<sup>-</sup> is formed and hence Ag<sup>+</sup> are less available in the solution and therefore copper cannot displace Ag from its complex ion.

64. (c) For bottom of ship to be protected, it is connected with more reactive metal than iron like magnesium. This technique is called cathodic protection.

65. (d) This is because zinc has higher oxidation potential than Ni, Cu and Sn.



The process of coating of iron surface with zinc is known as galvanization. Galvanized iron sheets maintain their lustre due to the formation of protective layer of basic zinc carbonate.

# 18

# Chemical Kinetics

## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Rate of reaction, rate laws and rate constant	first order reaction rate law	1	E	1	A						
	rate of reaction			1	E						
	difference between first and second order reaction					1	A				
Order of reaction and half life period	half life of zero order reaction					1	A				
	order of the reaction							1	A	1	A
	half life of first order reaction							1	A		
Theories of rate of reaction	collision frequency	1	E								
	effect of catalyst									1	E
LOD - Level of Difficulty	E - Easy	A - Average			D - Difficult			Qns - No. of Questions			

### Topic 1: Rate of Reaction, Rate Laws and Rate Constant

- The rate constant for a first order reaction is  $4.606 \times 10^{-3} \text{ s}^{-1}$ . The time required to reduce 2.0 g of the reactant to 0.2 g is : **[2020]**
  - 200 s
  - 500 s
  - 1000 s
  - 100 s
- If the rate constant for a first order reaction is  $k$ , the time ( $t$ ) required for the completion of 99% of the reaction is given by : **[2019]**
  - $t = 0.693/k$
  - $t = 6.909/k$
  - $t = 4.606/k$
  - $t = 2.303/k$
- For the chemical reaction  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   
the correct option is: **[2019]**

(a)  $-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

(b)  $-\frac{d[\text{N}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$

(c)  $-\frac{d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

(d)  $3 \frac{d[\text{H}_2]}{dt} = 2 \frac{d[\text{NH}_3]}{dt}$

- The correct difference between first and second order reactions is that **[2018]**
  - The rate of a first-order reaction does not depend on reactant concentrations, the rate of a second-order reaction does depend on reactant concentrations

- (b) The half-life of a first-order reaction does not depend on  $[A]_0$ , the half-life of a second-order reaction does depend on  $[A]_0$

(c) The rate of a first-order reaction does depend on reactant concentrations, the rate of a second-order reaction does not depend on reactant concentrations

(d) A first-order reaction can be catalyzed, a second-order reaction cannot be catalyzed

5. The rate constant of the reaction  $A \rightarrow B$  is  $0.6 \times 10^{-3}$  mole per second. If the concentration of A is 5 M then concentration of B after 20 minutes is : [2015 RS]

(a) 1.08 M (b) 3.60 M  
(c) 0.36 M (d) 0.72 M

6. In a reaction,  $A + B \rightarrow$  Product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentrations of both the reactants (A and B) are doubled. Rate law for the reaction can be written as : [2012]

(a) Rate =  $k[A][B]^2$  (b) Rate =  $k[A]^2[B]^2$   
(c) Rate =  $k[A][B]$  (d) Rate =  $k[A]^2[B]$

7. The rate of the reaction  $2N_2O_5 \rightarrow 4NO_2 + O_2$  can be written in three ways : [2011 MJ]

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5]$$

$$\frac{d[NO_2]}{dt} = k'[N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and  $k'$  and between k and  $k''$  are :

(a)  $k' = 2k$ ;  $k' = k$  (b)  $k' = 2k$ ;  $k'' = k/2$   
(c)  $k' = 2k$ ;  $k'' = 2k$  (d)  $k' = k$ ;  $k'' = k$

8. For the reaction  $N_2O_5(g) \rightarrow 2NO_2(g) + 1/2 O_2(g)$  the value of rate of disappearance of  $N_2O_5$  is given as  $6.25 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup>. The rate of formation of  $NO_2$  and  $O_2$  is given respectively as : [2010]

(a)  $6.25 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup> and  $6.25 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup>  
(b)  $1.25 \times 10^{-2}$  mol L<sup>-1</sup>s<sup>-1</sup> and  $3.125 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup>  
(c)  $6.25 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup> and  $3.125 \times 10^{-3}$  mol L<sup>-1</sup>s<sup>-1</sup>

9. The rate of the reaction  $2NO + Cl_2 \rightarrow 2NOCl$  is given by the rate equation rate =  $k[NO]^2[Cl_2]$  [2010]  
The value of the rate constant can be increased by:

(a) increasing the concentration of NO.  
(b) increasing the temperature.  
(c) increasing the concentration of the  $Cl_2$   
(d) doing all of these

10. For the reaction,  $N_2 + 3H_2 \rightarrow 2NH_3$ , [2009]

$\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>, the value of  $-\frac{d[H_2]}{dt}$  would be:

(a)  $4 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>  
(b)  $6 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>  
(c)  $1 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>  
(d)  $3 \times 10^{-4}$  mol L<sup>-1</sup>s<sup>-1</sup>

11. In the reaction [2009]

$$BrO_3^-(aq) + 5Br^- (aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine ( $Br_2$ ) is related to rate of disappearance of bromide ions as following:

(a)  $\frac{d[Br_2]}{dt} = -\frac{5}{3} \frac{d[Br^-]}{dt}$   
(b)  $\frac{d[Br_2]}{dt} = \frac{5}{3} \frac{d[Br^-]}{dt}$   
(c)  $\frac{d[Br_2]}{dt} = \frac{3}{5} \frac{d[Br^-]}{dt}$   
(d)  $\frac{d[Br_2]}{dt} = -\frac{3}{5} \frac{d[Br^-]}{dt}$

12. For the reaction  $2A + B \rightarrow 3C + D$  which of the following does not express the reaction rate ? [2006]

(a)  $-\frac{d[B]}{dt}$  (b)  $\frac{d[D]}{dt}$   
(c)  $-\frac{1}{2} \frac{d[A]}{dt}$  (d)  $-\frac{1}{3} \frac{d[C]}{dt}$

13. Consider the reaction [2006]

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

The equality relationship between  $\frac{d[NH_3]}{dt}$  and  $-\frac{d[H_2]}{dt}$  is

- (a)  $+\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[H_2]}{dt}$
- (b)  $+\frac{d[NH_3]}{dt} = -\frac{3}{2} \frac{d[H_2]}{dt}$
- (c)  $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$
- (d)  $\frac{d[NH_3]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt}$
14.  $3A \rightarrow 2B$ , rate of reaction  $\frac{d[B]}{dt}$  is equal to [2002]
- (a)  $-\frac{3}{2} \frac{d[A]}{dt}$  (b)  $-\frac{2}{3} \frac{d[A]}{dt}$   
 (c)  $-\frac{1}{3} \frac{d[A]}{dt}$  (d)  $+2 \frac{d[A]}{dt}$
15. For the reaction  $2N_2O_5 \rightarrow 4NO_2 + O_2$ , rate and rate constant are  $1.02 \times 10^{-4} \text{ mol lit}^{-1} \text{ s}^{-1}$  and  $3.4 \times 10^{-5} \text{ s}^{-1}$  respectively then concentration of  $N_2O_5$  at that time will be [2001]
- (a)  $1.732 \text{ M}$  (b)  $3 \text{ M}$   
 (c)  $3.4 \times 10^5 \text{ M}$  (d)  $1.02 \times 10^{-4} \text{ M}$
16. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant? [2000]
- $$\text{BrO}_3^-(\text{aq}) + \underline{5\text{Br}^-}(\text{aq}) + 6\text{H}^+(\text{aq}) \longrightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$$
- (a)  $\frac{d[\text{Br}_2]}{dt} = -\frac{5}{3} \frac{d[\text{Br}^-]}{dt}$
- (b)  $\frac{d[\text{Br}_2]}{dt} = -\frac{d[\text{Br}^-]}{dt}$
- (c)  $\frac{d[\text{Br}_2]}{dt} = \frac{3}{5} \frac{d[\text{Br}^-]}{dt}$
- (d)  $\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$
17. The rate of reaction depends upon the [1995]
- (a) volume (b) force  
 (c) pressure (d) conc. of reactants
- Topic 2: Order of Reaction and Half Life Period**
18. A first order reaction has a rate constant of  $2.303 \times 10^{-3} \text{ s}^{-1}$ . The time required for 40 g of this reactant to reduce to 10 g will be [NEET Odisha 2019]  
 [Given that  $\log_{10} 2 = 0.3010$ ]
- (a) 602 s (b) 230.3 s  
 (c) 301 s (d) 2000 s
19. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction [2018]
- (a) is halved (b) is doubled  
 (c) remains unchanged (d) is tripled
20. Mechanism of a hypothetical reaction [2017]  
 $X_2 + Y_2 \rightarrow 2XY$  is given below :
- (i)  $X_2 \rightarrow X + X$  (fast)  
 (ii)  $X + Y_2 \rightleftharpoons XY + Y$  (slow)  
 (iii)  $X + Y \rightarrow XY$  (fast)
- The overall order of the reaction will be :
- (a) 2 (b) 0  
 (c) 1.5 (d) 1
21. A first order reaction has a specific reaction rate of  $10^{-2} \text{ s}^{-1}$ . How much time will it take for 20 g of the reactant to reduce to 5 g ? [2017]
- (a) 138.6 sec (b) 346.5 sec  
 (c) 693.0 sec (d) 238.6 sec
22. The rate of a first -order reaction is  $0.04 \text{ mol l}^{-1} \text{s}^{-1}$  at 10 seconds and  $0.03 \text{ mol l}^{-1} \text{s}^{-1}$  at 20 seconds after initiation of the reaction. The half-life period of the reaction is [2016]
- (a) 24.1 s (b) 34.1 s  
 (c) 44.1 s (d) 54.1 s
23. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is : [2015]
- (a) First  
 (b) Second  
 (c) More than zero but less than first  
 (d) Zero
24. A reaction is 50% completed in 2 hours and 75% completed in 4 hours. The order of reaction is [NEET Kar. 2013]
- (a) 0 (b) 1  
 (c) 2 (d) 3
25. For a reaction between A and B the order with respect to A is 2 and the order with respect to B is 3. The concentrations of both A and B are doubled, the rate will increase by a factor of: [NEET Kar. 2013]
- (a) 10 (b) 12  
 (c) 16 (d) 32
26. In a zero-order reaction for every  $10^\circ$  rise of temperature, the rate is doubled. If the temperature is increased from  $10^\circ\text{C}$  to  $100^\circ\text{C}$ , the rate of the reaction will become : [2012]
- (a) 256 times (b) 512 times  
 (c) 64 times (d) 128 times

27. Which one of the following statements for the order of a reaction is incorrect? *[2011]*
- Order can be determined only experimentally.
  - Order is not influenced by stoichiometric coefficient of the reactants.
  - Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction.
  - Order of reaction is always whole number.
28. The unit of rate constant for a zero order reaction is *[2011 M]*
- $\text{mol L}^{-1} \text{s}^{-1}$
  - $\text{L mol}^{-1} \text{s}^{-1}$
  - $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$
  - $\text{s}^{-1}$
29. During the kinetic study of the reaction,  $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ , following results were obtained:

Run	$[\text{A}] / \text{mol L}^{-1}$	$[\text{B}] / \text{mol L}^{-1}$	Initial rate of formation of D/ $\text{mol L}^{-1} \text{min}^{-1}$
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Based on the above data which one of the following is correct? *[2010]*

- $\text{rate} = k [\text{A}]^2 [\text{B}]$
  - $\text{rate} = k[\text{A}] [\text{B}]$
  - $\text{rate} = k[\text{A}]^2 [\text{B}]^2$
  - $\text{rate} = k[\text{A}] [\text{B}]^2$
30. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is: *[2009]*
- $0.5 \times 10^{-2} \text{ s}^{-1}$
  - $0.5 \times 10^{-3} \text{ s}^{-1}$
  - $5.0 \times 10^{-2} \text{ s}^{-1}$
  - $5.0 \times 10^{-3} \text{ s}^{-1}$
31. For the reaction  $A + B \rightarrow$  products, it is observed that: *[2009]*
- On doubling the initial concentration of A only, the rate of reaction is also doubled and
  - On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by:

- $\text{rate} = k[\text{A}][\text{B}]^2$
- $\text{rate} = k[\text{A}]^2[\text{B}]^2$
- $\text{rate} = k[\text{A}][\text{B}]$
- $\text{rate} = k[\text{A}]^2[\text{B}]$

32. The bromination of acetone that occurs in acid solution is represented by this equation. *[2008]*
- $$\text{CH}_3\text{COCH}_3(\text{aq}) + \text{Br}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{Br}(\text{aq}) + \text{H}^+(\text{aq}) + \text{Br}^-(\text{aq})$$

These kinetic data were obtained for given reaction concentrations.

#### Initial Concentrations, M

$[\text{CH}_3\text{COCH}_3]$	$[\text{Br}_2]$	$[\text{H}^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of  $\text{Br}_2$ ,  $\text{Ms}^{-1}$

$$5.7 \times 10^{-5}$$

$$5.7 \times 10^{-5}$$

$$1.2 \times 10^{-4}$$

$$3.1 \times 10^{-4}$$

Based on these data, the rate equations is:

- $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$
- $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{Br}_2]$
- $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]^2$
- $\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{Br}_2][\text{H}^+]$

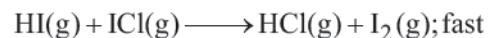
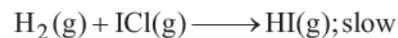
33. The reaction of hydrogen and iodine monochloride is given as: *[2007]*



The reaction is of first order with respect to  $\text{H}_2(\text{g})$  and  $\text{ICl}(\text{g})$ , following mechanisms were proposed. Mechanism A:



Mechanism B:



Which of the above mechanism(s) can be consistent with the given information about the reaction?

- A and B both
- neither A nor B
- A only
- B only

34. In a first-order reaction  $A \rightarrow B$ , if  $k$  is rate constant and initial concentration of the reactant A is 0.5 M, then the half-life is *[2007]*

- $\frac{\log 2}{k}$
- $\frac{\log 2}{k\sqrt{0.5}}$
- $\frac{\ln 2}{k}$
- $\frac{0.693}{0.5k}$

35. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately [2007]  
 (a) 45 minutes      (b) 60 minutes  
 (c) 40 minutes      (d) 50 minutes  
 $(\log 4 = 0.60, \log 5 = 0.69)$
36. For a first order reaction  $A \rightarrow B$  the reaction rate at reactant concentration of 0.01 M is found to be  $2.0 \times 10^{-5}$  mol L<sup>-1</sup> s<sup>-1</sup>. The half life period of the reaction is [2005]  
 (a) 30 s      (b) 220 s  
 (c) 300 s      (d) 347 s
37. The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is: [2005]  
 (a) 2      (b) -2  
 (c) 1      (d) -1
38. The rate of a first order reaction is  $1.5 \times 10^{-2}$  mol L<sup>-1</sup> min<sup>-1</sup> at 0.5 M concentration of the reactant. The half life of the reaction is [2004]  
 (a) 0.383 min      (b) 23.1 min  
 (c) 8.73 min      (d) 7.53 min
39. If the rate of the reaction is equal to the rate constant, the order of the reaction is [2003]  
 (a) 3      (b) 0  
 (c) 1      (d) 2
40. The reaction  $A \rightarrow B$  follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B? [2003]  
 (a) 2 hours      (b) 1 hour  
 (c) 0.5 hour      (d) 0.25 hour
41.  $3A \rightarrow B + C$ , it would be a zero order reaction when [2002]  
 (a) the rate of reaction is proportional to square of concentration of A  
 (b) the rate of reaction remains same at any concentration of A  
 (c) the rate remains unchanged at any concentration of B and C  
 (d) the rate of reaction doubles if concentration of B is increased to double
42. Half life of a first order reaction is 4 s and the initial concentration of the reactants is 0.12 M. The concentration of the reactant left after 16 s is [1999]  
 (a) 0.0075 M      (b) 0.06 M  
 (c) 0.03 M      (d) 0.015 M
43. The plot of concentration of the reactant vs. time for a reaction is a straight line with a negative slope. The reaction follows a [1996]  
 (a) zero order rate equation  
 (b) first order rate equation  
 (c) second order rate equation  
 (d) third order rate equation
44. A substance 'A' decomposes by a first order reaction starting initially with  $[A] = 2.00$  m and after 200 min,  $[A]$  becomes 0.15 m. For this reaction  $t_{1/2}$  is [1995]  
 (a) 53.72 min      (b) 50.49 min  
 (c) 48.45 min      (d) 46.45 min
45. Select the rate law that corresponds to data shown for the following reaction [1994]  
 $A + B \rightarrow \text{products.}$   
 Exp.    [A]    [B]    Initial rate  
 1    0.012    0.035    0.1  
 2    0.024    0.070    0.8  
 3    0.024    0.035    0.1  
 4    0.012    0.070    0.8  
 (a)  $\text{rate} = k[B]^3$       (b)  $\text{rate} = k[B]^4$   
 (c)  $\text{rate} = k[A][B]^3$       (d)  $\text{rate} = k[A]^2[B]^2$

### Topic 3: Theories of Rate of Reaction

46. An increase in the concentration of the reactants of a reaction leads to change in [2020]  
 (a) heat of reaction  
 (b) threshold energy  
 (c) collision frequency  
 (d) activation energy
47. For a reaction, activation energy  $E_a = 0$  and the rate constant at 200 K is  $1.6 \times 10^6$  s<sup>-1</sup>. The rate constant at 400 K will be [NEET Odisha 2019]  
 [Given that gas constant, R = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>]  
 (a)  $3.2 \times 10^6$  s<sup>-1</sup>      (b)  $3.2 \times 10^4$  s<sup>-1</sup>  
 (c)  $1.6 \times 10^6$  s<sup>-1</sup>      (d)  $1.6 \times 10^3$  s<sup>-1</sup>
48. The addition of a catalyst during a chemical reaction alters which of the following quantities? [2016]  
 (a) Entropy      (b) Internal energy  
 (c) Enthalpy      (d) Activation energy
49. The activation energy of a reaction can be determined from the slope of which of the following graphs? [2015]  
 (a)  $\frac{\ln K}{T}$  vs. T      (b)  $\ln K$  vs.  $\frac{l}{T}$   
 (c)  $\frac{T}{\ln K}$  vs.  $\frac{l}{T}$       (d)  $\ln K$  vs. T

50. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

[NEET 2013]

- (a) 269 kJ mol<sup>-1</sup>      (b) 34.7 kJ mol<sup>-1</sup>  
 (c) 15.1 kJ mol<sup>-1</sup>      (d) 342 kJ mol<sup>-1</sup>

51. A reaction having equal energies of activation for forward and reverse reaction has :

[NEET 2013]

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

52. Activation energy ( $E_a$ ) and rate constants ( $k_1$  and  $k_2$ ) of a chemical reaction at two different temperatures ( $T_1$  and  $T_2$ ) are related by :

[2012 MJ]

- (a)  $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$   
 (b)  $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$   
 (c)  $\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left( \frac{1}{T_2} + \frac{1}{T_1} \right)$   
 (d)  $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

53. For an endothermic reaction, energy of activation is  $E_a$  and enthalpy of reaction of  $\Delta H$  (both of these in kJ/mol). Minimum value of  $E_a$  will be.

[2010]

- (a) less than  $\Delta H$       (b) equal to  $\Delta H$   
 (c) more than  $\Delta H$       (d) equal to zero

54. The rate constants  $k_1$  and  $k_2$  for two different reactions are  $10^{16} \cdot e^{-2000/T}$  and  $10^{15} \cdot e^{-1000/T}$ , respectively. The temperature at which  $k_1 = k_2$  is :

- (a) 1000 K      (b)  $\frac{2000}{2.303}$  K      [2008]  
 (c) 2000 K      (d)  $\frac{1000}{2.303}$  K

55. The temperature dependence of rate constant ( $k$ ) of a chemical reaction is written in terms of Arrhenius equation,  $k = A e^{-E_a^*/RT}$ . Activation energy ( $E_a^*$ ) of the reaction can be calculated by plotting

[2003]

- (a)  $\log k$  vs  $\frac{1}{\log T}$       (b)  $k$  vs  $T$

- (c)  $k$  vs  $\frac{1}{\log T}$       (d)  $\log k$  vs  $\frac{1}{T}$

56. The activation energy for a simple chemical reaction  $A \rightarrow B$  is  $E_a$  in forward direction. The activation energy for reverse reaction [2003]

- (a) Is always double of  $E_a$   
 (b) Is negative of  $E_a$   
 (c) Is always less than  $E_a$   
 (d) Can be less than or more than  $E_a$

57. When a biochemical reaction is carried out in laboratory in the absence of enzyme then rate of reaction obtained is  $10^{-6}$  times, then activation energy of reaction in the presence of enzyme is

- (a)  $\frac{6}{RT}$       [2001]  
 (b) Different from  $E_a$  obtained in laboratory  
 (c)  $P$  is required  
 (d) Can't say anything

58. Activation energy of a chemical reaction can be determined by

[1998]

- (a) evaluating rate constant at standard temperature  
 (b) evaluating velocities of reaction at two different temperatures  
 (c) evaluating rate constants at two different temperatures  
 (d) changing concentration of reactants

59. In a reversible reaction the energy of activation of the forward reaction is 50 kcal. The energy of activation for the reverse reaction will be

[1996]

- (a) < 50 kcal  
 (b) either greater than or less than 50 kcal  
 (c) 50 kcal  
 (d) > 50 kcal

60. A chemical reaction is catalyzed by a catalyst  $X$ . Hence  $X$

[1995]

- (a) reduces enthalpy of the reaction  
 (b) decreases rate constant of the reaction  
 (c) increases activation energy of the reaction  
 (d) does not affect equilibrium constant of the reaction

61. For an exothermic reaction, the energy of activation of the reactants is

[1994]

- (a) equal to the energy of activation of products  
 (b) less than the energy of activation of products  
 (c) greater than the energy of activation of products  
 (d) Sometimes greater and sometimes less than that of the products

## ANSWER KEY

1	(b)	8	(b)	15	(b)	22	(a)	29	(d)	36	(d)	43	(a)	50	(b)	57	(b)
2	(c)	9	(b)	16	(d)	23	(a)	30	(b)	37	(b)	44	(a)	51	(b)	58	(c)
3	(c)	10	(d)	17	(d)	24	(b)	31	(a)	38	(b)	45	(a)	52	(b, d)	59	(b)
4	(b)	11	(d)	18	(a)	25	(d)	32	(a)	39	(b)	46	(c)	53	(c)	60	(d)
5	(d)	12	(d)	19	(b)	26	(b)	33	(d)	40	(b)	47	(c)	54	(d)	61	(b)
6	(d)	13	(a)	20	(c)	27	(d)	34	(c)	41	(b)	48	(d)	55	(d)		
7	(b)	14	(b)	21	(a)	28	(a)	35	(a)	42	(a)	49	(b)	56	(d)		

## Hints &amp; Solutions

1. (b) First order rate equation is

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$\Rightarrow 4.606 \times 10^{-3} = \frac{2.303}{t} \log \frac{2}{0.2}$$

$$\Rightarrow t = \frac{2.303}{4.606 \times 10^{-3}} \times \log 10 = \frac{10^3}{2} = 500 \text{ sec}$$

2. (c) For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

for 99% completion of the reaction,

$$t = \frac{2.303}{k} \log \frac{100}{100-99}$$

$$t = \frac{2.303}{k} \log 10^2$$

$$t = \frac{4.606}{k}$$

3. (c)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$-\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

4. (b)  $(t_{1/2})^{1^{\text{st}}} \text{ order} = \text{Independent of concentration}$

$$(t_{1/2})^{2^{\text{nd}}} \text{ order} \propto \frac{1}{[A]_0}$$

Half life for the second order reaction is

$$t_{1/2} = \frac{1}{K \times [A]_0}$$

5. (d) Rate constant  $k = 0.6 \times 10^{-3}$  mole per second.

(unit mole per second shows zero order reaction)  
For a zero order reaction

$$[A] = [A]_0 - kt$$

$$\text{and } [A_0] - [A] = [B] = kt \\ = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72 \text{ M}$$

6. (d) According to statement given in the question, it is clear that

$$r \propto [A]^2 \text{ and } r \propto [B]$$

That means, order of reaction with respect to B is 1 and w.r.t A is 2.

$$\text{Hence, Rate} = k[A]^2[B]^1$$

7. (b) Rate of disappearance of reactants = Rate of appearance of products

$$-\frac{1}{2} \frac{d(N_2O_5)}{dt} = \frac{1}{4} \frac{d(NO_2)}{dt} = \frac{d(O_2)}{dt}$$

$$\frac{1}{2} k(N_2O_5) = \frac{1}{4} k'(N_2O_5) = k''(N_2O_5)$$

$$\frac{k}{2} = \frac{k'}{4} = k''$$

$$k' = 2k, \quad k'' = \frac{k}{2}$$

8. (b)  $\text{N}_2O_5(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$

$$-\frac{d}{dt}[N_2O_5] = +\frac{1}{2} \frac{d}{dt}[NO_2] = 2 \frac{d}{dt}[O_2]$$

$$\frac{d}{dt}[NO_2] = 1.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1} \text{ and}$$

$$\frac{d}{dt}[O_2] = 3.125 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$$



9. (b)  $2\text{NO(g)} + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl(g)}$

$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$$

The value of rate constant can be increased by increasing the temperature and is independent of the initial concentration of the reactants.

10. (d) Rate of disappearance of  $\text{H}_2$  = rate of formation of  $\text{NH}_3$ .

$$-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\Rightarrow -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt} = \frac{3}{2} \times 2 \times 10^{-4}$$

$$= 3 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

11. (d) Rate of disappearance of  $\text{Br}^-$   
= rate of appearance of  $\text{Br}_2$

$$\Rightarrow -\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = \frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

$$\Rightarrow \frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$$

12. (d) In the given options,  $-\frac{d[\text{C}]}{3dt}$  will not represent the reaction rate. It should not have

-ve sign as it is product; since  $\frac{1}{3} \frac{d[\text{C}]}{dt}$  show the

rate of formation of product  $C$ , which will be positive.

13. (a) If we write rate of reaction in terms of concentration of  $\text{NH}_3$  and  $\text{H}_2$ , then

$$\text{Rate of reaction} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\text{So, } \frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$$

14. (b)  $3\text{A} \longrightarrow 2\text{B}$

Rate of appearance of  $B$  is equal to rate of disappearance of  $A$ .

$$\frac{1}{2} \frac{d[B]}{dt} = -\frac{1}{3} \frac{d[A]}{dt} \Rightarrow \frac{d[B]}{dt} = -\frac{2}{3} \frac{d[A]}{dt}$$

15. (b)  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

From the unit of rate constant, it is clear that the reaction follows first order kinetics. Hence, by rate law equation,  $r = k[\text{N}_2\text{O}_5]$

where  $r = 1.02 \times 10^{-4}$ ,  $k = 3.4 \times 10^{-5}$

$$1.02 \times 10^{-4} = 3.4 \times 10^{-5} [\text{N}_2\text{O}_5]$$

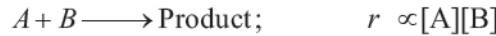
$$[\text{N}_2\text{O}_5] = 3\text{M}$$

16. (d) Rate of reaction

$$-\frac{1}{5} \frac{d[\text{Br}^-]}{dt} = +\frac{1}{3} \frac{d[\text{Br}_2]}{dt}$$

$$\frac{d[\text{Br}_2]}{dt} = -\frac{3}{5} \frac{d[\text{Br}^-]}{dt}$$

17. (d) The rate of a reaction is the speed at which the reactants are converted into products. It depends upon the concentration of reactants. e.g. for the reaction



By decreasing volume of gas or increasing pressure of it, concentration will increase. Hence, (a) and (c) are also correct options.

18. (a) For a first order reaction

$$\text{Half life period, } t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{2.303 \times 10^{-3}} \text{ s}^{-1}$$

$$= 300.91 \text{ s}$$

Now,  $40 \text{ g} \xrightarrow{t_{\frac{1}{2}}} 20 \text{ g} \xrightarrow{t_{\frac{1}{2}}} 10 \text{ g}$

So,  $40 \text{ g}$  substance requires 2 half life periods to reduce upto  $10 \text{ g}$

$$\therefore \text{Time taken in reduction} = 2 \times 300.91 \text{ s}$$

$$= 601.82 \approx 602 \text{ s}$$

$$19. (b) (t_{\frac{1}{2}})_{\text{zero}} = \frac{[\text{A}]_0}{2k}$$

$\therefore$  If  $[\text{A}]_0$  = doubled,  $t_{\frac{1}{2}}$  = doubled

20. (c) Overall rate =  $k[\text{X}][\text{Y}_2]$  ... (1)  
 $k$  = rate constant

Assuming step (i) to be reversible, its equilibrium constant,

$$k_{\text{eq}} = \frac{[\text{X}]^2}{[\text{X}_2]} \Rightarrow [\text{X}]^2 = k_{\text{eq}} [\text{X}_2];$$

$$[\text{X}] = k_{\text{eq}}^{\frac{1}{2}} [\text{X}_2]^{\frac{1}{2}} \quad \dots (2)$$

From eq (1) and (2)

$$\text{Rate} = kk_{\text{eq}}^{\frac{1}{2}} [\text{X}_2]^{\frac{1}{2}} [\text{Y}_2]$$

$$\text{Overall order} = \frac{1}{2} + 1 = \frac{3}{2} = 1.5$$



The overall reaction rate depends on the rate of the slowest step.

i.e., Overall rate = Rate of slowest step

21. (a) Half life for a first order reaction,

$$t_{1/2} = \frac{0.693}{K}$$

$$\text{So, } t_{1/2} = \frac{0.693}{10^{-2}} \text{ sec.}$$

Also, for the reduction of 20 g of reactant to 5 g, two half lives will be required.

∴ For 20 g of the reactant to reduce to 5 g, time taken,

$$t = 2 \times \frac{0.693}{10^{-2}} \text{ sec} = 138.6 \text{ sec.}$$



$$N = N_0 \left( \frac{1}{2} \right)^n$$

where  $N$  = mass after  $n$  number of half life

$n$  = number of half life

$N_0$  = Initial mass

22. (a) For a first order reaction

$$K = \frac{2.303}{(t_2 - t_1)} \log \frac{(a - x_1)}{(a - x_2)}$$

$$K = \frac{2.303}{(20 - 10)} \log \left( \frac{0.04}{0.03} \right)$$

$$K = \frac{2.303 \times 0.1249}{10}$$

$$\frac{0.6932}{t_{1/2}} = \frac{2.303 \times 0.1249}{10}$$

$$t_{1/2} = \frac{0.6932 \times 10}{2.303 \times 0.1249} = 24.1 \text{ sec}$$

23. (a)  $t_{1/2} = \frac{0.693}{k}$

For first order  $t_{1/2}$  is independent of initial concentration of reactant.

24. (b) For a first order reaction,

$$t_{75\%} = 2 \times t_{50\%}$$

25. (d) Rate<sub>1</sub> =  $k [A]^2[B]^3$

when concentrations of both A and B are doubled then

$$\text{Rate}_2 = k [2A]^2[2B]^3 = 32 k [A]^2[B]^3$$

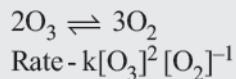
∴ Rate will increase by a factor of 32.

26. (b)  $\frac{r_{100^\circ C}}{r_{10^\circ C}} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512 \text{ times}$

27. (d) order of reaction can be zero, whole number or fractional.



The order w.r.t a reactant can be negative also as in this case:



28. (a) Rate =  $k [A]^0$

Unit of  $k$  = mol L<sup>-1</sup> sec<sup>-1</sup>

29. (d) In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence, it is second order with respect to B. In case of I & IV, keeping the concentration of [B] constant, when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. hence

$$\text{Rate} = k [A][B]^2$$

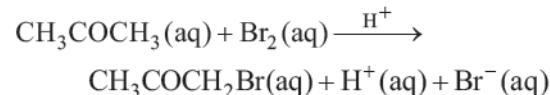
30. (b) For a first order reaction

$$t_{1/2} = \frac{0.693}{k}; k = \frac{0.693}{1386} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

31. (a) When concentration of A is doubled, rate is doubled. Hence order with respect to A is one. When concentrations of both A and B are doubled, rate increases by 8 times hence order with respect to B is 2.

$$\therefore \text{rate} = k [A]^1 [B]^2$$

32. (a) Rewriting the given data for the reaction



S. No.	Initial concen -ration of $\text{CH}_3\text{COCH}_3$ in M	Initial concentr -ation of $\text{Br}_2$ in M	Initial concentr -ation of $\text{H}^+$ in M	Rate of disappearance of $\text{Br}_2$ in $\text{M s}^{-1}$ i.e. $-\frac{d}{dt}[\text{Br}_2]$ or $\frac{dx}{dt}$
1	0.30	0.05	0.05	$5.7 \times 10^{-5}$
2	0.30	0.10	0.05	$5.7 \times 10^{-5}$
3	0.30	0.10	0.10	$1.2 \times 10^{-4}$
4	0.40	0.05	0.20	$3.1 \times 10^{-4}$

This reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (*i.e.* rate of disappearance of  $\text{Br}_2$ ).

From data (1) and (2) in which concentration of  $\text{CH}_3\text{COCH}_3$  and  $\text{H}^+$  remain unchanged and only the concentration of  $\text{Br}_2$  is doubled, there is no change in rate of reaction. It means the rate of reaction is independent of concentration of  $\text{Br}_2$ . Again from (2) and (3) in which  $(\text{CH}_3\text{COCH}_3)$  and  $(\text{Br}_2)$  remain constant but  $\text{H}^+$  increases from 0.05 M to 0.10 *i.e.* doubled, the rate of reaction changes from  $5.7 \times 10^{-5}$  to  $1.2 \times 10^{-4}$  (or  $12 \times 10^{-5}$ ), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to  $[\text{H}^+]$ . From (3) and (4), the rate should have doubled due to increase in conc of  $[\text{H}^+]$  from 0.10 M to 0.20 M but the rate has changed from  $1.2 \times 10^{-4}$  to  $3.1 \times 10^{-4}$ . This is due to change in concentration of  $\text{CH}_3\text{COCH}_3$  from 0.30 M to 0.40 M. Thus, the rate is directly proportional to  $[\text{CH}_3\text{COCH}_3]$ .

$$\text{rate} = k [\text{CH}_3\text{COCH}_3]^1 [\text{Br}_2]^0 [\text{H}^+]^1 \\ = k [\text{CH}_3\text{COCH}_3] [\text{H}^+].$$

33. (d) As the slowest step is the rate determining step thus the mechanism *B* will be more consistent with the given information. Also because it involve one molecule of  $\text{H}_2$  and one molecule of  $\text{ICl}$ , it can be expressed as :

$$r = k [\text{H}_2][\text{ICl}]$$

Which shows that the reaction is of first order w.r.t. both  $\text{H}_2$  &  $\text{ICl}$ .

34. (c) For a first order reaction

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

when  $t = t_{1/2}$

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a - a/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{\ln 2}{k}$$

35. (a) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

when  $t = 60$  and  $x = 60\%$

$$k = \frac{2.303}{60} \log \frac{100}{100-60} = \frac{2.303}{60} \log \frac{100}{40} = 0.0153$$

Now,

$$t_{1/2} = \frac{2.303}{0.0153} \log \frac{100}{100-50} = \frac{2.303}{0.0153} \times \log 2 \\ = \frac{2.303}{0.0153} \times 0.3010 = 45.31 \text{ min.}$$

36. (d) Given  $[A] = 0.01 \text{ M}$   
Rate =  $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ S}^{-1}$

For a first order reaction

$$\text{Rate} = k [A]$$

$$k = \frac{2.0 \times 10^{-5}}{[0.01]} = 2 \times 10^{-3}$$

$$t_{1/2} = \frac{0.693}{2 \times 10^{-3}} = 347 \text{ sec.}$$

37. (b) Rate<sub>1</sub> =  $k [A]^x [B]^y$  ... (1)

$$\frac{\text{Rate}_1}{4} = k [A]^x [2B]^y \quad \dots (2)$$

$$\text{or Rate}_1 = 4k [A]^x [2B]^y$$

From (1) and (2) we get

$$\frac{k[A]^x[B]^y}{4} = k[A]^x[2B]^y \\ \frac{[B]^y}{4} = [2B]^y$$

$$\text{or } \frac{1}{4} = \left( \frac{2B}{B} \right)^y \Rightarrow \frac{1}{4} = 2^y \text{ or } (2)^{-2} = 2^y$$

$$y = -2.$$

38. (b) For a first order reaction,  $A \rightarrow \text{products}$

$$r = k[A] \text{ or } k = \frac{r}{[A]}$$

$$\Rightarrow k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$$

$$\text{Further, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1 \text{ min.}$$

39. (b)  $\because r = k[A]^n$

$$\text{if } n = 0$$

$$r = k[A]^0$$

or  $r = k$  thus for zero order reactions rate is equal to the rate constant.

40. (b)  $A \rightarrow B$  For a first order reaction

$$\text{given } a = 0.8 \text{ mol}, \quad (a-x) = 0.8 - 0.6 = 0.2$$

$$k = \frac{2.303}{1} \log \frac{0.8}{0.2} \text{ or } k = 2.303 \log 4$$

again  $a = 0.9$ ,  $a - x = 0.9 - 0.675 = 0.225$

$$k = \frac{2.303}{t} \log \frac{0.9}{0.225}$$

$$2.303 \log 4 = \frac{2.303}{t} \log 4$$

Hence  $t = 1$  hour

41. (b) For reaction  $3A \longrightarrow B + C$

If it is zero order reaction  $r = k[A]^0$ , i.e. the rate remains same at any concentration of 'A'.

**NOTES**

For zero order reaction rate of reaction is independent of reactant concentration.

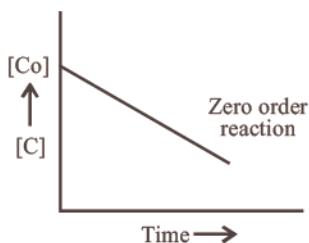
42. (a)  $t_{1/2} = 4$  s  $T = 16$

$$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \quad (\because T = n \times t_{1/2})$$

$$A = A_o \left( \frac{1}{2} \right)^n = 0.12 \times \left( \frac{1}{2} \right)^4 = \frac{0.12}{16} = 0.0075 \text{ M}$$

where  $A_o$  = initial concentration &  
 $A$  = concentration left after time  $t$ .

43. (a) For a zero order reaction, concentration decreases at a constant rate with time. Hence, the plot is a straight line with a negative slope.


**NOTES**

For zero order reaction

$$K = \frac{[C_0] - [C]}{t}$$

$$[C_0] = -Kt + [C_0]$$

$$\Rightarrow \text{slope} = -K, \text{ intercept} = [C_0]$$

44. (a) Given initial concentration ( $a$ ) = 2.00 m; Time taken ( $t$ ) = 200 min and final concentration ( $a - x$ ) = 0.15 m. For a first order reaction, rate constant,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{200} \log \frac{2.00}{0.15}$$

$$= \frac{2.303}{200} \times (0.301 + 0.824) = 1.29 \times 10^{-2} \text{ min}^{-1}$$

Further

$$(t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{1.29 \times 10^{-2}} = 53.49 \text{ min.}$$

45. (a) From data 1 and 3, it is clear that keeping (B) const, When [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. from 1 and 4, keeping [A] constant, when [B] is doubled, rate become 8 times. Hence  $\text{rate} \propto [B]^3$ .

46. (c) The number of collisions per second per unit volume of the reaction mixture is known as collision frequency ( $Z$ ). Collision frequency  $\propto$  no. of reacting molecules or atoms. Higher the concentration of reactant molecules higher is the probability of collision and so the collision frequency.

47. (c) From Arrhenius equation

$$\log \frac{k_{400}}{k_{200}} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

Since, given that  $E_a = 0$

$$\therefore \log \frac{k_{400}}{k_{200}} = 0$$

$$\Rightarrow \frac{k_{400}}{k_{200}} = 1$$

So,  $k_{400} = k_{200}$

So rate constant at 400,  $k = 1.6 \times 10^6 \text{ s}^{-1}$

48. (d) A catalyst provides an alternative route for the reaction with a lower activation energy.

49. (b) Arrhenius equation

$$K = A e^{-E_a/RT} \Rightarrow \ln K = \ln A - \frac{E_a}{RT}$$

$$\text{slope} = \frac{-E_a}{R}$$

so, activation energy of reaction can be

determined from the slope of  $\ln K$  vs  $\frac{1}{T}$

**NOTES**

Arrhenius Equation

$K = A e^{-E_a/RT}$ , where  $e^{-E_a/RT}$  represents the fraction of molecules

50. (b)  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{293} - \frac{1}{308} \right]$$

$$0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$$

$$E_a = \frac{0.3 \times 2.303 \times 8.314 \times 293 \times 308}{15}.$$

$$= 34673 \text{ J mol}^{-1} = 34.7 \text{ kJ mol}^{-1}$$

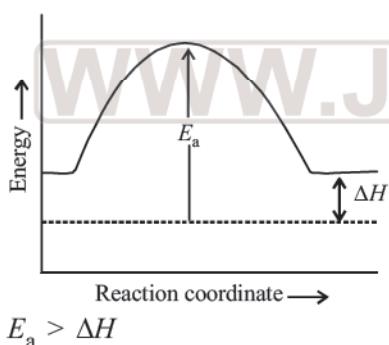
51. (b)  $\Delta H = E_{af} - E_{ab} = 0$

52. (b, d) According to Arrhenius equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{k_2}{k_1} = - \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

53. (c)



54. (d) Given,  $k_1 = 10^{16} \cdot e^{-\frac{2000}{T}}$

$$\text{and } k_2 = 10^{15} \cdot e^{-\frac{1000}{T}}$$

When  $k_1$  and  $k_2$  are equal at any temperature T, we have

$$10^{16} \cdot e^{-\frac{2000}{T}} = 10^{15} \cdot e^{-\frac{1000}{T}}$$

$$\text{or } 10 \times 10^{15} \cdot e^{-\frac{2000}{T}} = 10^{15} \cdot e^{-\frac{1000}{T}}$$

$$\text{or } 10 \cdot e^{-\frac{2000}{T}} = e^{-\frac{1000}{T}}$$

$$\text{or } \ln 10 - \frac{2000}{T} = -\frac{1000}{T}$$

or  $\ln 10 = \frac{2000}{T} - \frac{1000}{T}$

or  $2.303 \log 10 = \frac{1000}{T}$

or  $2.303 \times 1 \times T = 1000 \quad [\because \log 10 = 1]$

or  $T = \frac{1000}{2.303} K$

55. (d)  $k = A e^{-E_a/RT}$

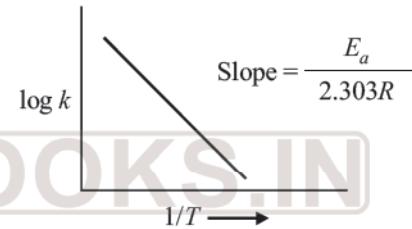
or  $\log k = \log A - \frac{E_a}{2.303 RT}$

Comparing the above equation with

$$y = mx + c$$

$$y = \log k, \quad x = \frac{1}{T}$$

Thus a plot of  $\log_{10} k$  vs  $1/T$  should be a straight line, with slope equal to  $-E_a / 2.303R$  and intercept equal to  $\log A$



$$\therefore \text{Slope} = \frac{-E_a}{2.303R}$$

or  $E_a = -2.303R \times \text{Slope}$

56. (d) The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.



As  $\Delta H = E_a$  (forward reaction) -  $E_a$  (backward reaction)

For exothermic reaction

$$\Delta H = -ve$$

$$\therefore -\Delta H = E_{a(f)} - E_{a(b)}$$

$$\text{or } E_{a(f)} = E_{a(b)} - \Delta H$$

$$\therefore E_{a(f)} < E_{a(b)}$$

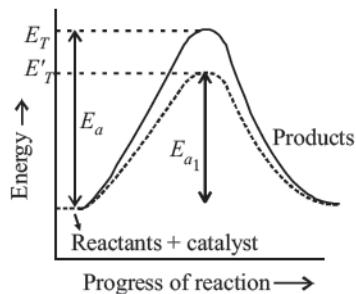
for endothermic reaction

$$\Delta H = + ve$$

$$\therefore \Delta H = E_{a(f)} - E_{a(b)} \text{ or } E_{a(f)} = \Delta H + E_{a(b)}$$

$$\therefore E_{a(f)} > E_{a(b)}$$

57. (b) The presence of enzyme (catalyst) increases the speed of reaction by lowering the energy barrier, i.e. a new path is followed with lower activation energy.



Here  $E_T$  is the threshold energy.

$E_a$  and  $E_{a1}$  is energy of activation of reaction in absence and presence of catalyst respectively.

58. (c) We know that the activation energy of chemical reaction is given by formula =

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

where  $k_1$  is the rate

constant at temperature  $T_1$  and  $k_2$  is the rate constant at temperature  $T_2$  and  $E_a$  is the activation energy. Therefore, activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

59. (b)  $\Delta H = E_{a(f)} - E_{a(b)}$

Thus, energy of activation for reverse reaction depend upon whether reaction is exothermic or endothermic

If reaction is exothermic,

$$\Delta H = -ve \quad E_{a(b)} > E_{a(f)}$$

If reaction is endothermic

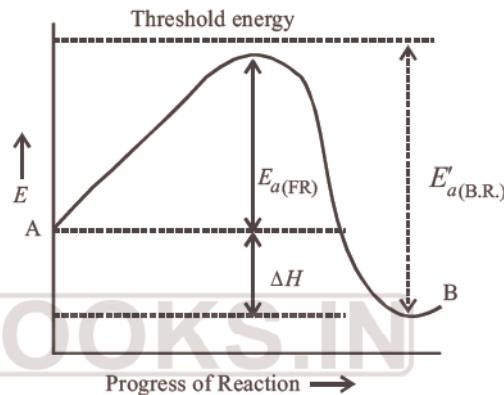
$$\Delta H = +ve \quad E_{a(b)} < E_{a(f)}$$

60. (d) A catalyst affects equally both forward and backward reactions, therefore it does not affect equilibrium constant of reaction.

61. (b)  $E_a$  (Forward) +  $\Delta H = E_a$  (backward)

For Exothermic reaction,  $\Delta H = -ve$  and

∴ activation energy of reactant is less than the energy of activation of products.



# 19

## Surface Chemistry

### Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Adsorption	characteristics of adsorption									1	E
Catalysis and theories of catalysis	catalysis							1	E		
Colloids and emulsions	zeta potential	1	E								
	colloidal solutions			1	A					1	E
	coagulation					1	E				

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

Qns - No. of Questions

#### Topic 1: Adsorption

- The correct option representing a Freundlich adsorption isotherm is **[NEET Odisha 2019]**
  - $\frac{x}{m} = kp^{-1}$
  - $\frac{x}{m} = kp^{0.3}$
  - $\frac{x}{m} = kp^{2.5}$
  - $\frac{x}{m} = kp^{-0.5}$
- Which one of the following characteristics is associated with adsorption ? **[2016]**
  - $\Delta G$  is negative but  $\Delta H$  and  $\Delta S$  are positive
  - $\Delta G$ ,  $\Delta H$  and  $\Delta S$  all are negative
  - $\Delta G$  and  $\Delta H$  are negative but  $\Delta S$  is positive
  - $\Delta G$  and  $\Delta S$  are negative but  $\Delta H$  is positive
- Which of the following statements is correct for the spontaneous adsorption of a gas? **[2014]**
  - $\Delta S$  is negative and, therefore,  $\Delta H$  should be highly positive
  - $\Delta S$  is negative and therefore,  $\Delta H$  should be highly negative
  - $\Delta S$  is positive and, therefore,  $\Delta H$  should be negative
  - $\Delta S$  is positive and, therefore,  $\Delta H$  should also be highly positive

- In Freundlich Adsorption isotherm, the value of  $1/n$  is **[2012]**
  - between 0 and 1 in all cases
  - between 2 and 4 in all cases
  - 1 in case of physical adsorption
  - 1 in case of chemisorption
- If  $x$  is amount of adsorbate and  $m$  is amount of adsorbent, which of the following relations is not related to adsorption process ? **[2011]**
  - $x/m = f(p)$  at constant  $T$ .
  - $x/m = f(T)$  at constant  $p$ .
  - $p = f(T)$  at constant  $(x/m)$ .
  - $\frac{x}{m} = p' T$
- The Langmuir adsorption isotherm is deduced using the assumption: **[2007]**
  - the adsorption sites are equivalent in their ability to adsorb the particles
  - the heat of adsorption varies with coverage
  - the adsorbed molecules interact with each other
  - the adsorption takes place in multilayers.

7. For adsorption of a gas on a solid, the plot of  $\log x/m$  vs  $\log p$  is linear with slope equal to ( $n$  being whole number) **[1994, 2006]**

  - $k$
  - $\log k$
  - $n$
  - $\frac{1}{n}$

8. According to the adsorption theory of catalysis, the speed of the reaction increases because **[2003]**

  - adsorption lowers the activation energy of the reaction
  - the concentration of reactant molecules at the active centres of the catalyst becomes high due to strong adsorption
  - in the process of adsorption, the activation energy of the molecules becomes large
  - adsorption produces heat which increases the speed of the reaction

9. Which is not correct regarding the adsorption of a gas on surface of solid? **[2001]**

  - On increasing temperature, adsorption increases continuously
  - Enthalpy and entropy changes are  $-ve$
  - Adsorption is more for some specific substances
  - This phenomenon is reversible

12. Which mixture of the solutions will lead to the formation of negatively charged colloidal  $[AgI]I^-$  sol.? **[2019]**

  - 50 mL of 1 M  $AgNO_3$  + 50 mL of 1.5 M  $KI$
  - 50 mL of 1 M  $AgNO_3$  + 50 mL of 2 M  $KI$
  - 50 mL of 2 M  $AgNO_3$  + 50 mL of 1.5 M  $KI$
  - 50 mL of 0.1 M  $AgNO_3$  + 50 mL of 0.1 M  $KI$

13. On which of the following properties does the coagulating power of an ion depend? **[2018]**

  - The magnitude of the charge on the ion alone
  - Size of the ion alone
  - The sign of charge on the ion alone
  - Both magnitude and sign of the charge on the ion

14. Fog is colloidal solution of **[2016]**

  - Liquid in gas
  - Gas in liquid
  - Solid in gas
  - Gas in gas

15. Which property of colloidal solution is independent of charge on the colloidal particles:- **[2014, 2015]**

  - Electrophoresis
  - Electro-osmosis
  - Tyndall effect
  - Coagulation

16. The protecting power of lyophilic colloidal sol.

## Topic 2: Catalysis and Theories of Catalysis

10. Which one of the following statements is not correct? **[2017]**

  - (a) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium
  - (b) Enzymes catalyse mainly bio-chemical reactions
  - (c) Coenzymes increase the catalytic activity of enzyme
  - (d) Catalyst does not initiate any reaction

## Topic 3: Colloids and Emulsions

11. Measuring Zeta potential is useful in determining which property of colloidal solution? **[2020]**

  - (a) Solubility
  - (b) Stability of the colloidal particles
  - (c) Size of the colloidal particles
  - (d) Viscosity

12. Which mixture of the solutions will lead to the formation of negatively charged colloidal  $[\text{AgI}]^{\text{I}^-}$  sol? [2019]  
(a) 50 mL of 1 M  $\text{AgNO}_3$  + 50 mL of 1.5 M  $\text{KI}$   
(b) 50 mL of 1 M  $\text{AgNO}_3$  + 50 mL of 2 M  $\text{KI}$   
(c) 50 mL of 2 M  $\text{AgNO}_3$  + 50 mL of 1.5 M  $\text{KI}$   
(d) 50 mL of 0.1 M  $\text{AgNO}_3$  + 50 mL of 0.1 M  $\text{KI}$

13. On which of the following properties does the coagulating power of an ion depend? [2018]  
(a) The magnitude of the charge on the ion alone  
(b) Size of the ion alone  
(c) The sign of charge on the ion alone  
(d) Both magnitude and sign of the charge on the ion

14. Fog is colloidal solution of [2016]  
(a) Liquid in gas      (b) Gas in liquid  
(c) Solid in gas      (d) Gas in gas

15. Which property of colloidal solution is independent of charge on the colloidal particles: [2014, 2015]  
(a) Electrophoresis      (b) Electro-osmosis  
(c) Tyndall effect      (d) Coagulation

16. The protecting power of lyophilic colloidal sol is expressed in terms of [2012]  
(a) Coagulation value  
(b) Gold number  
(c) Critical miscelle concentration  
(d) Oxidation number

17. Which one of the following forms micelles in aqueous solution above certain concentration? [2005]  
(a) Dodecyl trimethyl ammonium chloride  
(b) Glucose  
(c) Urea  
(d) Pyridinium chloride

18. Which of the following forms cationic micelles above certain concentration? [2004]  
(a) Sodium dodecyl sulphate  
(b) Sodium acetate  
(c) Urea  
(d) Cetyl trimethyl ammonium bromide

19. Position of non-polar and polar part in micelle is **[2002]**  
 (a) polar at outer surface and non-polar at inner surface  
 (b) polar at inner surface and non-polar at outer surface  
 (c) distributed all over the surface  
 (d) present in the surface only
20. Which is used for ending charge on colloidal solution? **[2000]**  
 (a) Electrons  
 (b) Electrolytes  
 (c) Positively charged ions  
 (d) Compounds
21. Hardy-Schulze rule explains the effect of electrolytes on the coagulation of colloidal solution. According to this rule, coagulation power of cations follow the order **[1999]**  
 (a)  $\text{Ba}^{+2} > \text{Na}^+ > \text{Al}^{+3}$  (b)  $\text{Al}^{+3} > \text{Na}^+ > \text{Ba}^{+2}$   
 (c)  $\text{Al}^{+3} > \text{Ba}^{+2} > \text{Na}^+$  (d)  $\text{Ba}^{+2} > \text{Al}^{+3} > \text{Na}^+$
22. At the Critical Micelle Concentration (CMC) the surfactant molecules **[1998]**  
 (a) decompose  
 (b) dissociate  
 (c) associate  
 (d) become completely soluble
23. The ability of an ion to bring about coagulation of a given colloid depends upon **[1997]**  
 (a) its size  
 (b) the magnitude of its charge  
 (c) the sign of the charge alone  
 (d) both magnitude and sign of its charge
24. During dialysis **[1996]**  
 (a) only solvent molecules can diffuse  
 (b) solvent molecules, ions and colloidal particles can diffuse  
 (c) all kinds of particles can diffuse through the semi-permeable membrane  
 (d) solvent molecules and ions can diffuse

## ANSWER KEY

1	(b)	4	(a)	7	(d)	10	(a)	13	(d)	16	(b)	19	(a)	22	(c)
2	(b)	5	(d)	8	(a)	11	(b)	14	(a)	17	(a)	20	(b)	23	(d)
3	(b)	6	(a)	9	(a)	12	(b)	15	(c)	18	(d)	21	(c)	24	(d)

## Hints & Solutions

1. (b) According to Freundlich isotherm

$$\frac{x}{m} = kp^{1/n}; \text{ where } (n > 1)$$

$$\text{So, } \frac{x}{m} = kp^{0.3} \text{ as } \frac{1}{n} = 0.3$$

So, answer is (b).



**NOTES** When  $\frac{1}{n} = 0$ ,  $\frac{x}{m} = \text{constant}$ , adsorption is independent of pressure.

When  $\frac{1}{n} = 1$ ,  $\frac{x}{m} = kp$ ,  $\frac{x}{m} \propto p$ , adsorption varies directly with pressure.

2. (b) Adsorption is spontaneous process, therefore change in the free energy ( $\Delta G$ ) for the process is negative.

According to Gibbs Helmholtz eqn.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta S$  is negative because adhering of gas molecules to the surface lowers the randomness.  
 $\therefore \Delta G$  can be  $-ve$  only when  $\Delta H$  is  $-ve$ .

3. (b) For adsorption  $\Delta S < 0$  and for a spontaneous change  $\Delta G = -ve$   
 hence  $\Delta H$  should be highly negative which is clear from the equation

$$\Delta G = \Delta H - T\Delta S$$

$$= -\Delta H - T(-\Delta S) = -\Delta H + T\Delta S$$

So if  $\Delta H$  is highly negative,  $\Delta G$  will also be  $(-ve)$

4. (a) According to Freundlich Adsorption isotherm

$$\frac{x}{m} = KP^n$$

at low pressure  $\frac{1}{n} = 1$

$$\therefore \frac{x}{m} \propto P^1$$

at high pressure  $\frac{1}{n} = 0$

$$\frac{x}{m} = \text{constant}$$

i.e. the value of n varies between 0 to 1

5. (d)  $\frac{x}{m} = f(P)$  at constant T and

$$\frac{x}{m} = f(T) \text{ at constant } T$$

Thus, it can be stated that for constant value of  $x/m$ , pressure and temperature can take different values or

$$P = f(T) \text{ at constant } (x/m).$$

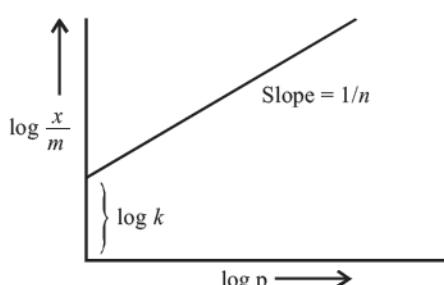
$$\text{But } \frac{x}{m} \neq P \times T$$

6. (a) Langmuir adsorption isotherm is based on the assumption that every adsorption site is equivalent and the ability of a particle to bind there is independent of whether or not nearby sites are occupied.

7. (d) According to Freundlich adsorption isotherm.

At intermediate pressure, extent of adsorption

$$\frac{x}{m} = kp^{1/n} \text{ or } \log \frac{x}{m} = \log k + \frac{1}{n} \log p;$$



plot of  $\log \frac{x}{m}$  vs  $\log p$  is linear with slope

$$= \frac{1}{n}$$

8. (a) A catalyst lowers the activation energy of the reaction.

$$\text{Rate of reaction} \propto \frac{1}{\text{activation energy}}$$

9. (a) On increasing temperature, adsorption of a gas on surface of solid decreases. Solid adsorb greater amount of substances at lower temperature.

10. (a) A catalyst speeds up both forward and backward reaction with the same rate.

So, equilibrium constant is not affected by the presence of a catalyst at any given temperature.

11. (b) In colloidal solution, the potential difference between the fixed layer and the diffused layer of opposite charge is known as Zeta potential.

Greater the Zeta potential more will be the stability of colloidal particle.

12. (b)  $\text{AgNO}_3 + \text{KI} \longrightarrow \text{AgI} + \text{KNO}_3$   
Negatively charged colloid

A solution of  $\text{AgNO}_3$  and KI will form a negatively charged colloidal sol,  $[\text{AgI}]I^-$ , only when KI is present in excess (i.e., KI behaves as a solvent).

Millimole of KI is maximum in option (2) ( $50 \times 2 = 100$ )

13. (d) According to Hardy Schulze rule, coagulating power of an ion depends on both magnitude and sign of the charge on the ion.



Greater the valence of the flocculating ion added, greater is the coagulating power.

14. (a) Fog is a colloidal system having dispersed phase as liquid and dispersion medium as gas.

15. (c) Tyndall effect is an optical property, and it is independent of charge on colloidal particles.

16. (b) The lyophobic sols are less stable than lyophilic sols. The lyophilic sols are thus used to protect the lyophobic sols. This property of lyophilic sols is known as protective action of lyophilic sols.

Which can be represented by gold number.

17. (a) Micelle formation is shown by surfactants detergents (Dodecyl trimethyl ammonium chloride) in their aqueous solutions.

18. (d) Cetyl trimethyl ammonium bromide,  $[C_{16}H_{33}(CH_3)_3N^+Br^-]$  is a cationic micelle



20. (b) On addition of electrolyte, charge of colloidal particles will get neutralized and coagulation will occur.
21. (c) According to this law the coagulating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion. The precipitating power of  $Al^{3+}$ ,  $Ba^{++}$ ,  $Na^+$  ions is in order  $Al^{3+} > Ba^{2+} > Na^+$ .
22. (c) The critical micelle concentration is the lowest concentration at which micelle formation appears. When surfactants are present above that CMC, they can act as emulsifiers that will solubilise a compound (oil, dirt, etc.) which is normally insoluble in the solvent being used.

23. (d) According to the Hardy Schulze rule, the coagulating effect of an ion on dispersed phase of opposite charge increases with the valency of the ion. Therefore, more the charge on oppositely charged ion, higher is the coagulation value.



Positive ion can coagulate negatively charged colloid and vice-versa. So, the ability depends on both magnitude and sign of its charge but the power of coagulation depends only on the magnitude of charge.

24. (d) Dialysis is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Colloidal particles cannot pass through animal membrane. Only solvent molecules and ions (in case of electrodialysis) can diffuse.

# 20

# General Principles and Processes of Isolation of Elements

 Trend Analysis with Important Topics & Sub-Topics 

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Occurrence of metals	occurrence of metals			1	E						
Metallurgical processes	metallurgical processes	1	A					1	E	1	A
	Ellingham diagram					1	A				
LOD - Level of Difficulty		E - Easy		A - Average		D - Difficult		Qns - No. of Questions			

## Topic 1: Occurrence of Metals

- Which one is malachite from the following ? **[2019]**
  - $\text{CuFeS}_2$
  - $\text{Cu}(\text{OH})_2$
  - $\text{Fe}_3\text{O}_4$
  - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
- "Metals are usually not found as nitrates in their ores". Out of the following two ((i) and (ii)) reasons which is/are true for the above observation ? **[2015]**
  - Metal nitrates are highly unstable.
  - Metal nitrates are highly soluble in water.
  - (i) and (ii) are false
  - (i) is false but (ii) is true
  - (i) is true but (ii) is false
  - (i) and (ii) are true
- Which one of the following is a mineral of iron? **[2012]**
  - Malachite
  - Cassiterite
  - Pyrolusite
  - Magnetite
- Identify the alloy containing a non-metal as a constituent in it. **[2012]**
  - Invar
  - Steel
  - Bell metal
  - Bronze

## Topic 2: Metallurgical Processes

- Identify the correct statement from the following: **[2020]**
  - Blister copper has blistered appearance due to evolution of  $\text{CO}_2$ .
  - Vapour phase refining is carried out for Nickel by Van Arkel method.
  - Pig iron can be moulded into a variety of shapes.
  - Wrought iron is impure iron with 4% carbon.
- Identify the incorrect statement. **[NEET Odisha 2019]**
  - Gangue is an ore contaminated with undesired materials.
  - The scientific and technological process used for isolation of the metal from its ore is known as metallurgy.
  - Minerals are naturally occurring chemical substances in the earth's crust.
  - Ores are minerals that may contain a metal.
- Considering Ellingham diagram, which of the following metals can be used to reduce alumina? **[2018]**
  - Fe
  - Zn
  - Cu
  - Mg

8. Extraction of gold and silver involves leaching with  $\text{CN}^-$  ion. Silver is later recovered by [2017]  
 (a) distillation  
 (b) zone refining  
 (c) displacement with Zn  
 (d) liquation
9. Match items of Column I with the items of Column II and assign the correct code : [2016]

Column-I	Column-II
(A) Cyanide process	(i) Ultrapure Ge
(B) Froth flotation	(ii) Dressing of $\text{ZnS}$ process
(C) Electrolytic reduction	(iii) Extraction of Al
(D) Zone refining	(iv) Extraction of Au
	(v) Purification of Ni

**Code :**

- | (A)       | (B)   | (C)   | (D)  |
|-----------|-------|-------|------|
| (a) (iv)  | (ii)  | (iii) | (i)  |
| (b) (ii)  | (iii) | (i)   | (v)  |
| (c) (i)   | (ii)  | (iii) | (iv) |
| (d) (iii) | (iv)  | (v)   | (i)  |

10. In the extraction of copper from its sulphide ore, the metal finally obtained by the reduction of cuprous oxide with : [2012, 2015 RS]  
 (a) iron (II) sulphide (b) carbon monoxide  
 (c) copper (I) sulphide (d) sulphur dioxide
11. Which of the following elements is present as the impurity to the maximum extent in the pig iron ?  
 (a) Manganese (b) Carbon [2011]  
 (c) Silicon (d) Phosphorus
12. The following reactions take place in the blast furnace in the preparation of impure iron. Identify the reaction pertaining to the formation of the slag. [2011 MJ]  
 (a)  $\text{Fe}_2\text{O}_3(\text{s}) + 3 \text{CO}(\text{g}) \rightarrow 2 \text{Fe}(\text{l}) + 3 \text{CO}_2(\text{g})$   
 (b)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
 (c)  $\text{CaO}(\text{s}) + \text{SiO}_2(\text{s}) \rightarrow \text{CaSiO}_3(\text{s})$   
 (d)  $2\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g})$

13. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true? [2007]  
 (a) The  $\Delta G_f^{\circ}$  of the sulphide is greater than those for  $\text{CS}_2$  and  $\text{H}_2\text{S}$ .  
 (b) The  $\Delta G_f^{\circ}$  is negative for roasting of sulphide ore to oxide.  
 (c) Roasting of the sulphide to the oxide is thermodynamically feasible.  
 (d) Carbon and hydrogen are suitable reducing agents for metal sulphides.

14. Sulphide ores of metals are usually concentrated by froth flotation process. Which one of the following sulphide ores offer an exception and concentrated by chemical leaching? [2007]  
 (a) Galena (b) Copper pyrite  
 (c) Sphalerite (d) Argentite

**Topic 3: Purification and Uses of Metals**

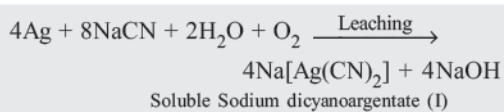
15. The metal oxide which cannot be reduced to metal by carbon is [NEET Kar. 2013]  
 (a)  $\text{Fe}_2\text{O}_3$  (b)  $\text{Al}_2\text{O}_3$   
 (c)  $\text{PbO}$  (d)  $\text{ZnO}$
16. Which of the following pairs of metals is purified by van Arkel method ? [2011]  
 (a) Ga and In (b) Zr and Ti  
 (c) Ag and Au (d) Ni and Fe
17. The method of zone refining of metals is based on the principle of [2003]  
 (a) Greater solubility of the impurity in the molten state than in the solid  
 (b) Greater mobility of the pure metal than that of the impurity  
 (c) Higher melting point of the impurity than that of the pure metal  
 (d) Greater noble character of the solid metal than that of the impurity
18. Method used for obtaining highly pure silicon used as a semiconductor material, is [1994, 96]  
 (a) Oxidation (b) Electrochemical  
 (c) Crystallization (d) Zone refining

**ANSWER KEY**

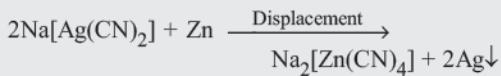
1	(d)	3	(d)	5	(c)	7	(d)	9	(a)	11	(b)	13	(d)	15	(b)	17	(a)		
2	(b)	4	(b)	6	(a)	8	(c)	10	(c)	12	(c)	14	(d)	16	(b)	18	(d)		

## Hints & Solutions

1. (d) Molachite is a green copper carbonate hydroxide mineral with chemical composition  $\text{CuCO}_3\text{C}_4(\text{OH})_2$ .
2. (b) Metal nitrates are highly soluble in water and are very stable for e.g.  $\text{NaNO}_3$  and  $\text{KNO}_3$ .
3. (d)  $[\text{Fe}_3\text{O}_4 \Rightarrow \text{Magnetite}]$   
 $[\text{CuCO}_3\text{Cu}(\text{OH})_2 - \text{Malachite}]$   
 $[\text{Pyrolusite} - \text{MnO}_2]$   $[\text{Cassiterite} - \text{SnO}_2]$ .
4. (b) Invar is a nickel iron alloy, Bell metal is an alloy of about 80% copper and 20% tin, Bronze is also an alloy of copper and tin.  
 Steel : It always have few % of carbon.
5. (c) The iron obtained from blast furnace contains about 4% carbon and smaller amount of impurities like S, P, Si, Mn. This form of iron is known as pig iron. It can be moulded into variety of shapes. Blister copper has blistered appearance due to evolution of  $\text{SO}_2$ . van Arkel method is used for refining of Zirconium or Titanium.
6. (a) Gangue is the commercially worthless material which is contaminating the ore.
7. (d) Mg has more  $-\Delta G$  value than alumina. So it will be in the lower part of Ellingham diagram. Metals which have more  $-\Delta G$  value can reduce those metal oxides which have less  $-\Delta G$  value.
8. (c) Zn being more reactive than Ag and Au, displaces them.

**NOTES**

Soluble cyanide compound can be treated with Zn to give metal by displacement.



9. (a) Highly electropositive metals like Al, K, Na etc. are extracted by the electrolytic reduction.
  - zone refining method is used for obtaining metals of high purity e.g. Ge.
  - Froth flotation process is suitable for sulphide ores.
  - Cyanide process is used for the extraction of gold.
10. (c)  $2\text{Cu}_2\text{S}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Cu}_2\text{O}(\text{s}) + 2\text{SO}_2(\text{g})$   
 The unchanged  $\text{Cu}_2\text{S}$ , mixed with  $\text{Cu}_2\text{O}$  and heated strongly in absence of air

11. (a)  $\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu} + \text{SO}_2$
12. (b) Pig iron or cast iron contains 3 – 5% carbon and varying amounts of Mn, Si, P and S which makes the iron hard and brittle.
13. (c) In blast furnace at about 1270 K, calcium carbonate is almost completely decomposed to give  $\text{CaO}$  which acts as a flux and combines with  $\text{SiO}_2$  present as impurity (gangue) in the ore to form calcium silicate (fusible slag)  
 $\text{CaO}(\text{s})(\text{basic flux}) + \text{SiO}_2(\text{s})(\text{acidic flux}) \longrightarrow \text{CaSiO}_3(\text{s})(\text{slag})$
14. (d) The sulphide ore is roasted to oxide before reduction because the  $\Delta G_f^\circ$  of most of the sulphides are greater than those of  $\text{CS}_2$  and  $\text{H}_2\text{S}$ , therefore, neither C nor H can reduce metal sulphide to metal. Further, the standard free energies of formation of oxide are much less than those of  $\text{SO}_2$ . Hence, oxidation of metal sulphides to metal oxide is thermodynamically favourable.
15. (d) Leaching is the selective dissolution of the desired mineral leaving behind the impurities in a suitable dissolving agent, e.g. Argentite or Silver glance,  $\text{Ag}_2\text{S}$  is an ore of silver. Silver is extracted from argentite by the mac-Arthur and Forest process (leaching process).  
 $\text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
16. (b) Al<sub>2</sub>O<sub>3</sub> cannot be reduced by carbon.

**NOTES**

In Ellingham diagram, place of aluminium oxidation is much below than that of carbon. Thus, carbon cannot reduce Al<sub>2</sub>O<sub>3</sub> to Aluminium metal.

17. (a) Zone refining is based on the difference in solubility of impurities in molten and solid state of the metal. This method is used for obtaining metals of very high purity.
18. (d) Si obtained by reduction of  $\text{SiCl}_4$  with  $\text{H}_2$  is further purified by zone refining method to get Si of very high purity.

**NOTES**

Silicon is purified by zone-refining process because the impurities present in it are more soluble in the liquid phase than in the solid phase.

# 21

## The *p*-Block Elements (Group 15, 16, 17 and 18)

### Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Nitrogen family	oxidation states in N compounds					1	A				
	acid strength of oxophosphorus acid									1	A
	chemical reactions of nitrogen / nitrogen compounds	1	A							1	E
Oxygen family	oxoacids of sulphur	1	A					1	A		
	stability order of hydrides			1	A						
Halogen family	preparation processes			1	A						
	structure of $\text{PCl}_5$			1	A						
	interhalogen compounds							1	A		
	bond dissociation enthalpy									1	E
	oxoacids/oxidation states/electron affinity					1	A			1	A
Noble gases	hybridisation and structures of noble gas compounds									1	A

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

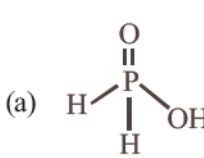
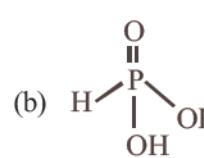
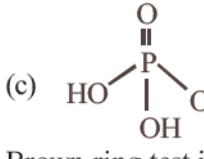
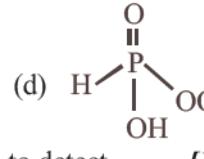
Qns - No. of Questions

#### Topic 1: Nitrogen Family

1. Urea reacts with water to form A which will decompose to form B. B when passed through  $\text{Cu}^{2+}$  (aq), deep blue colour solution C is formed. What is the formula of C from the following? [2020]
- (a)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$       (b)  $\text{Cu}(\text{OH})_2$   
 (c)  $\text{CuCO}_3 \text{ Cu}(\text{OH})_2$       (d)  $\text{CuSO}_4$

2. A compound 'X' upon reaction with  $\text{H}_2\text{O}$  produces a colorless gas 'Y' with rotten fish smell. Gas 'Y' is absorbed in a solution of  $\text{CuSO}_4$  to give  $\text{Cu}_3\text{P}_2$  as one of the products. Predict the compound 'X'. [NEET Odisha 2019]

- (a)  $\text{Ca}_3(\text{PO}_4)_2$       (b)  $\text{Ca}_3\text{P}_2$   
 (c)  $\text{NH}_4\text{Cl}$       (d)  $\text{As}_2\text{O}_3$

3. Which of the following oxoacids of phosphorus has strongest reducing property? **[NEET Odisha 2019]**
- (a)  $\text{H}_3\text{PO}_4$       (b)  $\text{H}_4\text{P}_2\text{O}_7$   
 (c)  $\text{H}_3\text{PO}_3$       (d)  $\text{H}_3\text{PO}_2$
4. The correct order of N-compounds in its decreasing order of oxidation states is **[2018]**
- (a)  $\text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl}$   
 (b)  $\text{HNO}_3, \text{NO}, \text{NH}_4\text{Cl}, \text{N}_2$   
 (c)  $\text{NH}_4\text{Cl}, \text{N}_2, \text{NO}, \text{HNO}_3$   
 (d)  $\text{HNO}_3, \text{NH}_4\text{Cl}, \text{NO}, \text{N}_2$
5. Which is the correct statement for the given acids? **[2016]**
- (a) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid  
 (b) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid  
 (c) Both are triprotic acids  
 (d) Both are diprotic acids
6. The product obtained as a result of a reaction of nitrogen with  $\text{CaC}_2$  is **[2016]**
- (a)  $\text{CaCN}_2$       (b)  $\text{CaCN}$   
 (c)  $\text{CaCN}_3$       (d)  $\text{Ca}_2\text{CN}$
7. Strong reducing behaviour of  $\text{H}_3\text{PO}_2$  is due to **[2015 RSJ]**
- (a) presence of one –OH group and two P–H bonds  
 (b) high electron gain enthalpy of phosphorus  
 (c) high oxidation state of phosphorus  
 (d) presence of two –OH groups and one P–H bond.
8. In which of the following compounds, nitrogen exhibits highest oxidation state? **[2012]**
- (a)  $\text{N}_2\text{H}_4$       (b)  $\text{NH}_3$   
 (c)  $\text{N}_3\text{H}$       (d)  $\text{NH}_2\text{OH}$
9. Which of the following statements is not valid for oxoacids of phosphorus? **[2012]**
- (a) Orthophosphoric acid is used in the manufacture of triple superphosphate.  
 (b) Hypophosphorous acid is a diprotic acid.  
 (c) All oxoacids contain tetrahedral four coordinated phosphorus.  
 (d) All oxoacids contain atleast one  $\text{P}=\text{O}$  and one  $\text{P}-\text{OH}$  group.
10. Oxidation states of P in  $\text{H}_4\text{P}_2\text{O}_5$ ,  $\text{H}_4\text{P}_2\text{O}_6$ , and  $\text{H}_4\text{P}_2\text{O}_7$ , are respectively: **[2010]**
- (a) +3, +5, +4      (b) +5, +3, +4  
 (c) +5, +4, +3      (d) +3, +4, +5
11. How many bridging oxygen atoms are present in  $\text{P}_4\text{O}_{10}$ ? **[2010]**
- (a) 5      (b) 6  
 (c) 4      (d) 2
12. Nitrogen forms  $\text{N}_2$ , but phosphorus is converted into  $\text{P}_4$  from P, the reason is **[2001]**
- (a) Triple bond is present between phosphorus atom  
 (b)  $\text{p}\pi - \text{p}\pi$  bonding is strong  
 (c)  $\text{p}\pi - \text{p}\pi$  bonding is weak  
 (d) Multiple bond is formed easily
13. Which of the following oxy-acids has the maximum number of hydrogens directly attached to phosphorus? **[1999]**
- (a)  $\text{H}_4\text{P}_2\text{O}_7$       (b)  $\text{H}_3\text{PO}_2$   
 (c)  $\text{H}_3\text{PO}_3$       (d)  $\text{H}_3\text{PO}_4$
14. Repeated use of which one of the following fertilizers would increase the acidity of the soil? **[1998]**
- (a) Urea  
 (b) Superphosphate of lime  
 (c) Ammonium sulphate  
 (d) Potassium nitrate
15. Which of the following species has the highest dipole moment? **[1997]**
- (a)  $\text{NH}_3$       (b)  $\text{PH}_3$   
 (c)  $\text{AsH}_3$       (d)  $\text{SbH}_3$
16. The structural formula of hypophosphorous acid is **[1997]**
- (a)   
 (b)   
 (c)   
 (d) 
17. Brown ring test is used to detect **[1994]**
- (a) Iodine      (b) Nitrate  
 (c) Iron      (d) Bromide
18. Which of the following fertilizers has the highest nitrogen percentage? **[1993]**
- (a) Ammonium sulphate  
 (b) Calcium cyanamide  
 (c) Urea  
 (d) Ammonium nitrate

19. Which one of the following substance is used in the laboratory for fast drying of neutral gases? **[1992]**
- Phosphorus pentoxide
  - Active charcoal
  - Anhydrous calcium chloride
  - $\text{Na}_3\text{PO}_4$ .
20. Number of electrons shared in the formation of nitrogen molecule is **[1992]**
- 6
  - 10
  - 2
  - 8
21. Sugarcane on reaction with nitric acid gives **[1992]**
- $\text{CO}_2$  and  $\text{SO}_2$
  - $(\text{COOH})_2$
  - 2  $\text{HCOOH}$  (two moles)
  - No reaction.
22. Nitrogen is relatively inactive element because **[1992]**
- Its atom has a stable electronic configuration
  - It has low atomic radius
  - Its electronegativity is fairly high
  - Dissociation energy of its molecule is fairly high
23.  $\text{H}_3\text{PO}_2$  is the molecular formula of an acid of phosphorus. Its name and basicity respectively are **[1992]**
- Phosphorus acid and two
  - Hypophosphorous acid and two
  - Hypophosphorous acid and one
  - Hypophosphoric acid and two
24. Aqueous solution of ammonia consists of **[1991]**
- $\text{H}^+$
  - $\text{OH}^-$
  - $\text{NH}_4^+$
  - $\text{NH}_4^+$  and  $\text{OH}^-$
25.  $\text{P}_2\text{O}_5$  is heated with water to give **[1991]**
- Hypophosphorous acid
  - Phosphorous acid
  - Hypophosphoric acid
  - Orthophosphoric acid
26. Basicity of orthophosphoric acid is **[1991]**
- 2
  - 3
  - 4
  - 5
27.  $\text{PCl}_3$  reacts with water to form **[1991]**
- $\text{PH}_3$
  - $\text{H}_3\text{PO}_3, \text{HCl}$
  - $\text{POCl}_3$
  - $\text{H}_3\text{PO}_4$
28.  $\text{PH}_4\text{I} + \text{NaOH}$  forms **[1991]**
- $\text{PH}_3$
  - $\text{NH}_3$
  - $\text{P}_4\text{O}_6$
  - $\text{P}_4\text{O}_{10}$
29. Pure nitrogen is prepared in the laboratory by heating a mixture of **[1991]**
- $\text{NH}_4\text{OH} + \text{NaCl}$
  - $\text{NH}_4\text{NO}_3 + \text{NaCl}$
  - $\text{NH}_4\text{Cl} + \text{NaOH}$
  - $\text{NH}_4\text{Cl} + \text{NaNO}_2$ .
30. Which of the following statements is not correct for nitrogen ? **[1990]**
- Its electronegativity is very high
  - $d$ -orbitals are available for bonding
  - It is a typical non-metal
  - Its molecular size is small
31. Of the following hydrides which one has the lowest boiling point ? **[1989]**
- $\text{AsH}_3$
  - $\text{SbH}_3$
  - $\text{PH}_3$
  - $\text{NH}_3$
32. Which of the following metal evolves hydrogen on reacting with cold dilute  $\text{HNO}_3$ ? **[1989]**
- Mg
  - Al
  - Fe
  - Cu.
33. Which one of the following compounds does not exist ? **[1989]**
- $\text{NCl}_5$
  - $\text{AsF}_5$
  - $\text{SbCl}_5$
  - $\text{PF}_5$
34. Each of the following is true about white and red phosphorus except that they **[1989]**
- Are both soluble in  $\text{CS}_2$
  - Can be oxidised by heating in air
  - Consist of the same kind of atoms
  - Can be converted into one another
35. When orthophosphoric acid is heated to  $600^\circ\text{C}$ , the product formed is **[1989]**
- $\text{PH}_3$
  - $\text{P}_2\text{O}_5$
  - $\text{H}_3\text{PO}_3$
  - $\text{HPO}_3$
36. Which of the following is a nitric acid anhydride? **[1988]**
- NO
  - $\text{NO}_2$
  - $\text{N}_2\text{O}_5$
  - $\text{N}_2\text{O}_3$ .

### Topic 2: Oxygen Family

37. Which of the following oxoacid of sulphur has  $-\text{O}-\text{O}-$  linkage? **[2020]**
- $\text{H}_2\text{SO}_4$ , sulphuric acid
  - $\text{H}_2\text{S}_2\text{O}_8$ , peroxodisulphuric acid
  - $\text{H}_2\text{S}_2\text{O}_7$ , pyrosulphuric acid
  - $\text{H}_2\text{SO}_3$ , sulphurous acid
38. Identify the correct formula of 'oleum' from the following. **[NEET Odisha 2019]**
- $\text{H}_2\text{S}_2\text{O}_8$
  - $\text{H}_2\text{S}_2\text{O}_7$
  - $\text{H}_2\text{SO}_3$
  - $\text{H}_2\text{SO}_4$

39. Which is the correct thermal stability order for  $H_2E$  ( $E = O, S, Se, Te$  and  $Po$ )? [2019]  
 (a)  $H_2S < H_2O < H_2Se < H_2Te < H_2Po$   
 (b)  $H_2O < H_2S < H_2Se < H_2Te < H_2Po$   
 (c)  $H_2Po < H_2Te < H_2Se < H_2S < H_2O$   
 (d)  $H_2Se < H_2Te < H_2Po < H_2O < H_2S$
40. In which pair of ions both the species contain  $S - S$  bond? [2017]  
 (a)  $S_4O_6^{2-}, S_2O_3^{2-}$     (b)  $S_2O_7^{2-}, S_2O_8^{2-}$   
 (c)  $S_4O_6^{2-}, S_2O_7^{2-}$     (d)  $S_2O_7^{2-}, S_2O_3^{2-}$
41. Nitrogen dioxide and sulphur dioxide have some properties in common. Which property is shown by one of these compounds, but not by the other? [2015]  
 (a) is a reducing agent  
 (b) is soluble in water  
 (c) is used as a food-preservative  
 (d) forms 'acid-rain'
42. Which of the statements given below is incorrect? [2015 RSJ]  
 (a)  $Cl_2O_7$  is an anhydride of perchloric acid  
 (b)  $O_3$  molecule is bent  
 (c)  $ONF$  is isoelectronic with  $O_2N^-$ .  
 (d)  $OF_2$  is an oxide of fluorine
43. Acidity of diprotic acids in aqueous solutions increases in the order : [2014]  
 (a)  $H_2S < H_2Se < H_2Te$   
 (b)  $H_2Se < H_2S < H_2Te$   
 (c)  $H_2Te < H_2S < H_2Se$   
 (d)  $H_2Se < H_2Te < H_2S$
44. Which of the following does not give oxygen on heating? [NEET 2013]  
 (a)  $Zn(ClO_3)_2$     (b)  $K_2Cr_2O_7$   
 (c)  $(NH_4)_2Cr_2O_7$     (d)  $KClO_3$
45. Sulphur trioxide can be obtained by which of the following reaction : [2012]  
 (a)  $CaSO_4 + C \xrightarrow{\Delta}$   
 (b)  $Fe_2(SO_4)_3 \xrightarrow{\Delta}$   
 (c)  $S + H_2SO_4 \xrightarrow{\Delta}$   
 (d)  $H_2SO_4 + PCI_5 \xrightarrow{\Delta}$
46. Which one of the following compounds is a peroxide? [2010]  
 (a)  $KO_2$     (b)  $BaO_2$   
 (c)  $MnO_2$     (d)  $NO_2$

47. Match List - I (substances) with List - II (processes) employed in the manufacture of the substances and select the correct option. [2010]

List - I		List - II	
Substances	Processes	Substances	Processes
1. Sulphuric acid	(i) Haber's process		
2. Steel	(ii) Bessemer's process		
3. Sodium hydroxide	(iii) Leblanc process		
4. Ammonia	(iv) Contact process		

**Code :**

1	2	3	4
(a) (iv)	(ii)	(iii)	(i)
(b) (i)	(iv)	(ii)	(iii)
(c) (i)	(ii)	(iii)	(iv)
(d) (iv)	(iii)	(ii)	(i)

48. Which of the following is the most basic oxide? [2006]

(a) $Sb_2O_3$	(b) $Bi_2O_3$
(c) $SeO_2$	(d) $Al_2O_3$

49. During its reactions, ozone [1999]

- (a) can only combine with hydrogen atoms
- (b) accepts electrons
- (c) loses electrons
- (d) shows the role of electrons to be irrelevant

50. Which of the following oxides will be the least acidic? [1996]

(a) $As_4O_6$	(b) $As_4O_{10}$
(c) $P_4O_{10}$	(d) $P_4O_6$

51. Oxidation of thiosulphate by iodine gives [1996]

- (a) tetrathionate ion
- (b) sulphide ion
- (c) sulphate ion
- (d) sulphite ion

52. About 20 km above the earth, there is an ozone layer. Which one of the following statements about ozone and ozone layer is true? [1995]

- (a) ozone has a triatomic linear molecule
- (b) it is harmful as it stops useful radiation
- (c) it is beneficial to us as it stops U.V radiation
- (d) conversion of  $O_3$  to  $O_2$  is an endothermic reaction

53. By passing  $H_2S$  gas in acidified  $KMnO_4$  solution, we get [1995]

- (a)  $S$
- (b)  $K_2S$
- (c)  $MnO_2$
- (d)  $K_2SO_3$

54. Polyanion formation is maximum in [1994]

- (a) Nitrogen
- (b) Oxygen
- (c) Sulphur
- (d) Boron

55. The acid which has a peroxy linkage is [1994]  
 (a) Sulphurous acid (b) Pyrosulphuric acid  
 (c) Dithionic acid (d) Caro's acid
56. Which would quickly absorb oxygen? [1991, 92]  
 (a) Alkaline solution of pyrogallol  
 (b) Conc.  $H_2SO_4$   
 (c) Lime water  
 (d) Alkaline solution of  $CuSO_4$
57. Oleum is [1991]  
 (a) Castor Oil (b) Oil of vitriol  
 (c) Fuming  $H_2SO_4$  (d) None of them
58. Oxygen will directly react with each of the following elements except [1989]  
 (a) P (b) Cl  
 (c) Na (d) S.
59. The gases respectively absorbed by alkaline pyrogallol and oil of cinnamon are [1989]  
 (a)  $O_3, CH_4$  (b)  $O_2, O_3$   
 (c)  $SO_2, CH_4$  (d)  $N_2O, O_3$ .
60. It is possible to obtain oxygen from air by fractional distillation because [1989]  
 (a) oxygen is in a different group of the periodic table from nitrogen  
 (b) oxygen is more reactive than nitrogen  
 (c) oxygen has higher b.p. than nitrogen  
 (d) oxygen has a lower density than nitrogen.
61. Hypo is used in photography to [1988]  
 (a) reduce  $AgBr$  grains to metallic silver  
 (b) convert metallic silver to silver salt  
 (c) remove undecomposed silver bromide as a soluble complex  
 (d) remove reduced silver

### Topic 3: Halogen Family

62. Match the following: [2019]  
 (a) Pure nitrogen (i) Chlorine  
 (b) Haber process (ii) Sulphuric acid  
 (c) Contact process (iii) Ammonia  
 (d) Deacon's process (iv) Sodium azide or Barium azide
- Which of the following is the correct option ?
- |                         |     |     |     |
|-------------------------|-----|-----|-----|
| (a)                     | (b) | (c) | (d) |
| (a) (i) (ii) (iii) (iv) |     |     |     |
| (b) (ii) (iv) (i) (iii) |     |     |     |
| (c) (iii) (iv) (ii) (i) |     |     |     |
| (d) (iv) (iii) (ii) (i) |     |     |     |
63. Identify the incorrect statement related to  $PCl_5$  from the following: [2019]  
 (a) Three equatorial P – Cl bonds make an angle of  $120^\circ$  with each other  
 (b) Two axial P – Cl bonds make an angle of  $180^\circ$  with each other  
 (c) Axial P – Cl bonds are longer than equatorial P – Cl bonds  
 (d)  $PCl_5$  molecule is non-reactive
64. Which of the following statements is not true for halogens? [2018]  
 (a) All form monobasic oxyacids  
 (b) All are oxidizing agents  
 (c) Chlorine has the highest electron-gain enthalpy  
 (d) All but fluorine shows positive oxidation states
65. Match the interhalogen compounds of column-I with the geometry in column II and assign the correct code. [2017]
- | Column-I   | Column-II                                |
|------------|--|
| 1. $XX'$   | (i) T-shape                              |
| 2. $XX'_3$ | (ii) Pentagonal bipyramidal              |
| 3. $XX'_5$ | (iii) Linear                             |
| 4. $XX'_7$ | (iv) Square-pyramidal<br>(v) Tetrahedral |
- Code :**
- |           |       |       |      |
|-----------|-------|-------|------|
| 1         | 2     | 3     | 4    |
| (a) (iii) | (i)   | (iv)  | (ii) |
| (b) (v)   | (iv)  | (iii) | (ii) |
| (c) (iv)  | (iii) | (ii)  | (i)  |
| (d) (iii) | (iv)  | (i)   | (ii) |
66. Among the following, the correct order of acidity is [2016]  
 (a)  $HClO_3 < HClO_4 < HClO_2 < HClO$   
 (b)  $HClO < HClO_2 < HClO_3 < HClO_4$   
 (c)  $HClO_2 < HClO < HClO_3 < HClO_4$   
 (d)  $HClO_4 < HClO_2 < HClO < HClO_3$
67. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules? [2016]  
 (a)  $I_2 > Br_2 > Cl_2 > F_2$  (b)  $Cl_2 > Br_2 > F_2 > I_2$   
 (c)  $Br_2 > I_2 > F_2 > Cl_2$  (d)  $F_2 > Cl_2 > Br_2 > I_2$

68. The variation of the boiling point of the hydrogen halides is in the order  $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$ .  
**[2015 RS]**

What explains the higher boiling point of hydrogen fluoride?

- (a) The electronegativity of fluorine is much higher than for other elements in the group.
- (b) There is strong hydrogen bonding between HF molecules
- (c) The bond energy of HF molecules is greater than in other hydrogen halides.
- (d) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.

69. Which is the strongest acid in the following :  
**[NEET 2013]**

- |                             |                             |
|-----------------------------|-----------------------------|
| (a) $\text{HClO}_3$         | (b) $\text{HClO}_4$         |
| (c) $\text{H}_2\text{SO}_3$ | (d) $\text{H}_2\text{SO}_4$ |

70. In which of the following arrangements the given sequence is not strictly according to the property indicated against it ?  
**[2012 MJ]**

- (a)  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$  : increasing acidic strength
- (b)  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$  : increasing  $pK_a$  values
- (c)  $\text{NH}_3 < \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$  : increasing acidic character
- (d)  $\text{CO}_2 < \text{SiO}_2 < \text{SnO}_2 < \text{PbO}_2$  : increasing oxidising power

71. The correct order of increasing bond angles in the following species are :  
**[2010]**

- (a)  $\text{Cl}_2\text{O} < \text{ClO}_2 < \text{ClO}_2^-$
- (b)  $\text{ClO}_2 < \text{Cl}_2\text{O} < \text{ClO}_2^-$
- (c)  $\text{Cl}_2\text{O} < \text{ClO}_2^- < \text{ClO}_2$
- (d)  $\text{ClO}_2^- < \text{Cl}_2\text{O} < \text{ClO}_2$

72. In the case of alkali metals, the covalent character decreases in the order:  
**[2009]**

- (a)  $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$
- (b)  $\text{MF} > \text{MCl} > \text{MI} > \text{MBr}$
- (c)  $\text{MI} > \text{MBr} > \text{MCl} > \text{MF}$
- (d)  $\text{MCl} > \text{MI} > \text{MBr} > \text{MF}$

73. Among the following which is the strongest oxidising agent?  
**[2009]**

- |                   |                  |
|-------------------|------------------|
| (a) $\text{Br}_2$ | (b) $\text{I}_2$ |
| (c) $\text{Cl}_2$ | (d) $\text{F}_2$ |

74. Which one of the following arrangements does not give the correct picture of the trends indicated against it ?  
**[2000, 2008]**

- (a)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Oxidizing power
- (b)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Electron gain enthalpy
- (c)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Bond dissociation energy

- (d)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Electronegativity.

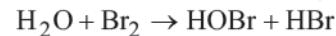
75. Which one of the following orders correctly represents the increasing acid strengths of the given acids?  
**[2005, 2007]**

- (a)  $\text{HOCl} < \text{HOCl} < \text{HOCl}_3 < \text{HOClO}_2$
- (b)  $\text{HOClO}_2 < \text{HOCl}_3 < \text{HOCl} < \text{HOCl}$
- (c)  $\text{HOCl}_3 < \text{HOClO}_2 < \text{HOCl} < \text{HOCl}$
- (d)  $\text{HOCl} < \text{HOCl} < \text{HOClO}_2 < \text{HOClO}_3$

76. Which one of the following orders is not in accordance with the property stated against it ?  
**[2006]**

- (a)  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$  : Acidic property in water
- (b)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Electronegativity
- (c)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Bond dissociation energy
- (d)  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  : Oxidising power

77. Which is the best description of the behaviour of bromine in the reaction given below? **[2004]**



- (a) Proton acceptor only
- (b) Both oxidized and reduced
- (c) Oxidized only
- (d) Reduced only

78. Which of the following statements is **not** true ?

- (a) HF is a stronger acid than HCl **[2003]**
- (b) Among halide ions, iodide is the most powerful reducing agent
- (c) Fluorine is the only halogen that does not show a variable oxidation state
- (d) HOCl is a stronger acid than HOBr

79. A one litre flask is full of brown bromine vapour. The intensity of brown colour of vapour will not decrease appreciably on adding to the flask some  
**[1998]**

- (a) pieces of marble
- (b) animal charcoal powder
- (c) carbon tetrachloride
- (d) carbon disulphide

80. Which one is the correct order of the size of iodine species?  
**[1997]**

- (a)  $\text{I} > \text{I}^+ > \text{I}^-$
- (b)  $\text{I} > \text{I}^- > \text{I}^+$
- (c)  $\text{I}^+ > \text{I}^- > \text{I}$
- (d)  $\text{I}^- > \text{I} > \text{I}^+$

81. Regarding  $F^-$  and  $Cl^-$  which of the following statements is/are correct? [1996]
- $Cl^-$  can give up an electron more easily than  $F^-$
  - $Cl^-$  is a better reducing agent than  $F^-$
  - $Cl^-$  is smaller in size than  $F^-$
  - $F^-$  can be oxidized more readily than  $Cl^-$
- (i) and (ii)
  - (i), (ii) and (iv)
  - (iii) and (iv)
  - only (i)
82. A certain compound ( $X$ ) when treated with copper sulphate solution yields a brown precipitate. On adding hypo solution, the precipitate turns white. The compound is [1994]
- $K_2CO_3$
  - $KI$
  - $KBr$
  - $K_3PO_4$
83. HI can be prepared by all the following methods, except [1994]
- $PI_3 + H_2O$
  - $KI + H_2SO_4$
  - $H_2 + I_2 \xrightarrow{Pt}$
  - $I_2 + H_2S$
84. Which among the following is paramagnetic? [1994]
- $Cl_2O$
  - $ClO_2$
  - $Cl_2O_7$
  - $Cl_2O_6$
85. Which one of the following oxides of chlorine is obtained by passing dry chlorine over silver chlorate at  $90^\circ C$ ? [1994]
- $Cl_2O$
  - $ClO_3$
  - $ClO_2$
  - $ClO_4$
86. The formula for calcium chlorite is [1994]
- $Ca(ClO_4)_2$
  - $Ca(ClO_3)_2$
  - $CaClO_2$
  - $Ca(ClO_2)_2$
87. A solution of potassium bromide is treated with each of the following. Which one would liberate bromine? [1993]
- Hydrogen iodide
  - Sulphur dioxide
  - chlorine
  - Iodine
88. When chlorine is passed over dry slaked lime at room temperature, the main reaction product is [1992]
- $Ca(ClO_2)_2$
  - $CaCl_2$
  - $CaOCl_2$
  - $Ca(OCl)_2$
89. In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with [1992]
- Carbon dioxide
  - Chlorine
  - Iodine
  - Sulphur dioxide
90. The bleaching action of chlorine is due to [1991]
- Reduction
  - Hydrogenation
  - Chlorination
  - Oxidation
91. Bleaching powder reacts with a few drops of dilute HCl to give [1989]
- chlorine
  - hypochlorous acid
  - calcium oxide
  - oxygen
92. Bleaching powder is obtained by the action of chlorine gas and [1988]
- dilute solution of  $Ca(OH)_2$
  - concentrated solution of  $Ca(OH)_2$
  - dry  $CaO$
  - dry slaked lime

#### Topic 4: Noble Gases

93. Match the compounds given in column I with the hybridisation and shape given in column II and mark the correct option. [2016]

Column-I	Column-II
1. $XeF_6$	(i) Distorted octahedral
2. $XeO_3$	(ii) Square planar
3. $XeOF_4$	(iii) Pyramidal
4. $XeF_4$	(iv) Square pyramidal

Code :

1	2	3	4
(a) (i)	(iii)	(iv)	(ii)
(b) (i)	(ii)	(iv)	(iii)
(c) (iv)	(iii)	(i)	(ii)
(d) (iv)	(i)	(ii)	(iii)

94. Identify the incorrect statement, regarding the molecule  $XeO_4$ : [NEET Kar. 2013]

- $XeO_4$  molecule is tetrahedral
- $XeO_4$  molecule is square planar
- There are four  $p\pi - d\pi$  bonds
- There are four  $sp^3 - p$ ,  $\sigma$  bonds

95. Noble gases do not react with other elements because [1994]

- They are mono atomic
- They are found in abundance
- The size of their atoms is very small
- They are completely paired up and stable electron shells

96. Which of the following statements is false ? [1994]

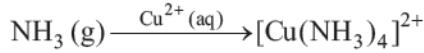
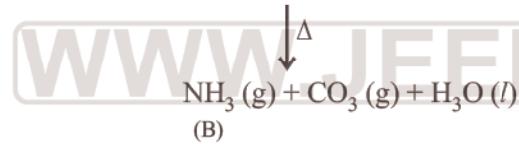
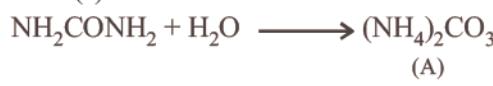
- Radon is obtained from the decay of radium
- Helium is inert gas
- Xenon is the most reactive among the rare gases
- The most abundant rare gas found in the

## ANSWER KEY

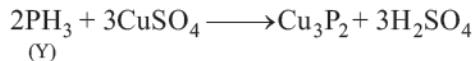
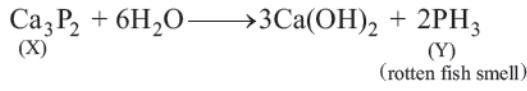
1	(a)	11	(b)	21	(b)	31	(c)	41	(c)	51	(a)	61	(c)	71	(d)	81	(d)	91	(a)
2	(b)	12	(c)	22	(d)	32	(a)	42	(d)	52	(c)	62	(d)	72	(c)	82	(b)	92	(d)
3	(d)	13	(b)	23	(c)	33	(a)	43	(a)	53	(a)	63	(d)	73	(d)	83	(b)	93	(a)
4	(a)	14	(c)	24	(d)	34	(a)	44	(c)	54	(c)	64	(d)	74	(b,c)	84	(b)	94	(b)
5	(b)	15	(a)	25	(d)	35	(d)	45	(b)	55	(d)	65	(a)	75	(d)	85	(c)	95	(d)
6	(a)	16	(a)	26	(b)	36	(c)	46	(b)	56	(a)	66	(b)	76	(c)	86	(d)	96	(d)
7	(a)	17	(b)	27	(b)	37	(b)	47	(a)	57	(c)	67	(b)	77	(b)	87	(c)		
8	(c)	18	(c)	28	(a)	38	(b)	48	(b)	58	(b)	68	(b)	78	(a)	88	(d)		
9	(b)	19	(a)	29	(d)	39	(c)	49	(a)	59	(b)	69	(b)	79	(a)	89	(b)		
10	(d)	20	(a)	30	(b)	40	(a)	50	(a)	60	(c)	70	(b)	80	(d)	90	(d)		

## Hints &amp; Solutions

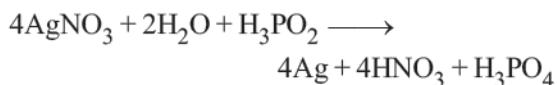
1. (a)



2. (b)



3. (d) Hypophosphorous acid is a good reducing agent as it contains two P-H bonds.

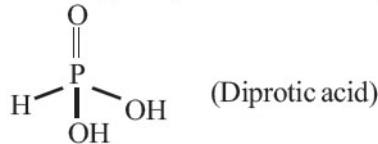
4. (a)  $\begin{array}{ccccccccc} +5 & +2 & 0 & -3 \\ \text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl} \end{array}$ 

Nitrogen in its elemental form has zero oxidation state.

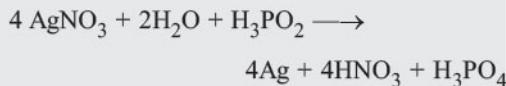
5. (b) Phosphinic acid as shown in structure below has one P—OH bond, thus, it is monobasic or monoprotic



Phosphonic acid as shown in structure has two P—OH bonds, thus, it is dibasic or diprotic

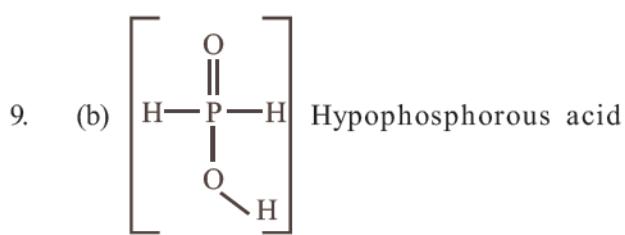
6. (a)  $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C}$ 

7. (a) The acids which contain P-H bond have strong reducing properties.

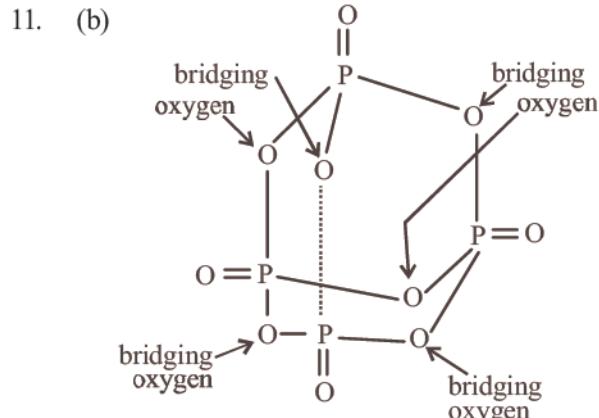
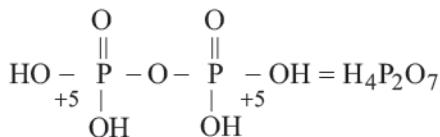
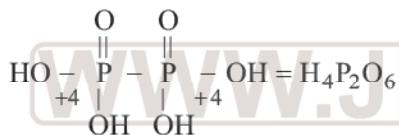
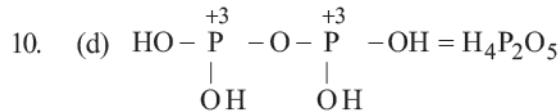
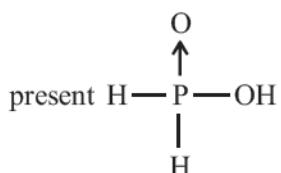
H<sub>3</sub>PO<sub>2</sub> acid is good reducing agent as it contains two P—H bonds and reduces, for example, AgNO<sub>3</sub> to metallic silver.

8. (c) Compound Oxidation number of nitrogen

N <sub>2</sub> H <sub>4</sub>	=	-2
NH <sub>3</sub>	=	-3
N <sub>3</sub> H	=	-1/3
NH <sub>2</sub> OH	=	-1



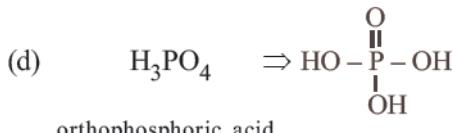
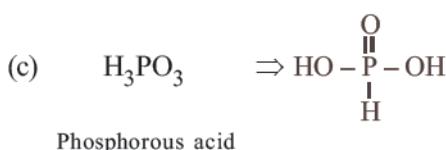
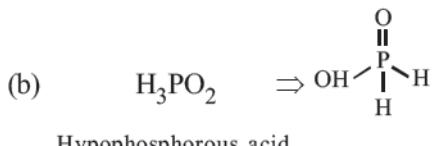
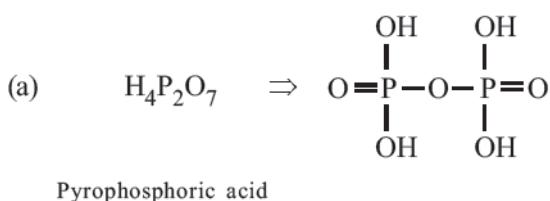
$(\text{H}_3\text{PO}_2)$  is a monobasic acid. i.e., it has only one ionisable hydrogen atom or one OH is



i.e. 6-bridging oxygen.

12. (c) Nitrogen form  $\text{N}_2$  (i.e.  $\text{N} \equiv \text{N}$ ) but phosphorus form  $\text{P}_4$ , because in  $\text{P}_2$ ,  $\text{p}_\pi - \text{p}_\pi$  bonding is present which is a weaker bonding.

13. (b)

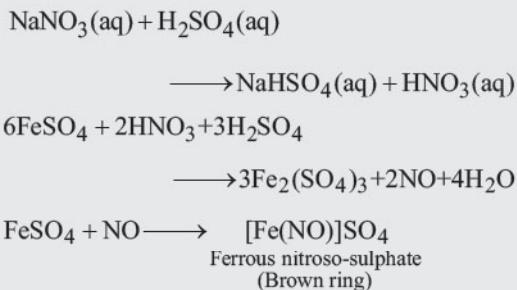


14. (c) Ammonium sulphate is a salt of weak base and strong acid, so it produces acidity. Hence aqueous solution of ammonium sulphate increases the acidity of soil.

15. (a) Order of dipole moment decreases as  $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$   
(Based upon electronegativity)

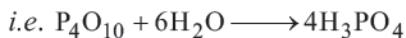
16. (a) We know that empirical formula of hypophosphorus acid is  $\text{H}_3\text{PO}_2$ . In this only one ionisable hydrogen atom is present i.e. it is monobasic. Therefore option (a) is correct structural formula of it.

17. (b) Brown ring test is done for the confirmation of  $\text{NO}_3^-$  ions.



18. (c) Urea (46.6%N). % of N in other compound are :  $(\text{NH}_4)_2\text{SO}_4 = 21.2\%$ ;  
 $\text{CaCN}_2 = 35.0\%$  and  $\text{NH}_4\text{NO}_3 = 35.0\%$

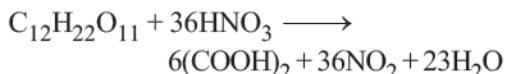
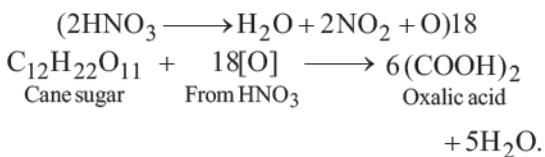
19. (a) Phosphorus pentoxide has great affinity for water. It forms ortho phosphoric acid on absorbing water



It is thus used as a powerful dehydrating or drying agent.

20. (a) Nitrogen molecule is diatomic containing a triple bond between two N atoms,  $\ddot{\text{N}} \equiv \ddot{\text{N}}$ . Therefore, nitrogen molecule is formed by sharing six electrons.

21. (b) Cane sugar is oxidised to oxalic acid



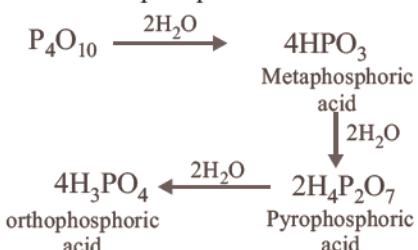
22. (d)  $\text{N}_2$  molecule contains triple bond between N atoms having very high dissociation energy ( $946 \text{ kJ mol}^{-1}$ ) due to which it is relatively inactive.

23. (c)  $\text{H}_3\text{PO}_2$  is named as hypophosphorous acid. As it contains only one P–OH group, its basicity is one.

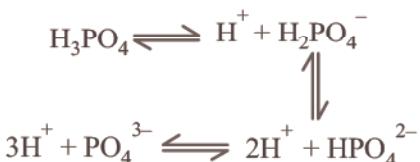
24. (d) Aqueous solution of ammonia is obtained by passing  $\text{NH}_3$  in  $\text{H}_2\text{O}$  which gives  $\text{NH}_4^+$  and  $\text{OH}^-$  ions.



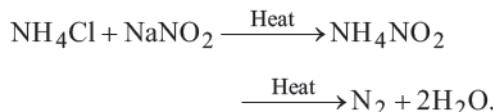
25. (d)  $\text{P}_2\text{O}_5$  have great affinity for water. The final product is orthophosphoric acid.



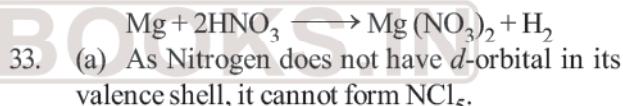
26. (b) It is a tribasic acid as all the three hydrogen atoms are ionisable. It forms three series of salts.



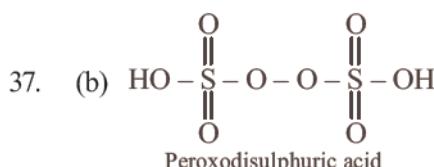
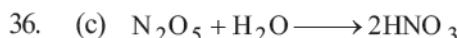
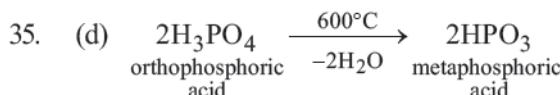
27. (b)  $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$
28. (a)  $\text{PH}_4\text{I} + \text{NaOH} \rightarrow \text{NaI} + \text{PH}_3 + \text{H}_2\text{O}$
29. (d) Pure nitrogen in the lab can be obtained by heating ammonium nitrate. Ammonium nitrate is not a stable compound it dissociate to give nitrogen.



30. (b) In case of nitrogen, *d*-orbitals are not available.
31. (c)  $\text{NH}_3$  undergoes H-bonding and hence has the highest b.p. Among the remaining hydrides *i.e.*  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$  the b.p. increases as the size of the element increases and hence the magnitude of the van der Waal's forces of attraction increases. Thus,  $\text{PH}_3$  has the lowest b.p.
32. (a) Magnesium and manganese are the metals that produce hydrogen with dilute nitric acid

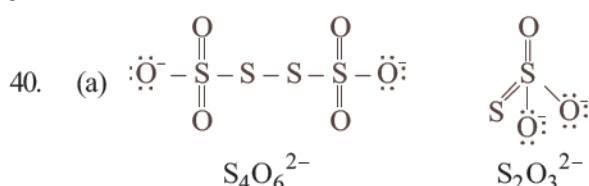


34. (a) Red phosphorus is not soluble in  $\text{CS}_2$ , only white P is soluble.



**NOTES**  
Peroxosulphuric acid is also known as Marshall's acid and is one of the most powerful peroxy acid oxidant.

38. (b) Oleum is  $\text{H}_2\text{S}_2\text{O}_7$ .
39. (c) On going down the group, bond dissociation enthalpy of the hydrides of oxygen family decreases. Therefore, thermal stability also decreases.



41. (c)  $\text{SO}_2$  is widely used in food and drinks industries for its property as a preservative and antioxidant while  $\text{NO}_2$  is not used as food preservative.

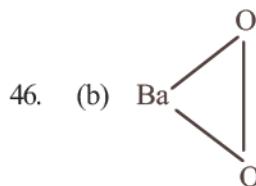
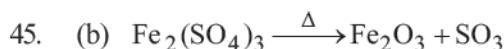
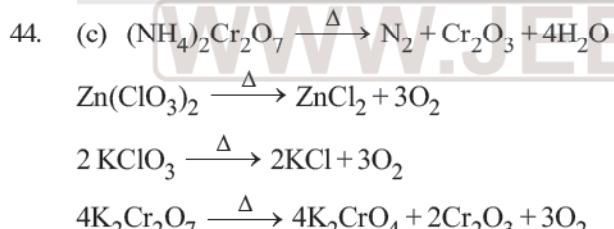
42. (d)  $\text{OF}_2$ ; among the following O and F, F is more electronegative than oxygen.

So  $\text{OF}_2$  cannot be called oxide because in that case fluorine is in +1 oxidation state which is not possible, so  $\text{OF}_2$  is called oxygen difluoride.

43. (a) The weakening of M—H bond with increase in size of M (where M = S, Se, Te) explains the acid character of hydrides.



On moving down the group, atomic size increases hence, bond length increases and hence, removal tendency of H also increases.

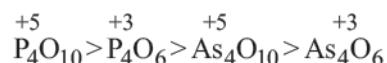


47. (a)
- |                      |                         |
|----------------------|-------------------------|
| (1) Sulphuric acid   | (iv) Contact process    |
| (2) Steel            | (ii) Bessemer's process |
| (3) Sodium hydroxide | (iii) Leblanc process   |
| (4) Ammonia          | (i) Haber's process     |

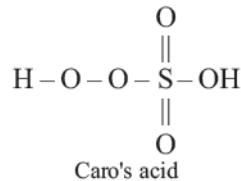
48. (b) More the oxidation state of the central atom (metal), more is its acidity. Hence,  $\text{SeO}_2$  (O. S. of Se = +4) is acidic. Further for a given O.S., the basic character of the oxides increases with the

increasing size of the central atom. Thus  $\text{Al}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  are amphoteric and  $\text{Bi}_2\text{O}_3$  is basic.

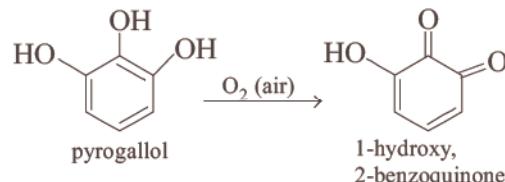
49. (a) Since ozone can easily lose oxygen atom (nascent oxygen), it acts as a powerful oxidising agent, and hence, reacts with hydrogen atoms.
50. (a) As the O.N. of the central atom of the compounds increases, acidic strength of that compound also increases and on moving from top to bottom in groups acidic strength of oxides also decrease due to decreasing electronegativity in groups.



51. (a)  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$   
Tetrathionate
52. (c) Ozone layer is beneficial to us, because it stops harmful ultraviolet radiations to reach the earth.
53. (a)  $2\text{KMnO}_4 + 5\text{H}_2\text{S} + 3\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{S} + 8\text{H}_2\text{O}$ .  
Thus, in this reaction sulphur (S) is produced.
54. (c) Due to greater tendency for catenation, sulphur shows property of polyanion formation to a greater extent. For example, in polysulphides such as  $\text{S}_3^{2-}, \text{S}_4^{2-}, \text{S}_5^{2-}$
55. (d) Caro's acid is  $\text{H}_2\text{SO}_5$  which contains one S—O—O—H peroxy linkage. It is also known as permonosulphuric acid.



56. (a) Upon oxidation, pyrogallol forms hydroxy-quinone and many other higher molecular mass products.

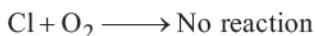
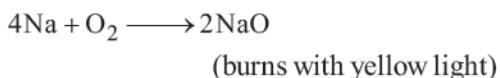




Hydroxy groups are strong activators of aromatic systems, hence pyrogallol is reactive enough to react with oxygen in air.

57. (c) Oleum is  $H_2S_2O_7$  ( $H_2SO_4 + SO_3$ ) which is obtained by dissolving  $SO_3$  in  $H_2SO_4$  and is called fuming sulphuric acid.

58. (b)  $S + O_2 \rightarrow SO_2$  (burns with blue light)



Chlorine does not react directly with oxygen.

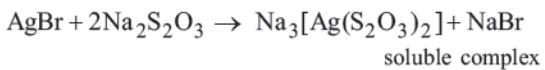
59. (b) Alkaline pyrogallol absorbs  $O_2$  and oil of cinnamon absorbs  $O_3$ .

60. (c) Oxygen has higher b.pt. than nitrogen therefore it can be obtained from air by fractional distillation.



Air is liquified by making use of the joule-Thomson effect (cooling by expansion of the gas). Water vapour and  $CO_2$  are removed by solidification. The remaining constituents of liquid air i.e., liquid oxygen and liquid nitrogen are separated by means of fractional distillation.

61. (c) Undecomposed  $AgBr$  forms a soluble complex with hypo



62. (d)

63. (d)  $PCl_5$  is very reactive due to the presence of weak axial bonds. It is used in the synthesis of various organic compounds.

64. (d) Due to high electronegativity and small size, F forms only one oxoacid,  $HOF$  known as fluoric (I) acid.



Flourine has  $-1$  oxidation state in most of its compound. Oxidation number of F is  $+1$  in  $HOF$ .

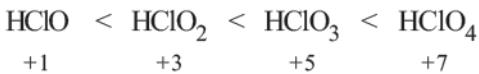
65. (a)  $XX' \rightarrow$  Linear (e.g.  $ClF$ ,  $BrF$ )

$XX'_3 \rightarrow$  T-Shape (e.g.  $ClF_3$ ,  $BrF_3$ )

$XX'_5 \rightarrow$  Square pyramidal (e.g.  $BrF_5IF_5$ )

$XX'_7 \rightarrow$  Pentagonal bipyramidal (e.g.  $IF_7$ )

66. (b) Acidic strength increases as the oxidation number of central atom increases.



67. (b) Bond dissociation enthalpy decreases as the bond distance increases from  $F_2$  to  $I_2$ . This is due to increase in the size of the atom, on moving from F to I.

F – F bond dissociation enthalpy is smaller than Cl – Cl and even smaller than Br – Br. This is because F atom is very small and hence the three lone pairs of electrons on each F atom repel the bond pair holding the F-atoms in  $F_2$  molecules. The increasing order of bond dissociation enthalphy is



68. (b) The H-bonding is present in HF due to high electronegativity of fluorine atom. While H-bonding is not present in HI, HBr and HCl.

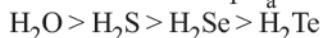
69. (b)  $HClO_4$  is the strongest acid amongst all because the oxidation state of Cl is maximum (+7).

70. (b) If acidic nature is high,  $K_a$  is high and  $pK_a$  is low

	$H_2O$	$H_2S$
$K_a$	$1.8 \times 10^{-6}$	$1.3 \times 10^{-7}$
$K_a$	$1.3 \times 10^{-4}$	$2.3 \times 10^{-3}$

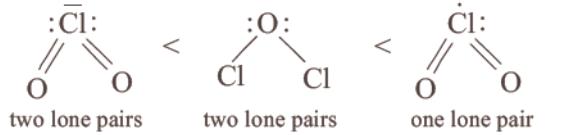
since  $pK_a = -\log K_a$

Hence the order of  $pK_a$  will be



71. (d) (i) As the number of lone pair of electrons increases, bond angle decreases due to repulsion between  $lp - lp$ .

- (ii) As the electronegativity of the central atom increases, bond angle increases. Hence, the correct order of bond angle:



72. (c)  $MI > MBr > MCl > MF$ . As the size of the anion decreases covalency decreases.

73. (d) Standard reduction potential of halogens are positive and decreases from fluorine to iodine. Therefore, halogens act as strong oxidising agent and their oxidising power decreases from fluorine to iodine.

74. (b and c)

- (a) The oxidising power of halogen follow the order  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .
- (b) The correct order of electron gain enthalpy of halogens is  $\text{Cl}_2 > \text{F}_2 > \text{Br}_2 > \text{I}_2$ . The low value of  $\text{F}_2$  than  $\text{Cl}_2$  is due to its small size.
- (c) The correct order of bond dissociation energies of halogens is  $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$ .
- (d) It is the correct order of electronegativity values of halogens.
- $$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$$

75. (d)  $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$



As the oxidation number of the central atom increases, strength of acid also increases.

76. (c) Bond dissociation energy of fluorine is less because of its small size and repulsion between electrons of two atoms. So option (c) is wrong order. The correct order is



77. (b)  $\text{H}_2\text{O} + \text{Br}_2 \longrightarrow \text{HOBr} + \text{HBr}$

Thus, here oxidation number of Br increases from 0 to +1 and also decreases from 0 to -1. Thus, it is oxidised as well as reduced.

78. (a) F is more electronegative than Cl therefore HF bond is stronger than HCl and hence proton is not given off easily. Hence HF is the weakest hydrohalic acid.

79. (a) Brown bromine vapour will not react with

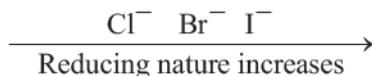
- (a) Pieces of marble ( $\text{CaCO}_3$ ).
- (b) Animal charcoal powder can adsorb it.
- (c) In carbon tetrachloride solution it will dissolve.

(d) In carbon disulphide solution, bromine will dissolve and thus, intensity of brown colour will decrease.

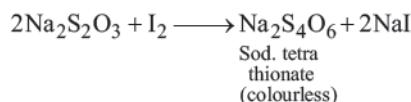
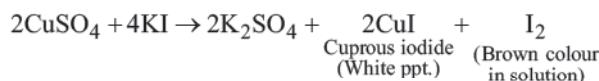
80. (d) We know that positive ion is always smaller and negative ion is always larger than the corresponding atom. Therefore the correct order of the size is  $\text{I}^- > \text{I} > \text{I}^+$

81. (d) The halide ions act as reducing agents.  $\text{F}^-$  ion does not show any reducing nature but  $\text{Cl}^-$ ,

$\text{Br}^-$  &  $\text{I}^-$  ion act as reducing agents and their reducing nature is in increasing order



82. (b) KI reacts with  $\text{CuSO}_4$  solution to produce cuprous iodide (white precipitate) and  $\text{I}_2$  (which gives brown colour). Iodine reacts with hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) solution. Decolourisation of solution shows the appearance of white precipitate.

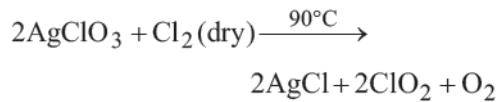


83. (b) HI cannot be prepared by heating iodides with concentrated  $\text{H}_2\text{SO}_4$ . The reaction between KI &  $\text{H}_2\text{SO}_4$  is as follows:



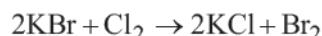
84. (b)  $\text{ClO}_2$  contains 7 + 12 i.e. 19 electrons (valence) which is an odd number, i.e. there is (are) free electron(s). Hence it is paramagnetic in nature.

85. (c) Pure  $\text{ClO}_2$  is obtained by passing dry  $\text{Cl}_2$  over  $\text{AgClO}_3$  at  $90^\circ\text{C}$ .



86. (d) Calcium chlorite is  $\text{Ca}(\text{ClO}_2)_2$

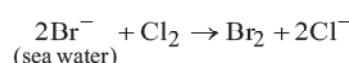
87. (c) A stronger oxidising agent ( $\text{Cl}_2$ ) displaces a weaker oxidising agent ( $\text{Br}_2$ ) from its salt solution.



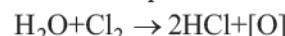
88. (d)



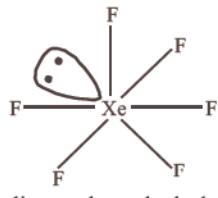
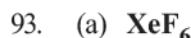
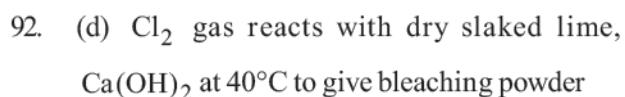
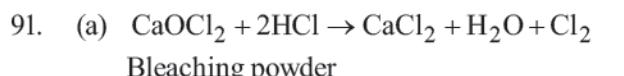
89. (b) Bromide in the mother liquor is oxidised to  $\text{Br}_2$  by  $\text{Cl}_2$  which is a stronger oxidising agent.



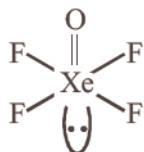
90. (d) Bleaching action of chlorine is due to oxidation in presence of moisture. It is permanent



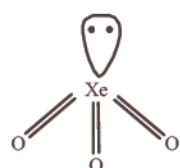
Colouring matter + [O]  $\rightarrow$  colourless matter



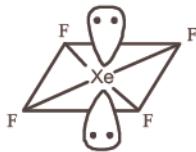
distorted octahedral



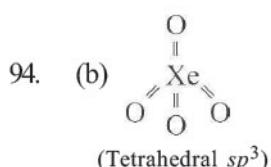
Square pyramidal



Pyramidal



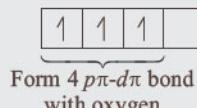
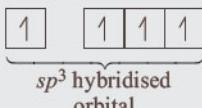
Square planar



Xe : Ground state

[Kr]  $4d^{10}5s^25p^65d^0$

Xe : Excited state



4  $sp^3$  hybridised orbitals form 4 sigma bond with oxygen.

95. (d) On account of highly stable  $ns^2np^6$  configuration in the valence shell. These elements have no tendency either to lose, gain or share electrons with atoms of other elements i.e., their combining capacity or valency is zero. Further all the orbitals in the atoms of these elements are doubly occupied i.e electrons are not available for sharing.

96. (d) The most abundant rare gas found in the atmosphere is argon and not helium.

# 22

# The *d*-and *f*-Block Elements



Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Characteristics of <i>d</i> -block elements	d-d transition and paramagnetism					1	A				
	catalytic activities/oxidation states/reducing properties	1	A								
Compounds of transition metals	properties of $\text{KMnO}_4$							1	E		
	properties of $\text{K}_2\text{Cr}_2\text{O}_7$									1	E
	reactions of copper									1	E
Lanthanoids and actinoids	characteristics of actinoids							1	E		
	electronic configuration									1	A
LOD - Level of Difficulty	E - Easy	A - Average			D - Difficult		Qns - No. of Questions				

## Topic 1: Characteristics of *d*-Block Elements

- Identify the incorrect statement. *[2020]*
  - The transition metals and their compounds are known for their catalytic activity due to their ability to adopt multiple oxidation states and to form complexes.
  - Interstitial compounds are those that are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.
  - The oxidation states of chromium in  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  are not the same.
  - $\text{Cr}^{2+}$  ( $d^4$ ) is a stronger reducing agent than  $\text{Fe}^{2+}$  ( $d^6$ ) in water.

- Match the catalyst with the process *[NEET Odisha 2019]*

Catalyst	Process
(i) $\text{V}_2\text{O}_5$	(a) The oxidation of ethyne to ethanal
(ii) $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$	(b) Polymerisation of alkynes
(iii) $\text{PdCl}_2$	(c) Oxidation of $\text{SO}_2$ in the manufacture of $\text{H}_2\text{SO}_4$
(iv) Nickel complexes	(d) Polymerisation of ethylene

Which of the following is the correct option?

- (i)-(c), (ii)-(a), (iii)-(d), (iv)-(b)
- (i)-(c), (ii)-(d), (iii)-(a), (iv)-(b)
- (i)-(a), (ii)-(b), (iii)-(c), (iv)-(d)
- (i)-(a), (ii)-(c), (iii)-(b), (iv)-(d)

3. Which one of the following ions exhibits  $d-d$  transition and paramagnetism as well? [2018]
- (a)  $\text{CrO}_4^{2-}$       (b)  $\text{Cr}_2\text{O}_7^{2-}$   
 (c)  $\text{MnO}_4^{2-}$       (d)  $\text{MnO}_4^-$
4. Magnetic moment 2.84 B.M. is given by :-  
 (At. nos, Ni=28, Ti=22, Cr=24, Co=27) [2015]
- (a)  $\text{Ti}^{3+}$       (b)  $\text{Cr}^{2+}$   
 (c)  $\text{Co}^{2+}$       (d)  $\text{Ni}^{2+}$
5. The number of  $d$ -electrons in  $\text{Fe}^{2+}$  ( $Z = 26$ ) is not equal to the number of electrons in which one of the following? [2015]
- (a)  $p$ -electrons in  $\text{Cl}$  ( $Z = 17$ )  
 (b)  $d$ -electrons in  $\text{Fe}$  ( $Z = 26$ )  
 (c)  $p$ -electrons in  $\text{Ne}$  ( $Z = 10$ )  
 (d)  $s$ -electrons in  $\text{Mg}$  ( $Z = 12$ )
6. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium ? [2015 RS]
- (a)  $3s\ 4s\ 3p\ 3d$       (b)  $4s\ 3s\ 3p\ 3d$   
 (c)  $3s\ 3p\ 3d\ 4s$       (d)  $3s\ 3p\ 4s\ 3d$
7. Magnetic moment 2.83 BM is given by which of the following ions ?  
 (At. nos. Ti=22, Cr=24, Mn=25, Ni=28):- [2014]
- (a)  $\text{Ti}^{3+}$       (b)  $\text{Ni}^{2+}$   
 (c)  $\text{Cr}^{3+}$       (d)  $\text{Mn}^{2+}$
8. Reason of lanthanoid contraction is:- [2014]
- (a) Negligible screening effect of ' $f$ ' orbitals  
 (b) Increasing nuclear charge  
 (c) Decreasing nuclear charge  
 (d) Decreasing screening effect
9. Which of the following lanthanoid ions is diamagnetic ?  
 (At nos. Ce=58, Sm=62, Eu=63, Yb=70) [NEET 2013]
- (a)  $\text{Sm}^{2+}$       (b)  $\text{Eu}^{2+}$   
 (c)  $\text{Yb}^{2+}$       (d)  $\text{Ce}^{2+}$
10. Sc ( $Z=21$ ) is a transition element but Zn ( $Z=30$ ) is not because [NEET Kar. 2013]
- (a) both Sc and Zn do not exhibit variable oxidation states  
 (b) both  $\text{Sc}^{3+}$  and  $\text{Zn}^{2+}$  ions are colourless and form white compounds  
 (c) in case of Sc,  $3d$  orbitals are partially filled but in Zn these are completely filled  
 (d) last electron is assumed to be added to  $4s$  level in case of Zn
11. Which one of the following does not correctly represent the correct order of the property indicated against it? [2012 M]
- (a)  $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$  : increasing number of oxidation states  
 (b)  $\text{Ti}^{3+} < \text{V}^{3+} < \text{Cr}^{3+} < \text{Mn}^{3+}$  : increasing magnetic moment  
 (c)  $\text{Ti} < \text{V} < \text{Cr} < \text{Mn}$  : increasing melting points  
 (d)  $\text{Ti} < \text{V} < \text{Mn} < \text{Cr}$  : increasing  $2^{\text{nd}}$  ionization enthalpy
12. Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential ( $E_{\text{M}^{2+}/\text{M}}^\circ$ ) value has a positive sign? [2012 M]
- (a)  $\text{Co}$  ( $Z=27$ )      (b)  $\text{Ni}$  ( $Z=28$ )  
 (c)  $\text{Cu}$  ( $Z=29$ )      (d)  $\text{Fe}$  ( $Z=26$ )
13. The catalytic activity of transition metals and their compounds is ascribed mainly to : [2012 M]
- (a) their magnetic behaviour  
 (b) their unfilled  $d$ -orbitals  
 (c) their ability to adopt variable oxidation state  
 (d) their chemical reactivity
14. For the four successive transition elements (Cr, Mn, Fe and Co), the stability of +2 oxidation state will be there in which of the following order? [2011]
- (a)  $\text{Mn} > \text{Fe} > \text{Cr} > \text{Co}$   
 (b)  $\text{Fe} > \text{Mn} > \text{Co} > \text{Cr}$   
 (c)  $\text{Co} > \text{Mn} > \text{Fe} > \text{Cr}$   
 (d)  $\text{Cr} > \text{Mn} > \text{Co} > \text{Fe}$

15. Which of the following ions will exhibit colour in aqueous solutions? **[2010]**
- (a)  $\text{La}^{3+}$  ( $Z=57$ )      (b)  $\text{Ti}^{3+}$  ( $Z=22$ )  
 (c)  $\text{Lu}^{3+}$  ( $Z=71$ )      (d)  $\text{Sc}^{3+}$  ( $Z=21$ )
16. Which one of the following ions has electronic configuration  $[\text{Ar}] 3d^6$ ? **[2010]**
- (a)  $\text{Ni}^{3+}$       (b)  $\text{Mn}^{3+}$   
 (c)  $\text{Fe}^{3+}$       (d)  $\text{Co}^{3+}$   
 (At. Nos. Mn = 25, Fe = 26, Co = 27, Ni = 28)
17. Which of the following pairs has the same size? **[2010]**
- (a)  $\text{Fe}^{2+}, \text{Ni}^{2+}$       (b)  $\text{Zr}^{4+}, \text{Ti}^{4+}$   
 (c)  $\text{Zr}^{4+}, \text{Hf}^{4+}$       (d)  $\text{Zn}^{2+}, \text{Hf}^{4+}$
18. Which of the following oxidation states is the most common among the lanthanoids? **[2010]**
- (a) 3      (b) 4  
 (c) 2      (d) 5
19. Which one of the elements with the following outer orbital configurations may exhibit the largest number of oxidation states? **[2009]**
- (a)  $3d^5 4s^1$       (b)  $3d^5 4s^2$   
 (c)  $3d^2 4s^2$       (d)  $3d^3 4s^2$
20. Out of  $\text{TiF}_6^{2-}$ ,  $\text{CoF}_6^{3-}$ ,  $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$  ( $Z$  of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are: **[2009]**
- (a)  $\text{Cu}_2\text{Cl}_2$  and  $\text{NiCl}_4^{2-}$   
 (b)  $\text{TiF}_6^{2-}$  and  $\text{Cu}_2\text{Cl}_2$   
 (c)  $\text{CoF}_6^{3-}$  and  $\text{NiCl}_4^{2-}$   
 (d)  $\text{TiF}_6^{2-}$  and  $\text{CoF}_6^{3-}$
21. The correct order of decreasing second ionisation enthalpy of Ti (22), V(23), Cr(24) and Mn (25) is : **[2008]**
- (a)  $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$       (b)  $\text{V} > \text{Mn} > \text{Cr} > \text{Ti}$   
 (c)  $\text{Mn} > \text{Cr} > \text{Ti} > \text{V}$       (d)  $\text{Ti} > \text{V} > \text{Cr} > \text{Mn}$
22. Which one of the following ions is the most stable in aqueous solution? **[2007]**
- (a)  $\text{V}^{3+}$       (b)  $\text{Ti}^{3+}$   
 (c)  $\text{Mn}^{3+}$       (d)  $\text{Cr}^{3+}$   
 (At.No. Ti = 22, V = 23, Cr = 24, Mn = 25)
23. In which of the following pairs are both the ions coloured in aqueous solutions ? **[2006]**
- (a)  $\text{Sc}^{3+}, \text{Ti}^{3+}$       (b)  $\text{Sc}^{3+}, \text{Co}^{2+}$   
 (c)  $\text{Ni}^{2+}, \text{Cu}^{+}$       (d)  $\text{Ni}^{2+}, \text{Ti}^{3+}$   
 (At.no.: Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)
24. The aqueous solution containing which one of the following ions will be colourless? (Atomic number: Sc = 21, Fe = 26, Ti = 22, Mn = 25) **[2005]**
- (a)  $\text{Sc}^{3+}$       (b)  $\text{Fe}^{2+}$   
 (c)  $\text{Ti}^{3+}$       (d)  $\text{Mn}^{2+}$
25. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionization enthalpy? **[2005]**
- (a) Vanadium ( $Z=23$ )  
 (b) Chromium ( $Z=24$ )  
 (c) Manganese ( $Z=25$ )  
 (d) Iron ( $Z=26$ )
26. Among the following series of transition metal ions, the one where all metal ions have  $3d^2$  electronic configuration is (At. nos. Ti = 22; V = 23; Cr = 24; Mn = 25) **[2004]**
- (a)  $\text{Ti}^{3+}, \text{V}^{2+}, \text{Cr}^{3+}, \text{Mn}^{4+}$   
 (b)  $\text{Ti}^{+}, \text{V}^{4+}, \text{Cr}^{6+}, \text{Mn}^{7+}$   
 (c)  $\text{Ti}^{4+}, \text{V}^{3+}, \text{Cr}^{2+}, \text{Mn}^{3+}$   
 (d)  $\text{Ti}^{2+}, \text{V}^{3+}, \text{Cr}^{4+}, \text{Mn}^{5+}$
27. The basic character of the transition metal monoxides follows the order  
 (Atomic No., Ti = 22, V = 23, Cr = 24, Fe = 26) **[2003]**
- (a)  $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$   
 (b)  $\text{VO} > \text{CrO} > \text{TiO} > \text{FeO}$   
 (c)  $\text{CrO} > \text{VO} > \text{FeO} > \text{TiO}$   
 (d)  $\text{TiO} > \text{FeO} > \text{VO} > \text{CrO}$

28. Which one of the following characteristics of the transition metals is associated with their catalytic activity? **[2003]**
- Variable oxidation states
  - High enthalpy of atomization
  - Parmagnetic behaviour
  - Colour of hydrated ions
29. Which of the following shows maximum number of oxidation states? **[2002]**
- Cr
  - Fe
  - Mn
  - V
30. Of the following transition metals, the maximum numbers of oxidation states are exhibited by:
- Chromium ( $Z=24$ ) **[2000]**
  - Manganese ( $Z=25$ )
  - Iron ( $Z=26$ )
  - Titanium ( $Z=22$ )
31. Which of the following forms colourless compound? **[2000]**
- $\text{Sc}^{3+}$
  - $\text{V}^{3+}$
  - $\text{Ti}^{3+}$
  - $\text{Cr}^{3+}$
32. Which one of the following elements shows maximum number of different oxidation states in its compounds? **[1998]**
- Eu
  - La
  - Ge
  - Am
33. Which one of the following ionic species will impart colour to an aqueous solution? **[1998]**
- $\text{Ti}^{4+}$
  - $\text{Cu}^+$
  - $\text{Zn}^{2+}$
  - $\text{Cr}^{3+}$
34. The common oxidation states of Ti are **[1994]**
- $+2, +3$
  - $+3, +4$
  - $-3, -4$
  - $+2, +3, +4$
35. The electronic configuration of Cu (atomic number 29) is **[1991]**
- $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 3d^9$
  - $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$
  - $1s^2, 2s^2 2p^6, 3p^2 3p^6, 4s^2 4p^6, 5s^2 5p^1$
  - $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2 4p^6 3d^3$
36. The electronic configurations of four elements are given below. Which element does not belong to the same family as others? **[1989]**
- $[\text{Xe}]4f^{14} 5d^{10} 6s^2$
  - $[\text{Kr}]4d^{10} 5s^2$
  - $[\text{Ne}]3s^2 3p^5$
  - $[\text{Ar}]3d^{10} 4s^2$
37. Which one of the following is an ore of silver? **[1988]**
- Argentite
  - Stibnite
  - Haematite
  - Bauxite
38. Which of the following metals corrodes readily in moist air? **[1988]**
- Gold
  - Silver
  - Nickel
  - Iron

**Topic 2: Compounds of Transition Metals**

39. Name the gas that can readily decolourise acidified  $\text{KMnO}_4$  solution: **[2017]**
- $\text{SO}_2$
  - $\text{NO}_2$
  - $\text{P}_2\text{O}_5$
  - $\text{CO}_2$
40. Which one of the following statements is correct when  $\text{SO}_2$  is passed through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution? **[2016]**
- The solution turns blue
  - The solution is decolourized
  - $\text{SO}_2$  is reduced
  - Green  $\text{Cr}_2(\text{SO}_4)_3$  is formed
41. When copper is heated with conc.  $\text{HNO}_3$  it produces **[2016]**
- $\text{Cu}(\text{NO}_3)_2$  and  $\text{NO}_2$
  - $\text{Cu}(\text{NO}_3)_2$  and NO
  - $\text{Cu}(\text{NO}_3)_2$ , NO and  $\text{NO}_2$
  - $\text{Cu}(\text{NO}_3)_2$  and  $\text{N}_2\text{O}$
42. Which of the following processes does not involve oxidation of iron? **[2015]**
- Decolourization of blue  $\text{CuSO}_4$  solution by iron
  - Formation of  $\text{Fe}(\text{CO})_5$  from Fe
  - Liberation of  $\text{H}_2$  from steam by iron at high temperature
  - Rusting of iron sheets
43. Assuming complete ionization, same moles of which of the following compounds will require

- the least amount of acidified  $\text{KMnO}_4$  for complete oxidation [2015 RS]
- (a)  $\text{FeSO}_4$       (b)  $\text{FeSO}_3$   
 (c)  $\text{FeC}_2\text{O}_4$       (d)  $\text{Fe}(\text{NO}_2)_2$
44. The pair of compounds that can exist together is: [2014]
- (a)  $\text{FeCl}_3, \text{SnCl}_2$       (b)  $\text{HgCl}_2, \text{SnCl}_2$   
 (c)  $\text{FeCl}_2, \text{SnCl}_2$       (d)  $\text{FeCl}_3, \text{KI}$
45. In acidic medium,  $\text{H}_2\text{O}_2$  changes  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{CrO}_5$  which has two ( $-\text{O}-\text{O}$ ) bonds. Oxidation state of Cr in  $\text{CrO}_5$  is:- [2014]
- (a) +5      (b) +3  
 (c) +6      (d) -10
46. The reaction of aqueous  $\text{KMnO}_4$  with  $\text{H}_2\text{O}_2$  in acidic conditions gives: [2014]
- (a)  $\text{Mn}^{4+}$  and  $\text{O}_2$       (b)  $\text{Mn}^{2+}$  and  $\text{O}_2$   
 (c)  $\text{Mn}^{2+}$  and  $\text{O}_3$       (d)  $\text{Mn}^{4+}$  and  $\text{MnO}_2$
47.  $\text{KMnO}_4$  can be prepared from  $\text{K}_2\text{MnO}_4$  as per the reaction:
- $$3\text{MnO}_4^{2-} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_4^- + \text{MnO}_2 + 4\text{OH}^-$$
- The reaction can go to completion by removing  $\text{OH}^-$  ions by adding. [NEET 2013]
- (a) KOH      (b)  $\text{CO}_2$   
 (c)  $\text{SO}_2$       (d) HCl
48. Which of the statements is not true? [2012]
- (a) On passing  $\text{H}_2\text{S}$  through acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, a milky colour is observed.  
 (b)  $\text{Na}_2\text{Cr}_2\text{O}_7$  is preferred over  $\text{K}_2\text{Cr}_2\text{O}_7$  in volumetric analysis.  
 (c)  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in acidic medium is orange.  
 (d)  $\text{K}_2\text{Cr}_2\text{O}_7$  solution becomes yellow on increasing the pH beyond 7.
49. Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution turns green when  $\text{Na}_2\text{SO}_3$  is added to it. This is due to the formation of: [2011]
- (a)  $\text{Cr}_2(\text{SO}_4)_3$       (b)  $\text{CrO}_4^{2-}$   
 (c)  $\text{Cr}_2(\text{SO}_3)_3$       (d)  $\text{CrSO}_4$
50. Copper sulphate dissolves in excess of KCN to give [2006]
- (a)  $[\text{Cu}(\text{CN})_4]^{3-}$       (b)  $[\text{Cu}(\text{CN})_4]^{2-}$   
 (c)  $\text{Cu}(\text{CN})_2$       (d) CuCN
51. German silver is an alloy of [2000]
- (a) Fe, Cr, Ni      (b) Cu, Zn, Ag  
 (c) Cu, Zn, Ni      (d) Cu, Sn, Al
52. Which of the following combines with Fe (II) ions to form a brown complex? [2000]
- (a) NO      (b)  $\text{N}_2\text{O}$   
 (c)  $\text{N}_2\text{O}_3$       (d)  $\text{N}_2\text{O}_5$
53. On heating chromite ( $\text{FeCr}_2\text{O}_4$ ) with  $\text{Na}_2\text{CO}_3$  in air, which of the following product is obtained? [1999]
- (a)  $\text{Na}_2\text{Cr}_2\text{O}_7$       (b) FeO  
 (c)  $\text{Fe}_3\text{O}_4$       (d)  $\text{Na}_2\text{CrO}_4$
54. The addition of excess of aqueous  $\text{HNO}_3$  to a solution containing  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  produces [1999]
- (a)  $\text{Cu}^+$       (b)  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$   
 (c)  $\text{Cu}(\text{OH})_2$       (d)  $\text{Cu}(\text{NO}_3)_2$
55. An acidic solution of 'X' does not give precipitate on passing  $\text{H}_2\text{S}$  through it. 'X' gives white precipitate when  $\text{NH}_4\text{OH}$  is added to it. The white precipitate dissolves in excess of NaOH solution. Pure 'X' fumes in air and dense white fumes are obtained when a glass rod dipped in  $\text{NH}_4\text{OH}$  is put in the fumes. Compound 'X' can be [1999]
- (a)  $\text{ZnCl}_2$       (b)  $\text{FeCl}_3$   
 (c)  $\text{AlCl}_3$       (d)  $\text{SnCl}_2$
56. Which one of the following elements constitutes a major impurity in pig iron? [1998]
- (a) Silicon      (b) Oxygen  
 (c) Sulphur      (d) Graphite
57.  $\text{K}_2\text{Cr}_2\text{O}_7$  on heating with aqueous NaOH gives [1997]
- (a)  $\text{CrO}_4^{2-}$       (b)  $\text{Cr}(\text{OH})_3$   
 (c)  $\text{Cr}_2\text{O}_7^{2-}$       (d)  $\text{Cr}(\text{OH})_2$
58.  $\text{CrO}_3$  dissolves in aqueous NaOH to give [1997]
- (a)  $\text{Cr}_2\text{O}_7^{2-}$       (b)  $\text{CrO}_4^{2-}$   
 (c)  $\text{Cr}(\text{OH})_3$       (d)  $\text{Cr}(\text{OH})_2$
59. Cuprous compounds such as  $\text{CuCl}$ ,  $\text{CuCN}$  and  $\text{CuSCN}$  are the only salts stable in water due to [1996]
- (a) high hydration energy of  $\text{Cu}^+$  ions  
 (b) their inherent tendency to not disproportionate  
 (c) diamagnetic nature  
 (d) insolubility in water
60. Stainless steel contains iron and [1995]
- (a) Cr + Ni      (b) Cr + Zn  
 (c) Zn + Pb      (d) Fe + Cr + Ni

61. The most durable metal plating on iron to protect against corrosion is **[1994]**  
 (a) Nickel plating      (b) Tin plating  
 (c) Copper plating      (d) Zinc plating
62. When  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is heated, the gas evolved is **[1994]**  
 (a)  $\text{N}_2$       (b)  $\text{NO}_2$   
 (c)  $\text{O}_2$       (d)  $\text{N}_2\text{O}$
63. When  $\text{CuSO}_4$  is electrolysed using platinum electrodes, **[1993]**  
 (a) Copper is liberated at cathode, sulphur at anode  
 (b) Copper is liberated at cathode, oxygen at anode  
 (c) Sulphur is liberated at cathode, oxygen at anode  
 (d) Oxygen is liberated at cathode, copper at anode
64. Cinnabar is an ore of **[1991]**  
 (a) Hg      (b) Cu  
 (c) Pb      (d) Zn
65. The composition of 'golden spangles' is **[1990]**  
 (a)  $\text{PbCrO}_4$       (b)  $\text{PbI}_2$   
 (c)  $\text{As}_2\text{S}_3$       (d)  $\text{BaCrO}_4$
66. Prussian blue is formed when **[1989]**  
 (a) Ferrous sulphate reacts with  $\text{FeCl}_3$   
 (b) Ferric sulphate reacts with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (c) Ferrous ammonium sulphate reacts with  $\text{FeCl}_3$   
 (d) Ammonium sulphate reacts with  $\text{FeCl}_3$
67. Photographic films and plates have an essential ingredient of **[1989]**  
 (a) Silver nitrate      (b) Silver bromide  
 (c) Sodium chloride      (d) Oleic acid
68. Nitriding is the process of surface hardening of steel by treating it in an atmosphere of **[1989]**  
 (a)  $\text{NH}_3$       (b)  $\text{O}_3$   
 (c)  $\text{N}_2$       (d)  $\text{H}_2\text{S}$
69. While extracting an element from its ore, the ore is ground and leached with dil. potassium cyanide solution to form the soluble product potassium argento cyanide. The element is **[1989]**  
 (a) Lead      (b) Chromium  
 (c) Manganese      (d) Silver
70. A blue colouration is not obtained when **[1989]**  
 (a) Ammonium hydroxide dissolves in copper sulphate  
 (b) Copper sulphate solution reacts with  $\text{K}_4[\text{Fe}(\text{CN})_6]$   
 (c) Ferric chloride reacts with sod. ferrocyanide  
 (d) Anhydrous  $\text{CuSO}_4$  is dissolved in water
- Topic 3: Lanthanoids and Actinoids**
71. The reason for greater range of oxidation states in actinoids is attributed to :- **[2017]**  
 (a) actinoid contraction  
 (b)  $5f$ ,  $6d$  and  $7s$  levels having comparable energies  
 (c)  $4f$  and  $5d$  levels being close in energies  
 (d) the radioactive nature of actinoids
72. The electronic configurations of Eu(Atomic No. 63), Gd(Atomic No. 64) and Tb (Atomic No. 65) are **[2016]**  
 (a)  $[\text{Xe}]4f^76s^2$ ,  $[\text{Xe}]4f^86s^2$  and  $[\text{Xe}]4f^85d^16s^2$   
 (b)  $[\text{Xe}]4f^75d^16s^2$ ,  $[\text{Xe}]4f^75d^16s^2$  and  $[\text{Xe}]4f^96s^2$   
 (c)  $[\text{Xe}]4f^65d^16s^2$ ,  $[\text{Xe}]4f^75d^16s^2$  and  $[\text{Xe}]4f^85d^16s^2$   
 (d)  $[\text{Xe}]4f^76s^2$ ,  $[\text{Xe}]4f^75d^16s^2$  and  $[\text{Xe}]4f^96s^2$
73. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii ? (Numbers in the parenthesis are atomic numbers). **[2015]**  
 (a) Zr (40) and Nb (41) (b) Zr (40) and Hf (72)  
 (c) Zr (40) and Ta (73) (d) Ti (22) and Zr (40)
74. Gadolinium belongs to  $4f$  series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium ? **[1997, NEET Kar. 2013, 2015 RS]**  
 (a)  $[\text{Xe}]4f^86d^2$       (b)  $[\text{Xe}]4f^95s^1$   
 (c)  $[\text{Xe}]4f^75d^16s^2$       (d)  $[\text{Xe}]4f^65d^26s^2$

75. Which of the following exhibit only +3 oxidation state ? **[2012 MJ]**
- U
  - Th
  - Ac
  - Pa
76. Identify the incorrect statement among the following: **[2007]**
- Lanthanoid contraction is the accumulation of successive shrinkages.
  - As a result of lanthanoid contraction, the properties of 4d series of the transition elements have no similarities with the 5d series of elements.
  - Shielding power of 4f electrons is quite weak.
  - There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.
77. The main reason for larger number of oxidation states exhibited by the actinoids than the corresponding lanthanoids, is **[2005, 2006]**
- more energy difference between 5f and 6d orbitals than between 4f and 5d orbitals.
  - lesser energy difference between 5f and 6d orbitals than between 4f and 5d orbitals.
  - larger atomic size of actinoids than the lanthanoids.
  - greater reactive nature of the actinoids than the lanthanoids.
78. Lanthanoids are **[2004]**
- 14 elements in the sixth period (atomic no. = 90 to 103) that are filling 4f sublevel
  - 14 elements in the seventh period (atomic no. = 90 to 103) that are filling 5f sublevel
  - 14 elements in the sixth period (atomic no. = 58 to 71) that are filling 4f sublevel
  - 14 elements in the seventh period (atomic no. = 58 to 71) that are filling 4f sublevel
79. The correct order of ionic radii of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  is **[2003]**
- $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$
  - $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
  - $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
  - $\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$
- (Atomic nos. Y=39, La=57, Eu=63, Lu=71)
80. General electronic configuration of lanthanides is **[1991, 2002]**
- $(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2$
  - $(n-2)f^{10-14}(n-1)d^{0-1}ns^2$
  - $(n-2)f^{0-14}(n-1)d^{10}ns^2$
  - $(n-2)d^{0-1}(n-1)f^{1-14}ns^2$
81. Which of the following statement is not correct? **[2001]**
- $\text{La(OH)}_3$  is less basic than  $\text{Li(OH)}_3$
  - La is actually an element of transition series rather lanthanides
  - Atomic radius of Zr and Hf are same because of lanthanide contraction
  - In lanthanide series ionic radius of  $\text{Ln}^{+3}$  ions decreases
82. The lanthanide contraction is responsible for the fact that **[1997]**
- Zr and Y have about the same radius
  - Zr and Nb have similar oxidation state
  - Zr and Hf have about the same radius
  - Zr and Zn have the same oxidation states
- (Atomic numbers : Zr=40, Y=39, Nb=41, Hf=72, Zn=30)
83. Actinides **[1994]**
- Are all synthetic elements
  - Include element 104
  - Have any short lived isotopes
  - Have variable valency
84. Among the lanthanides the one obtained by synthetic method is **[1994]**
- Lu
  - Pm
  - Pr
  - Gd

## ANSWER KEY

1	(c)	10	(c)	19	(b)	28	(a)	37	(a)	46	(b)	55	(a)	64	(a)	73	(b)	82	(c)
2	(b)	11	(c)	20	(b)	29	(c)	38	(d)	47	(b)	56	(d)	65	(b)	74	(c)	83	(d)
3	(c)	12	(c)	21	(a)	30	(b)	39	(a)	48	(b)	57	(a)	66	(b)	75	(c)	84	(b)
4	(d)	13	(c)	22	(d)	31	(a)	40	(d)	49	(a)	58	(b)	67	(b)	76	(b)		
5	(a)	14	(a)	23	(d)	32	(d)	41	(a)	50	(a)	59	(d)	68	(a)	77	(b)		
6	(d)	15	(b)	24	(a)	33	(d)	42	(b)	51	(c)	60	(d)	69	(d)	78	(c)		
7	(b)	16	(d)	25	(c)	34	(b)	43	(a)	52	(a)	61	(d)	70	(b)	79	(c)		
8	(a)	17	(c)	26	(d)	35	(b)	44	(c)	53	(d)	62	(a)	71	(b)	80	(a)		
9	(c)	18	(a)	27	(a)	36	(c)	45	(c)	54	(b)	63	(b)	72	(d)	81	(a)		

## Hints &amp; Solutions

1. (c) Oxidation state of Cr in  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  is + 6 i.e. oxidation states are same.
2. (b) (i)  $\text{V}_2\text{O}_5$ : Used in the oxidation of  $\text{SO}_2$  in the manufacture of  $\text{H}_2\text{SO}_4$  by contact process.  
(ii)  $\text{TiCl}_4 + \text{Al}(\text{CH}_3)_3$ : Used in the polymerization of ethylene.  
(iii)  $\text{PdCl}_2$ : Used in the oxidation of ethyne to ethanal.  
(iv) Nickel complexes: Used in the polymerization of alkynes.
3. (c)  $\text{CrO}_4^{2-}$        $\text{Cr}^{6+}$  diamagnetic  
 $\text{Cr}_2\text{O}_7^{2-}$        $\text{Cr}^{6+}$  diamagnetic  
 $\text{MnO}_4^-$        $\text{Mn}^{7+}$  diamagnetic  
 $\text{MnO}_4^{2-}$        $\text{Mn}^{6+}$  paramagnetic
- $3d$   

1			
---	--	--	--
- Thus, unpaired electron is present, so  $d-d$  transition is possible.
- For tetrahedral geometry:
- Before transition                  After transition
- (Left)  $3d$  orbital contains 5 electrons. It splits into  $t_{2g}$  (3 electrons) and  $e_g$  (2 electrons).  
(Right)  $3d$  orbital contains 5 electrons. It splits into  $t_{2g}$  (3 electrons) and  $e_g$  (2 electrons).
4. (d) Magnetic moment = 2.84 B.M. This indicates that 2 unpaired electrons are present.
- For  $\text{Ni}^{2+} = 4s^0 3d^8$ 

1	1	1	1	1
---	---	---	---	---
- Number of unpaired electrons ( $n$ ) = 2  
Hence,  $\text{Ni}^{2+}$  gives magnetic moment of 2.84 B.M.
5. (a)  $\text{Fe}^{2+} = 3d^6$  (number of ' $d$ ' electrons = 6)  
In  $\text{Cl} = 1s^2 2s^2 2p^6 3s^2 3p^5$   
total  $p$  electrons = 11, which are not equal to number of ' $d$ ' electrons in  $\text{Fe}^{2+}$   
\text{Ne} = 1s^2 2s^2 2p^6 = 6  
s-electrons in  $\text{Mg} = 1s^2 2s^2 2p^6 3s^2 = 6$
6. (d)  $(n+l)$  rule can be used. Titanium is a multi electron system  
 $(n+l)$        $3s$        $<$        $3p$        $<$        $4s$        $<$        $3d$   
                      ↓                    ↓                    ↓                    ↓  
                      (3+0)      (3+1)      (4+0)      (3+2)  
                      ||                    ||                    ||                    ||  
                      3                    4                    4                    5
- NOTES If  $(n+l)$  values are same, then value of "n" has to be considered. The orbital with lower  $n$  value is filled first.
7. (b) Magnetic moment  
 $\mu = \sqrt{n(n+2)}$   
 $2.83 = \sqrt{n(n+2)}$   
On solving  $n=2$   
 $\text{Ni}^{2+}$  has two unpaired electrons.

8. (a) The shape of *f*-orbitals is very much diffused and they have poor shielding effect.
- NOTES** The effective nuclear charge increases due to imperfect shielding of one electron by another in the same subshell which causes the contraction in the size of electron charge cloud. This contraction in size is known as lanthanoid contraction.
9. (c)  $\text{Sm}^{2+}$  ( $Z=62$ )  
 $[\text{Xe}]4f^6 6s^2 - 6$  unpaired  $e^-$   
 $\text{Eu}^{2+}$  ( $Z=63$ )  
 $[\text{Xe}]4f^7 6s^2 - 7$  unpaired  $e^-$   
 $\text{Yb}^{2+}$  ( $Z=70$ )  
 $[\text{Xe}]4f^{14} 6s^2 - 0$  unpaired  $e^-$   
 $\text{Ce}^{2+}$  ( $Z=58$ )  
 $[\text{Xe}]4f^1 5d^1 6s^2 - 2$  unpaired  $e^-$   
Only  $\text{Yb}^{2+}$  is diamagnetic.
10. (c) A transition element must have incomplete *d*-subshell. Zinc has completely filled *d* subshell having  $3d^{10}$  configuration. Hence do not show properties of transition elements to any appreciable extent except for their ability to form complexes.
11. (c) The melting points of the transition elements first rise to a maximum and then fall as the atomic number increases, manganese have abnormally low melting points.
12. (c)  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34$  volt,  
Other has -ve  $E_{\text{R.P.}}^\circ$ .  
 $E_{\text{Co}^{++}/\text{Co}}^\circ = -0.28$   
 $E_{\text{Ni}^{++}/\text{Ni}}^\circ = -0.25$   
 $E_{\text{Fe}^{++}/\text{Fe}}^\circ = -0.44$
13. (c) The transition metals and their compounds are used as catalysts because of the variable oxidation states. Due to this, they easily absorb and re-emit wide range of energy to provide the necessary activation energy.
14. (a)  $\text{Cr}^{2+} = \boxed{1\ 1\ 1\ 1\ 1}$   
 $\text{Mn}^{2+} = \boxed{1\ 1\ 1\ 1\ 1}$   
 $\text{Fe}^{2+} = \boxed{1\ 1\ 1\ 1\ 1}$   
 $\text{Co}^{2+} = \boxed{1\ 1\ 1\ 1\ 1}$
- $\text{Mn}^{2+}$  is most stable due to half-filled configuration. Hence, only option (a) can be the correct answer.

15. (b)  $\text{La}^{3+} : 54 e^- = [\text{Xe}]$   
 $\text{To}^{3+} : 19 e^- = [\text{Ar}] 3d^1$  (Colour)  
 $\text{Lu}^{3+} : 68 e^- = [\text{Xe}] 4f^{14}$   
 $\text{Sc}^{3+} : 18 e^- = [\text{Ar}]$
16. (d)  $\text{Ni}^{3+} : [\text{Ar}] 3d^7$   
 $\text{Mn}^{3+} : [\text{Ar}] 3d^4$   
 $\text{Fe}^{3+} : [\text{Ar}] 3d^5$   
 $\text{Co}^{3+} : [\text{Ar}] 3d^6$
17. (c) Due to lanthanide contraction, the size of Zr and Hf (atom and ions) become nearly similar
18. (a) +3 oxidation state is most common for lanthanoids. But occasionally +2 and +4 states are also obtained due to extra stability of empty, half-filled or filled *f*-subshell.
19. (b)  $\text{Mn} : 3d^5 4s^2$   $\boxed{1\ 1\ 1\ 1\ 1}\quad \boxed{4s}$   
The no. of various oxidation states possible are +2, +3, +4, (+5), +6, +7.
20. (b) In  $\text{TiF}_6^{2-}$  – Ti is in +4 O.S.;  $3d^0$  = colourless  
In  $\text{CoF}_6^{3-}$  – Co is in +3 O.S.;  $3d^5$  = coloured  
In  $\text{Cu}_2\text{Cl}_2$  – Cu is in +1 O.S.;  $3d^{10}$  – colourless  
In  $\text{NiCl}_4^{2-}$  – Ni is in +2 O.S.;  $3d^8$  – coloured
- NOTES** The colour exhibited by transition metal ions is due to the presence of unpaired electrons in *d*-orbitals which permits the *d* - *d* excitation of electrons.
21. (a) Ti;  $Z(22)$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$   
V;  $Z(23)$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$   
Cr;  $Z(24)$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$   
Mn;  $Z(25)$  is  $1s^2 2s^2 2p^6 3s^2 3d^5 4s^2$   
The second electron in all the cases (except Cr) is taken out from  $4s$ -orbital and for Cr it is taken from half-filled  $3d$ -orbital. The force required for removal of second electron will be more for Mn than others (except for Cr) due to having more positive charge. Based on this, we find the correct order  $\text{Mn} > \text{V} > \text{Ti}$ .  
*i.e.*  $\text{Cr} > \text{Mn} > \text{V} > \text{Ti}$ .
22. (d)  $\text{V}^{3+} = \boxed{1\ 1\ \quad\quad\quad}$   
 $\text{Ti}^{3+} = \boxed{1\ \quad\quad\quad}$   
 $\text{Mn}^{3+} = \boxed{1\ 1\ 1\ 1\ \quad}$   
 $\text{Cr}^{3+} = \boxed{1\ 1\ 1\ \quad\quad}$

$\text{Cr}^{3+}$  will be most stable in aqueous solution according to crystal field theory. It has  $t_{2g}^3$  configuration, which is most stable among the given options.

23. (d)  $\text{Sc}^{3+}$ :  $1s^2, 2s^2p^6, 3s^2p^6d^0, 4s^0$ ; no unpaired electron.

$\text{Cu}^+$ :  $1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^0$ ; no unpaired electron.

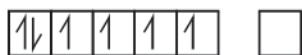
$\text{Ni}^{2+}$ :  $1s^2, 2s^2p^6, 3s^2p^6d^8, 4s^0$ ; 2 unpaired electron present.

$\text{Ti}^{3+}$ :  $1s^2, 2s^2p^6, 2s^2p^6d^1, 4s^0$ ; 1 unpaired electron present

$\text{Co}^{2+}$ :  $1s^2, 2s^2p^6, 3s^2p^6d^7, 4s^0$ ; 3 unpaired electron present

So, from the given option, the only correct combination is  $\text{Ni}^{2+}$  and  $\text{Ti}^{3+}$

24. (a)  $\text{Sc}^{3+} \rightarrow 3d^0 4s^0$   
 $\text{Fe}^{2+} \rightarrow 3d^6 4s^0$



4 unpaired  $e^-$   
 $\text{Ti}^{3+} \rightarrow 3d^1 4s^0$



$\text{Mn}^{2+} \rightarrow 3d^5 4s^0$



5 unpaired  $e^-$

In  $\text{Sc}^{3+}$  there is no unpaired electron. So the aqueous solution of  $\text{Sc}^{3+}$  will be colourless.

25. (c) For third ionization enthalpy electronic configuration of

		3d	4s
<sub>23</sub> V <sup>2+</sup>	$-4s^0 3d^3$	[1 1 1      ]	
<sub>24</sub> Cr <sup>2+</sup>	$-4s^0 3d^4$	[1 1 1 1    ]	
<sub>25</sub> Mn <sup>2+</sup>	$-4s^0 3d^5$	[1 1 1 1 1]	
<sub>26</sub> Fe <sup>2+</sup>	$-4s^0 3d^6$	[1 1 1 1 1]	

Mn has most stable configuration due to half filled  $d$ -orbital. Hence, 3rd ionization energy will be highest for Mn.

26. (d) The electronic configuration of different species given in the option (d) are :

$\text{Ti}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

$\text{V}^{3+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

$\text{Cr}^{4+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

$\text{Mn}^{5+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

27. (a) The basic character of the transition metal monoxide is  $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$  because basic character of oxides decrease with increase in atomic number.

**NOTES** Oxides of transitional metals in low oxidation state i.e., +2 and +3 are generally basic except  $\text{Cr}_2\text{O}_3$ .

28. (a) Transition metals have the ability to utilize  $(n-1)d$ -orbitals. Thus variable oxidation states enables the transition element to associate with the reactants in different forms.

29. (c)  $\text{Mn}$ :  $[\text{Ar}] 3d^5 4s^2$

Shows +2, +3, +4, +5, +6 & +7 oxidation states

30. (b) Manganese shows max. no. of oxidation states,

+2, +3, +4, +5, +6, +7

Other metals shows the following oxidation states

$\text{Cr} = +2, +3, +4, +5, +6$

$\text{Fe} = +2, +3$

$\text{Ti} = +2, +3, +4$

31. (a)  $\text{Sc}^{3+} \rightarrow [\text{Ar}]^{18} 3d^0$ ;  $\text{V}^{3+} \rightarrow [\text{Ar}]^{18} 3d^2$

$\text{Ti}^{3+} \rightarrow [\text{Ar}]^{18} 3d^1$ ;  $\text{Cr}^{3+} \rightarrow [\text{Ar}]^{18} 3d^3$

Scandium ion doesn't contain any unpaired electron in d orbitals hence it forms colourless compound.

32. (d)  $\text{Eu} = +2, +3$

$\text{La} = +3$

$\text{Gd} = +3$

$\text{Am} = +2, +3, +4, +5, +6$

33. (d) We know that chromium (III) salts dissolve in water to give violet solution. The violet colour is due to the hydrated chromium (III) in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

34. (b)  $\text{Ti}(22) = [\text{Ar}] 3d^2 4s^2$

minimum oxidation state is +2 and maximum oxidation state is +4.

$\text{Ti}^{4+} = [\text{Ar}]$

Hence, it is most stable state of Ti.

$\text{Ti}^{3+} = [\text{Ar}] 3d^1$

It acts as a good reducing agent as it can readily oxidized to  $\text{Ti}^{4+}$  ion.

$\text{Ti}^{2+} = [\text{Ar}] 3d^2$

It is the most unstable form.

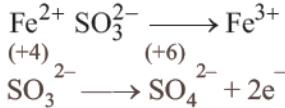
Thus, +3 and +4 are the common oxidation states.



The minimum oxidation state of transition metals is equal to the number of electrons in  $4s$  shell and the maximum oxidation state is equal to the sum of the  $4s$  and  $3d$  electrons.

35. (b) Electronic configuration of Cu (29) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$  and not  $1s^2, 2s^2 2p^6 3s^2 3p^6 4s^2, 3d^9$  due to extra stability of fully filled orbitals.
36. (c)  $[Ne]3s^2 3p^5$  is the electronic configuration of a  $p$ -block element whereas other configurations are those of  $d$ -block elements
37. (a) Argentite or silver glance ( $Ag_2S$ ) is an ore of Ag.
38. (d) In moist air, corrosion of iron takes place in the form of rust ( $Fe_2O_3 + Fe(OH)_3$ ). As iron is most reactive among all.
39. (a) Potassium permanganate has a purple colour. When sulphur dioxide reacts with potassium permanganate, the solution decolourises.  

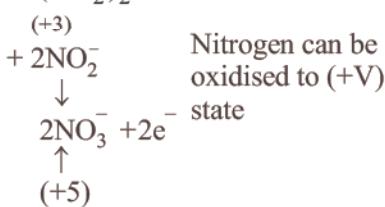
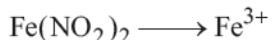
$$5SO_2 + 2KMnO_4 + 2H_2O \rightarrow 2H_2SO_4 + 2MnSO_4 + K_2SO_4$$
40. (d)  $K_2Cr_2O_7 + SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$   
green colour
41. (a) Less active metals like Cu, Ag etc. react with conc. acid and form nitrate and nitrogen dioxide.
42. (b) Formation of  $Fe(CO)_5$  from Fe involves no change in oxidation state of iron.
43. (a) Considering the same moles of compounds  $Fe^{2+} SO_4^{2-}$  only  $Fe^{2+}$  is oxidised by  $KMnO_4$ .  $SO_4^{2-}$  in which sulphur is in highest oxidation state cannot be oxidised.



Sulphur can be oxidised to (+6) i.e to  $SO_4^{2-}$

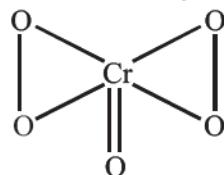
In  $FeC_2O_4 \longrightarrow Fe^{3+}$

Carbon can be oxidised to (+IV) i.e to  $CO_2$



44. (c) Both are reducing agents.

45. (c) The structure of  $CrO_5$  is



Hence,  $CrO_5$  has two proxy linkage.

Now suppose the oxi. no. of Cr is  $x$  then

$$x + (-1 \times 4) + (-2) = 0$$

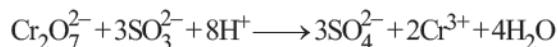
$$\therefore x = +6$$

46. (b)  $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$   
*i.e. Mn<sup>2+</sup> ion and O<sub>2</sub>.*

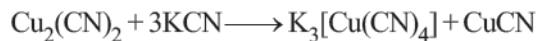
47. (b) HCl and  $SO_2$  are reducing agents and can reduce  $MnO_4^-$ .  $CO_2$  which is neither oxidising nor reducing will provide only acidic medium. It can shift reaction in forward direction and reaction can go to completion.

48. (b)  $Na_2Cr_2O_7$  is hygroscopic in nature and therefore accurate weighing is not possible in normal atmospheric conditions. A hygroscopic substance absorbs moisture from atmosphere and this could lead to inaccuracies in weight.

49. (a) The green colour appears due to the formation of  $Cr^{3+}$  ion



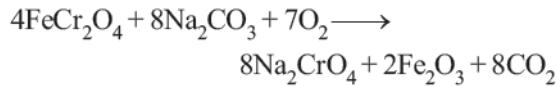
50. (a) Copper sulphate on treatment with excess of KCN forms complex  $K_3[Cu(CN)_4]$  or  $[Cu(CN)_4]^{3-}$



51. (c) German Silver Composition : Cu = 56%, Zn = 24%, Ni = 20%

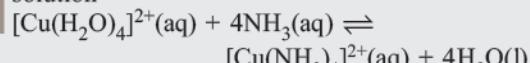
52. (a) We know that when nitrogen oxide (NO) combines with Fe (II) ions, a brown complex is formed. This reaction is called brown ring test

53. (d) By heating chromite with  $Na_2CO_3$ ,  $Na_2CrO_4$  is obtained

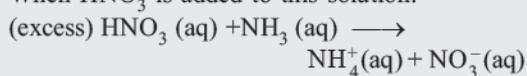


54. (b) When excess of aq.  $\text{HNO}_3$  to  $[\text{C}_4(\text{H}_3)_4]^{2+}$  produces  $[(4\text{H}_2\text{O})_4]^{2+}$ .

Following equilibrium exist in the given aqueous solution

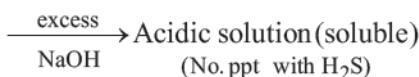


When  $\text{HNO}_3$  is added to this solution:

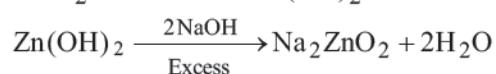
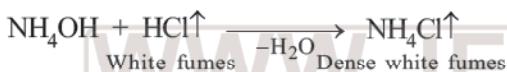
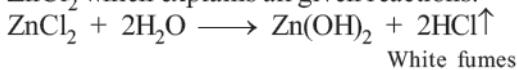


Thus, amount of  $\text{NH}_3(\text{aq})$  will reduce drastically. With a simple application of Le Chatelier's principle, the equilibrium will shift towards left in the first reaction. Hence,  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  will form.

55. (a)  $X \xrightarrow{\text{NH}_4\text{OH}}$  White ppt

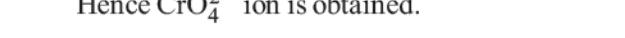


Given reactions (white precipitate with  $\text{H}_2\text{S}$  in presence of  $\text{NH}_4\text{OH}$ ) indicate that 'X' should be  $\text{ZnCl}_2$ , which explains all given reactions.



56. (d) Pig iron is the most impure form of iron and contain highest proportion of carbon (2.5–4%).

57. (a)  $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaOH} \rightarrow \text{K}_2\text{CrO}_4 + \text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$   
Hence  $\text{CrO}_4^{2-}$  ion is obtained.



Hence  $\text{CrO}_4^{2-}$  ion is obtained.



59. (d) Although  $\text{Cu}^{2+}$  state is more stable than  $\text{Cu}^+$ , but  $\text{Cu}^+$  ion can be stabilized by formation of insoluble substances such as  $\text{CuCl}$ ,  $\text{CuCN}$  and  $\text{CuSCN}$ .  $\text{Cu}^{2+}$  is more stable than  $\text{Cu}^+$  because of its high hydration energy.

60. (d) Stainless steel contains 73% Fe, 18% Cr and 8% Ni.

61. (d) Galvanisation is the process of deposition of zinc metal on the surface of Fe to prevent it from rusting. Zinc forms a protective layer of basic carbonate ( $\text{ZnCO}_3$ ,  $\text{Zn}(\text{OH})_2$ ) on it.

62. (a)  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \xrightarrow{\text{Heat}} \text{Cr}_2\text{O}_3 + \text{N}_2 + 4\text{H}_2\text{O}$

63. (b)  $\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$ ;  
 $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$   
At cathode :  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$   
At anode :  $4\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$

64. (a) Cinnabar ( $\text{HgS}$ ) is an ore of  $\text{Hg}$ .  
65. (b)  $\text{PbI}_2$  is yellow and is called golden spangles.  
66. (b) Potassium ferrocyanide solution is added to  $\text{Fe}^{3+}$  ions in solution to give deep blue solution or precipitate.  
 $2\text{Fe}_2(\text{SO}_4)_3 + 3\text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow$   
 $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 6\text{K}_2\text{SO}_4$   
Prussian blue

67. (b)  $\text{AgBr}$  is highly photosensitive and is used in photographic films and plates.  
68. (a) When steel is heated in presence of  $\text{NH}_3$ , iron nitride on the surface of steel is formed which imparts a hard coating. This process is called nitriding.  
69. (d) Cyanide process is used in the metallurgy of  $\text{Ag}$ .

$2\text{Ag}_2\text{S} + 8\text{NaCN} + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow$   
 $4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH} + 2\text{S}$

$2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Zn} \longrightarrow$   
 $\text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag} \downarrow$

70. (b)  $2\text{CuSO}_4 + \text{K}_4[\text{Fe}(\text{CN})_6] \longrightarrow$   
 $\text{Cu}_2[\text{Fe}(\text{CN})_6] + 2\text{K}_2\text{SO}_4$   
Chocolate ppt.

71. (b) Minimum or comparable energy gap between  $5f$ ,  $6d$  and  $7s$  subshell makes electron excitation easier, hence there is a greater range of oxidation states in actinoids.  
72. (d)  $\text{Eu}(63) = [\text{Xe}]4f^7 6s^2$   
 $\text{Gd}(64) = [\text{Xe}]4f^7 5d^1 6s^2$   
 $\text{Tb}(65) = [\text{Xe}]4f^9 6s^2$   
73. (b) Zr (40) and Hf (72) are in the same group (4). Because of lanthanoid contraction, they have nearly same atomic radii.  
74. (c)  $\text{Gd}(64) = [\text{Xe}]4f^7 5d^1 6s^2$   
75. (c)  $\text{Ac}(89) = [\text{Rn}] [6d^1] [7s^2]$   
76. (b) Due to lanthanoid contraction the properties of  $4d$  series of the transition element have similarities with the  $5d$  series of elements.

There is a steady decrease in the radii as the atomic number of the lanthanide elements increases. For every additional proton added in nucleus the corresponding electron goes to  $4f$  subshell.

77. (b) Lesser energy difference between  $5f$  and  $6d$  orbitals than between  $4f$  and  $5d$  orbitals result in larger no. of oxidation state.
78. (c) Lanthanides are  $4f$ -series elements starting from cerium ( $Z = 58$ ) to lutetium ( $Z = 71$ ). These are placed in the sixth period and in third group.
79. (c) In lanthanide series there is a regular decrease in the atomic as well as ionic radii of trivalent ions ( $M^{3+}$ ) as the atomic number increases. Although the atomic radii do show some irregularities but ionic radii decreases from La(103 pm) to Lu(86pm).
80. (a) The Lanthanides are transition metals from atomic numbers 58 (Ce) to 71(Lu).  
Hence the electronic configuration becomes :  

$$(n-2)f^{1-14}(n-1)s^2p^6d^{0-1}ns^2.$$
81. (a) La(OH)<sub>3</sub> is more basic than Li(OH)<sub>3</sub>. In lanthanides, the basic character of hydroxides decreases as the ionic radius decreases.
82. (c) We know that regular decrease in the size of the atoms and ions is called lanthanide contraction. In vertical column of transition elements there is a very small change in size and some times size is found to be same from second member to third member. The similarity in size of the atoms of Zr and Hf is evident due to the fact of lanthanide contraction. Therefore, Zr and Hf both have same radius 160 pm.
83. (d) Actinides have variable valency due to very small difference in energies of  $5f$ ,  $6d$  and  $7s$  orbitals. Actinides are the elements from atomic number 89 to 103.
84. (b) Pm is obtained by synthetic method.  
 NOTES Promethium is not present in nature. It is synthetic radioactive lanthanoid.

# 23

# Coordination Compounds



Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Coordination number, nomenclature and isomerism of coordination compounds	isomerism					1	A				
	primary/secondary valency							1	D		
Magnetic moment, valence bond theory and crystal field theory	ligand strength	1	E								
	magnetic moment	1	A			1	A				
	crystal field theory			1	A			1	D		
	complex formation							1	A		
	geometry/hybridisation and magnetic behaviour					1	A	1	A		
LOD - Level of Difficulty	E - Easy	A - Average		D - Difficult		Qns - No. of Questions					

## Topic 1: Coordination Number, Nomenclature and Isomerism of Coordination Compounds

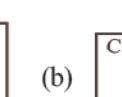
- The type of isomerism shown by the complex  $[\text{CoCl}_2(\text{en})_2]$  is [2018]
  - Geometrical isomerism
  - Coordination isomerism
  - Linkage isomerism
  - Ionization isomerism
- The correct order of the stoichiometries of  $\text{AgCl}$  formed when  $\text{AgNO}_3$  in excess is treated with the complexes :  $\text{CoCl}_3 \cdot 6\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 5\text{NH}_3$ ,  $\text{CoCl}_3 \cdot 4\text{NH}_3$  respectively is : [2017]
  - $3\text{AgCl}, 1\text{AgCl}, 2\text{AgCl}$
  - $3\text{AgCl}, 2\text{AgCl}, 1\text{AgCl}$
- Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test of chloride ions with silver nitrate at  $25^\circ\text{C}$ ? [2015]
  - $\text{CoCl}_3 \cdot 4\text{NH}_3$
  - $\text{CoCl}_3 \cdot 5\text{NH}_3$
  - $\text{CoCl}_3 \cdot 6\text{NH}_3$
  - $\text{CoCl}_3 \cdot 3\text{NH}_3$
- The sum of coordination number and oxidation number of the metal  $M$  in the complex  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$  (where  $\text{en}$  is ethylenediamine) is: [2015 RS]
  - 9
  - 6
  - 7
  - 8
- The name of complex ion,  $[\text{Fe}(\text{CN})_6]^{3-}$  is :

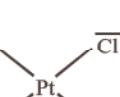
- |  |                              |   |
|--|------------------------------|---|
| (a) Hexacyanoiron (III) ion  | <b>[2015 RS]</b>             | with the composition of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ is due to : |
| (b) Hexacyanitoferrate (III) ion   |                              | <b>[2010]</b>   |
| (c) Tricyanoferrate (III) ion  |                              |   |
| (d) Hexacyanidoferrate (III) ion   |                              |   |
| 6. Number of possible isomers for the complex $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ will be (en = ethylenediamine)  | (a) 2 (b) 1 <b>[2015 RS]</b> |   |
|  | (c) 3 (d) 4                  |   |
| 7. An excess of $\text{AgNO}_3$ is added to 100 mL of a 0.01 M solution of dichlorotetraaquachromium (III) chloride. The number of moles of $\text{AgCl}$ precipitated would be : <b>[NEET 2013]</b> |                              |   |
| (a) 0.002 (b) 0.003  |                              |   |
| (c) 0.01 (d) 0.001   |                              |   |
| 8. The correct IUPAC name for $[\text{CrF}_2(\text{en})_2]\text{Cl}$ is: <b>[NEET Kar. 2013]</b>   |                              |   |
| (a) Chlorodifluoridobis (ethylene diamine) chromium (III)  |                              |   |
| (b) Chlorodifluoridoethylenediaminechromium (III) chloride   |                              |   |
| (c) Difluoridobis (ethylene diamine) chromium (III) chloride   |                              |   |
| (d) Difluorobis-(ethylene diamine) chromium (III) chloride   |                              |   |
| 9. In a particular isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^0$ , the Cl-Co-Cl angle is $90^\circ$ , the isomer is known as <b>[NEET Kar. 2013]</b>   |                              |   |
| (a) Linkage isomer (b) Optical isomer  |                              |   |
| (c) <i>cis</i> -isomer (d) Position isomer   |                              |   |
| 10. The complexes $[\text{Co}(\text{NH}_3)_6]$ $[\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ are the examples of which type of isomerism? <b>[2011]</b>        |                              |   |
| (a) Linkage isomerism  |                              |   |
| (b) Ionization isomerism   |                              |   |
| (c) Coordination isomerism   |                              |   |
| (d) Geometrical isomerism  |                              |   |
| 11. The complex, $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$ will have how many geometrical isomers ? <b>[2011]</b>   |                              |   |
| (a) 3 (b) 4  |                              |   |
| (c) 0 (d) 2  |                              |   |
| 12. The existence of two different coloured complexes  |                              |   |

17. Which one of the following is expected to exhibit optical isomerism?  
(en = ethylenediamine) [2005]

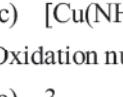
  - cis-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]
  - trans-[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]
  - cis-[Co(en)<sub>2</sub>Cl<sub>2</sub>]
  - trans-[Co(en)<sub>2</sub>Cl<sub>2</sub>]

18. Which of the following is considered to be an anticancer species ? [2004]

(a) 

(b) 

(c) 

(d) 

19. Which of the following coordination compounds would exhibit optical isomerism? [2004]

  - pentaamminenitrocobalt(III) iodide
  - diamminedichloroplatinum(II)
  - trans-dicyanobis (ethylenediamine) chromium(III) chloride
  - tris-(ethylenediamine) cobalt (III) bromide

20. Which one of the following octahedral complexes will not show geometric isomerism?  
(A and B are monodentate ligands) [2003]

  - [MA<sub>5</sub>B]
  - [MA<sub>2</sub>B<sub>4</sub>]
  - [MA<sub>3</sub>B<sub>3</sub>]
  - [MA<sub>4</sub>B<sub>2</sub>]

21. According to IUPAC nomenclature sodium nitroprusside is named as [2003]

  - Sodium pentacyanonitrosyl ferrate (III)
  - Sodium nitroferrocyanide
  - Sodium nitroferrocyanide
  - Sodium pentacyanonitrosyl ferrate (II)

22. The hypothetical complex chloridodiaquatriammine cobalt (III) chloride can be represented as [2002]

  - [CoCl(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>
  - [Co(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)Cl<sub>3</sub>]

23. Which of the following will give maximum number of isomers? [2001]

  - [Ni(C<sub>2</sub>O<sub>4</sub>)(en)<sub>2</sub>]<sup>2-</sup>
  - [Ni(en)(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>
  - [Cr(SCN)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup>
  - [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]

24. Which of the following will exhibit maximum ionic conductivity? [2001]

  - K<sub>4</sub>[Fe(CN)<sub>6</sub>]
  - [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub>
  - [Cu(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>
  - [Ni(CO)<sub>4</sub>]

25. Oxidation number of Ni in [Ni(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>4-</sup> is [2001]

  - 3
  - 4
  - 2
  - 6

26. Which one of the following complexes will have four different isomers ? [2000]

  - [Co(en)<sub>2</sub>Cl<sub>2</sub>]Cl
  - [Co(en)(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl
  - [Co(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl
  - [Co(en)<sub>3</sub>]Cl<sub>3</sub>

27. In which of the following compounds does iron exhibit zero oxidation state? [1999]

  - [Fe(H<sub>2</sub>O)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>
  - K<sub>3</sub>[Fe(CN)<sub>6</sub>]
  - K<sub>4</sub>[Fe(CN)<sub>6</sub>]
  - [Fe(CO)<sub>5</sub>]

28. The total number of possible isomers for the complex compound [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>] [Pt<sup>II</sup>Cl<sub>4</sub>] [1998]

  - 3
  - 6
  - 5
  - 4

29. IUPAC name of [Pt(NH<sub>3</sub>)<sub>3</sub>(Br)(NO<sub>2</sub>)Cl]Cl is [1998]

  - Triamminechlorobromonitroplatinum (IV) chloride
  - Triamminebromonitrochloroplatinum (IV) chloride
  - Triamminebromochloronitroplatinum (IV) chloride
  - Triaminenitrochlorobromoplatinum (IV) chloride

30. A coordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of  $\text{AgNO}_3$  solution, we get two moles of  $\text{AgCl}$  precipitate. The ionic formula for this complex would be **[1998]**
- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}] [(\text{NH}_3)\text{Cl}]$
  - $[\text{Co}(\text{NH}_3)_5\text{Cl}] [\text{Cl}(\text{NO}_2)]$
  - $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)] \text{Cl}_2$
  - $[\text{Co}(\text{NH}_3)_5] [(\text{NO}_2)_2\text{Cl}_2]$
31. The formula for the complex, dichlorobis (urea) copper (II) is **[1997]**
- $[\text{Cu}\{\text{O}=\text{C}(\text{NH}_2)_2\}] \text{Cl}_2$
  - $[\text{Cu}\{\text{O}=\text{C}(\text{NH}_2)_2\}\text{Cl}]\text{Cl}$
  - $[\text{CuCl}_2\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]$
  - $[\text{CuCl}_2][\{\text{O}=\text{C}(\text{NH}_2)_2\}]_2$
32. The number of geometrical isomers of the complex  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$  is **[1997]**
- 2
  - 3
  - 4
  - zero
33. Among the following, the compound that is both paramagnetic and coloured, is **[1996]**
- $\text{KMnO}_4$
  - $\text{CuF}_2$
  - $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - $\text{K}_2\text{Cr}_2\text{O}_7$
34. The number of geometrical isomers for  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is **[1995]**
- 2
  - 1
  - 3
  - 4
35.  $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  is called **[1994]**
- Potassium alumino oxalate
  - Potassium trioxalatoaluminate (III)
  - Potassium aluminium (III) oxalate
  - Potassium trioxalato aluminate (VI)
36. Among the following complexes, optical activity is possible in **[1994]**
- $[\text{Co}(\text{NH}_3)_6]^{3+}$
  - $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cl}_2]^+$
  - $[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_2]^+$
  - $[\text{Co}(\text{CN})_5\text{NC}]$
37. An example of double salt is **[1989]**
- Bleaching powder
  - $\text{K}_4[\text{Fe}(\text{CN})_6]$
  - Hypo
  - Potash alum
- Topic 2: Magnetic Moment, Valence Bond Theory and Crystal Field Theory**
38. Which of the following is the correct order of increasing field strength of ligands to form coordination compounds? **[2020]**
- $\text{SCN}^- < \text{F}^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-}$
  - $\text{F}^- < \text{SCN}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$
  - $\text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{SCN}^- < \text{F}^-$
  - $\text{SCN}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$
39. The calculated spin only magnetic moment of  $\text{Cr}^{2+}$  ion is **[2020]**
- 4.90 BM
  - 5.92 BM
  - 2.84 BM
  - 3.87 BM
40. The Crystal Field Stabilisation Energy (CFSE) for  $[\text{CoCl}_6]^{4-}$  is  $18000 \text{ cm}^{-1}$ . The CFSE for  $[\text{CoCl}_4]^{2-}$  will be **[NEET Odisha 2019]**
- $8000 \text{ cm}^{-1}$
  - $6000 \text{ cm}^{-1}$
  - $16000 \text{ cm}^{-1}$
  - $18000 \text{ cm}^{-1}$
41. What is the **correct** electronic configuration of the central atom in  $\text{K}_4[\text{Fe}(\text{CN})_6]$  based on crystal field theory? **[2019]**
- $t_{2g}^4 e_g^2$
  - $t_{2g}^6 e_g^0$
  - $e_g^3 t_{2g}^3$
  - $e_g^4 t_{2g}^2$
42. The geometry and magnetic behaviour of the complex  $[\text{Ni}(\text{CO})_4]$  are **[2018]**
- Square planar geometry and diamagnetic
  - Tetrahedral geometry and diamagnetic
  - Tetrahedral geometry and paramagnetic
  - Square planar geometry and paramagnetic

43. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code : **[2018]**

Column I	Column II
a. $\text{Co}^{3+}$	i. $\sqrt{8}$ BM
b. $\text{Cr}^{3+}$	ii. $\sqrt{35}$ BM
c. $\text{Fe}^{3+}$	iii. $\sqrt{3}$ BM
d. $\text{Ni}^{2+}$	iv. $\sqrt{24}$ BM
	v. $\sqrt{15}$ BM
a      b      c      d	
(a) iv	v
(b) i	ii
(c) iii	v
(d) iv	i
	ii      iii

44.  $\text{HgCl}_2$  and  $I_2$  both when dissolved in water containing  $I^-$  ions, the pair of species formed is:

- (a)  $\text{HgI}_2, \text{I}^-$       (b)  $\text{HgI}_4^{2-}, \text{I}_3^-$  **[2017]**  
 (c)  $\text{Hg}_2\text{I}_2, \text{I}^-$       (d)  $\text{HgI}_2, \text{I}_3^-$

45. Correct increasing order for the wavelengths of absorption in the visible region the complexes of  $\text{Co}^{3+}$  is :- **[2017]**

- (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}, [\text{Co}(\text{en})_3]^{3+}, [\text{Co}(\text{NH}_3)_6]^{3+}$   
 (b)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}, [\text{Co}(\text{NH}_3)_6]^{3+}, [\text{Co}(\text{en})_3]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}, [\text{Co}(\text{en})_3]^{3+}, [\text{Co}(\text{H}_2\text{O})_6]^{3+}$   
 (d)  $[\text{Co}(\text{en})_3]^{3+}, [\text{Co}(\text{NH}_3)_6]^{3+}, [\text{Co}(\text{H}_2\text{O})_6]^{3+}$

46. Pick out the correct statement with respect to  $[\text{Mn}(\text{CN})_6]^{3-}$  **[2017]**

- (a) It is  $sp^3d^2$  hybridised and tetrahedral  
 (b) It is  $d^2sp^3$  hybridised and octahedral  
 (c) It is  $dsp^2$  hybridised and square planar  
 (d) It is  $sp^3d^2$  hybridised and octahedral

47. Which of these statements about  $[\text{Co}(\text{CN})_6]^{3-}$  is true ? **[2015]**

- (a)  $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a low-spin configuration.  
 (b)  $[\text{Co}(\text{CN})_6]^{3-}$  has four unpaired electrons and will be in a high spin configuration.

- (c)  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a high-spin configuration.

- (d)  $[\text{Co}(\text{CN})_6]^{3-}$  has no unpaired electrons and will be in a low-spin configuration.

48. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE): **[2014]**

- (a)  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$       (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

49. Which of the following complexes is used as an anti-cancer agent: **[2014]**

- (a) *mer*- $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (b) *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$   
 (c) *cis*- $\text{K}_2[\text{PtCl}_2\text{Br}_2]$  (d)  $\text{Na}_2\text{CoCl}_4$

50. A magnetic moment of 1.73 BM will be shown by one among the following : **[NEET 2013]**

- (a)  $[\text{Ni}(\text{CN})_4]^{2-}$       (b)  $[\text{TiCl}_4]$   
 (c)  $[\text{CoCl}_6]^{4-}$       (d)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

51. Which is diamagnetic? **[NEET Kar. 2013]**

- (a)  $[\text{Fe}(\text{CN})_6]^{3-}$       (b)  $[\text{Co}(\text{F}_6)]^{3-}$   
 (c)  $[\text{Ni}(\text{CN})_4]^{2-}$       (d)  $[\text{NiCl}_4]^{2-}$

52. The anion of acetylacetone (acac) forms  $\text{Co}(\text{acac})_3$  chelate with  $\text{Co}^{3+}$ . The rings of the chelate are **[NEET Kar. 2013]**

- (a) three membered      (b) five membered  
 (c) four membered      (d) six membered

53. Which among the following is a paramagnetic complex? **[NEET Kar. 2013]**

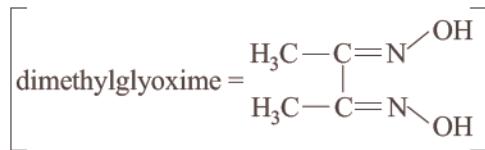
- (a)  $[\text{Mo}(\text{CO})_6]$       (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Pt}(\text{en})\text{Cl}_2]$       (d)  $[\text{CoBr}_4]^{2-}$   
 (At. No. of Mo = 42, Pt = 78)

54. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour ? **[2012]**

- (a)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$       (b)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$   
 (c)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$       (d)  $[\text{Co}(\text{NH}_3)_6]^{3+}$

55. Red precipitate is obtained when ethanol solution of dimethylglyoxime is added to ammoniacal Ni(II). Which of the following statements is not true ? **[2012 M]**

- (a) Red complex has a square planar geometry.  
 (b) Complex has symmetrical H-bonding  
 (c) Red complex has a tetrahedral geometry.  
 (d) Dimethylglyoxime functions as bidentate ligand.



56. Low spin complex of  $d^6$ -cation in an octahedral field will have the following energy : [2012 M]

- (a)  $\frac{-12}{5}\Delta_0 + P$       (b)  $\frac{-12}{5}\Delta_0 + 3P$   
 (c)  $\frac{-2}{5}\Delta_0 + 2P$       (d)  $\frac{-2}{5}\Delta_0 + P$

( $\Delta_0$  = Crystal Field Splitting Energy in an octahedral field, P = Electron pairing energy)

57. Of the following complex ions, which is diamagnetic in nature ? [2011]

- (a)  $[\text{NiCl}_4]^{2-}$       (b)  $[\text{Ni}(\text{CN})_4]^{2-}$   
 (c)  $[\text{CuCl}_4]^{2-}$       (d)  $[\text{CoF}_6]^{3-}$

58. The  $d$ -electron configurations of  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  are  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$ , respectively. Which one of the following will exhibit minimum paramagnetic behaviour? [2011]

- (a)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$       (b)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

(At. nos. Cr = 24, Mn = 25, Fe = 26, Co = 27)

59. Which of the following complex compounds will exhibit highest paramagnetic behaviour? [2011M]

(At. No. : Ti = 22, Cr = 24, Co = 27, Zn = 30)

- (a)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$       (b)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$       (d)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$

60. Which of the following complex ion is not expected to absorb visible light ? [2010]

- (a)  $[\text{Ni}(\text{CN})_4]^{2-}$       (b)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

61. Crystal field stabilization energy for high spin  $d^4$  octahedral complex is: [2010]

- (a)  $-1.8 \Delta_0$       (b)  $-1.6 \Delta_0 + P$   
 (c)  $-1.2 \Delta_0$       (d)  $-0.6 \Delta_0$

62. Which of the following complex ions is expected to absorb visible light? [2009]

- (a)  $[\text{Ti}(\text{en})_2(\text{NH}_3)_2]^{4+}$   
 (b)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$   
 (d)  $[\text{Sc}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$

(At. no. Zn = 30, Sc = 21, Ti = 22, Cr = 24)

63. Which of the following complexes exhibits the highest paramagnetic behaviour ? [2008]

- (a)  $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^+$   
 (b)  $[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+}$   
 (c)  $[\text{Co}(\text{ox})_2(\text{OH})_2]^-$   
 (d)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$

where gly = glycine, en = ethylenediamine and bpy = bipyridyl moieties)

(At. nos. Ti = 22, V = 23, Fe = 26, Co = 27)

64. In which of the following coordination entities the magnitude  $\Delta_0$  (CFSE in octahedral field) will be maximum? [2008]

- (a)  $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$       (b)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Co}(\text{CN})_6]^{3-}$       (d)  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$

(At. No. Co = 27)

65. The  $d$ -electron configurations of  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  are  $3d^4$ ,  $3d^5$ ,  $3d^6$  and  $3d^8$  respectively. Which one of the following aqua complexes will exhibit the minimum paramagnetic behaviour?

- [2007]
- (a)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       (b)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$   
 (c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$       (d)  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

(At. No. Cr = 24, Mn = 25, Fe = 26, Ni = 28)

66.  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (at no. of Cr = 24) has a magnetic moment of 3.83 B. M. The correct distribution of 3d electrons in the chromium of the complex is  
 (a)  $3d_{xy}^1, \left(3d_{x^2-y^2}\right)^1, 3d_{yz}^1$  [2006]  
 (b)  $3d_{xy}^1, 3d_{yz}^1, 3d_{xz}^1$   
 (c)  $3d_{xy}^1, 3d_{yz}^1, 3d_z^1 2$   
 (d)  $(3d_{x^2-y^2}^2)^1, 3d_z^2, 3d_{xz}^1$
67. Which one of the following is an inner orbital complex as well as diamagnetic in behaviour? (Atomic number: Zn = 30, Cr = 24, Co = 27, Ni = 28) [2005]  
 (a)  $[\text{Zn}(\text{NH}_3)_6]^{2+}$  (b)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$   
 (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  (d)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$
68. Among  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{Ni}(\text{CN})_4]^{2-}$ ,  $[\text{NiCl}_4]^{2-}$  species, the hybridization states of the Ni atom are, respectively (At. No. of Ni = 28) [2004]  
 (a)  $sp^3, dsp^2, dsp^2$  (b)  $sp^3, dsp^2, sp^3$   
 (c)  $sp^3, sp^3, dsp^2$  (d)  $dsp^2, sp^3, sp^3$
69.  $\text{CN}^-$  is a strong field ligand. This is due to the fact that [2004]  
 (a) it carries negative charge  
 (b) it is a pseudohalide  
 (c) it can accept electrons from metal species  
 (d) it forms high spin complexes with metal species
70. Considering  $\text{H}_2\text{O}$  as a weak field ligand, the number of unpaired electrons in  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  will be (At. no. of Mn = 25) [2004]  
 (a) three (b) five  
 (c) two (d) four
71. The number of unpaired electrons in the complex ion  $[\text{CoF}_6]^{3-}$  is (Atomic no.: Co = 27) [2003]  
 (a) Zero (b) 2  
 (c) 3 (d) 4
72. Atomic number of Cr and Fe are respectively 25 and 26, which of the following is paramagnetic? [2002]  
 (a)  $[\text{Cr}(\text{CO})_6]$  (b)  $[\text{Fe}(\text{CO})_5]$   
 (c)  $[\text{Fe}(\text{CN})_6]^{-4}$  (d)  $[\text{Cr}(\text{NH}_3)_6]^{+3}$
73.  $\text{CuSO}_4$  when reacts with KCN forms  $\text{CuCN}$ , which is insoluble in water. It is soluble in excess of KCN due to formation of the following complex [2002]  
 (a)  $\text{K}_2[\text{Cu}(\text{CN})_4]$  (b)  $\text{K}_3[\text{Cu}(\text{CN})_4]$   
 (c)  $\text{CuCN}_2$  (d)  $\text{Cu}[\text{K Cu}(\text{CN})_4]$
74. Which statement is incorrect? [2001]  
 (a)  $[\text{Ni}(\text{CO})_4]$  – Tetrahedral, paramagnetic  
 (b)  $[\text{Ni}(\text{CN})_4]^{2-}$  – Square planar, diamagnetic  
 (c)  $[\text{Ni}(\text{CO})_4]$  – Tetrahedral, diamagnetic  
 (d)  $[\text{NiCl}_4]^{2-}$  – Tetrahedral, paramagnetic
75. Which one of the following will show paramagnetism corresponding to 2 unpaired electrons? (Atomic numbers : Ni = 28, Fe = 26)  
 (a)  $[\text{Fe F}_6]^{3-}$  (b)  $[\text{Ni Cl}_4]^{2-}$  [1999]  
 (c)  $[\text{Fe}(\text{CN})_6]^{3-}$  (d)  $[\text{Ni}(\text{CN})_4]^{2-}$
76. The number of unpaired electrons in the complex  $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$  is (Atomic number Cr = 24)  
 (a) 4 (b) 1 [1999]  
 (c) 2 (d) 3
77. Which of the following statements is correct ? (Atomic number of Ni = 28) [1997]  
 (a)  $[\text{Ni}(\text{CO})_4]$  is diamagnetic and  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are paramagnetic  
 (b)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{NiCl}_4]^{2-}$  is paramagnetic  
 (c)  $[\text{Ni}(\text{CO})_4]$  and  $[\text{NiCl}_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CN})_4]^{2-}$  is paramagnetic  
 (d)  $[\text{NiCl}_4]^{2-}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$  are diamagnetic and  $[\text{Ni}(\text{CO})_4]$  is paramagnetic
78. Which of the following is common donor atom in ligands? [1995]  
 (a) arsenic (b) nitrogen  
 (c) oxygen (d) both 'b' and 'c'
79. The complex ion  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is formed by  $sp^3d^2$  hybridisation. Hence, the ion should possess  
 (a) Octahedral geometry [1990]  
 (b) Tetrahedral geometry  
 (c) Square planar geometry  
 (d) Tetragonal geometry.

## Topic 3: Organometallic Compounds

80. Iron carbonyl,  $[\text{Fe}(\text{CO})_5]$  is **[2018]**  
 (a) Tetranuclear      (b) Mononuclear  
 (c) Dinuclear      (d) Trinuclear
81. An example of a sigma bonded organometallic compound is : **[2017]**  
 (a) Grignard's reagent (b) Ferrocene  
 (c) Cobaltocene      (d) Ruthenocene
82. Which of the following has longest C–O bond length? (Free C–O bond length in CO is  $1.128\text{\AA}$ )  
**[2016]**  
 (a)  $[\text{Ni}(\text{CO})_4]$       (b)  $[\text{Co}(\text{CO})_4]^-$   
 (c)  $[\text{Fe}(\text{CO})_4]^{2-}$       (d)  $[\text{Mn}(\text{CO})_6]^+$
83. Which of the following carbonyls will have the strongest C – O bond ? **[2011 M]**  
 (a)  $[\text{Mn}(\text{CO})_6]^+$       (b)  $[\text{Cr}(\text{CO})_6]$   
 (c)  $[\text{V}(\text{CO})_6]^-$       (d)  $[\text{Fe}(\text{CO})_5]$
84. Which of the following does **not** have a metal–carbon bond? **[2004]**  
 (a)  $\text{Al}(\text{OC}_2\text{H}_5)_3$       (b)  $\text{C}_2\text{H}_5\text{MgBr}$   
 (c)  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$  (d)  $[\text{Ni}(\text{CO})_4]$
85. Among the following, which is **not** the  $\pi$ -bonded organometallic compound? **[2003]**  
 (a)  $(\text{CH}_3)_4\text{Sn}$   
 (b)  $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$   
 (c)  $\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2$   
 (d)  $\text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2$
86. Which of the following organometallic compound is  $\sigma$  and  $\pi$  bonded? **[2001]**  
 (a)  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$   
 (b)  $\text{Fe}(\text{CH}_3)_3$   
 (c)  $\text{K}[\text{PtCl}_3(\eta^2-\text{C}_2\text{H}_4)]$   
 (d)  $[\text{Co}(\text{CO})_5\text{NH}_3]^{2+}$
87. Which of the following may be considered to be an organometallic compound? **[1996]**  
 (a) Nickel tetracarbonyl  
 (b) Chlorophyll  
 (c)  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$   
 (d)  $[\text{Co}(\text{en})_3]\text{Cl}_3$

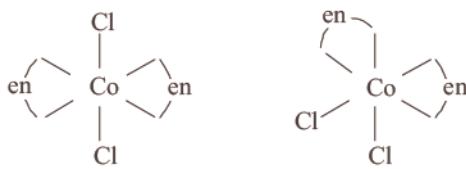
## ANSWER KEY

<b>1</b>	(b)	<b>10</b>	(c)	<b>19</b>	(d)	<b>28</b>	(d)	<b>37</b>	(d)	<b>46</b>	(b)	<b>55</b>	(c)	<b>64</b>	(c)	<b>73</b>	(b)	<b>82</b>	(c)
<b>2</b>	(a)	<b>11</b>	(a)	<b>20</b>	(a)	<b>29</b>	(c)	<b>38</b>	(d)	<b>47</b>	(d)	<b>56</b>	(b)	<b>65</b>	(b)	<b>74</b>	(a)	<b>83</b>	(a)
<b>3</b>	(d)	<b>12</b>	(b)	<b>21</b>	(a)	<b>30</b>	(c)	<b>39</b>	(a)	<b>48</b>	(b)	<b>57</b>	(b)	<b>66</b>	(b)	<b>75</b>	(b)	<b>84</b>	(a)
<b>4</b>	(a)	<b>13</b>	(d)	<b>22</b>	(a)	<b>31</b>	(c)	<b>40</b>	(a)	<b>49</b>	(b)	<b>58</b>	(c)	<b>67</b>	(c)	<b>76</b>	(d)	<b>85</b>	(a)
<b>5</b>	(d)	<b>14</b>	(a)	<b>23</b>	(c)	<b>32</b>	(a)	<b>41</b>	(b)	<b>50</b>	(d)	<b>59</b>	(b)	<b>68</b>	(b)	<b>77</b>	(b)	<b>86</b>	(d)
<b>6</b>	(c)	<b>15</b>	(b)	<b>24</b>	(a)	<b>33</b>	(b)	<b>42</b>	(b)	<b>51</b>	(c)	<b>60</b>	(a)	<b>69</b>	(b)	<b>78</b>	(d)	<b>87</b>	(a)
<b>7</b>	(d)	<b>16</b>	(a)	<b>25</b>	(c)	<b>34</b>	(a)	<b>43</b>	(a)	<b>52</b>	(d)	<b>61</b>	(d)	<b>70</b>	(b)	<b>79</b>	(a)		
<b>8</b>	(c)	<b>17</b>	(c)	<b>26</b>	(b)	<b>35</b>	(b)	<b>44</b>	(b)	<b>53</b>	(d)	<b>62</b>	(b)	<b>71</b>	(d)	<b>80</b>	(b)		
<b>9</b>	(c)	<b>18</b>	(c)	<b>27</b>	(d)	<b>36</b>	(b)	<b>45</b>	(d)	<b>54</b>	(a)	<b>63</b>	(c)	<b>72</b>	(d)	<b>81</b>	(a)		

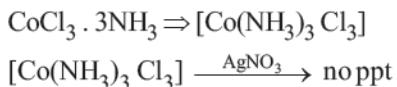
# Hints & Solutions

1. (b)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \xrightarrow{\text{AgNO}_3}$   
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \xrightarrow{\text{AgNO}_3}$   
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \xrightarrow{\text{AgNO}_3}$
- 3 mol of AgCl  
2 mol of AgCl  
1 mol of AgCl  
Complexes are respectively  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

2. (a) In the given complex, the CN of Co is 6, and the complex has octahedral geometry.



3. (d)  $\text{CoCl}_3 \cdot 3\text{NH}_3$  will not give test for chloride ions with silver nitrate due to absence of ionisable chloride atoms.

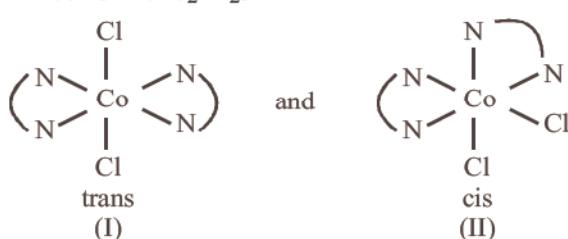


**NOTES** Secondary valence is fixed for a metal/ion. For  $\text{Co}^{3+}$ , it is six.

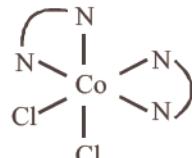
4. (a)  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$   
 $\text{C}_2\text{O}_4$  = bidentate ligand, carry -2 charge  
en = bidentate ligand, carry 0 charge  
 $\therefore \text{M carry} + 3 \text{ charge; coordination number} = 6$   
 $\therefore \text{Sum} = +3 + 6 = 9$

5. (d) Hexacyanidoferate (III) ion.

6. (c)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$



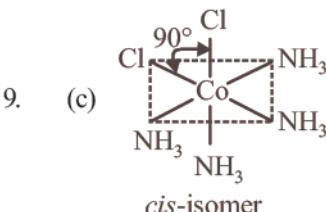
Mirror image of (II)



7. (d)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{NO}_3$

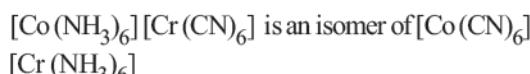
$$\begin{aligned} \text{Molarity} &= \frac{\text{wt}}{\text{mol. mass}} \times \frac{1000}{\text{vol.}} \\ \frac{\text{wt}}{\text{mol. mass}} &= \text{molarity} \times \frac{\text{vol.}}{1000} = \frac{0.01 \times 100}{1000} \\ &= 0.001 \end{aligned}$$

8. (c) IUPAC name of  $[\text{CrF}_2(\text{en})_2]\text{Cl}$  is Difluoridobis(ethylenediamine) chromium (III) chloride.



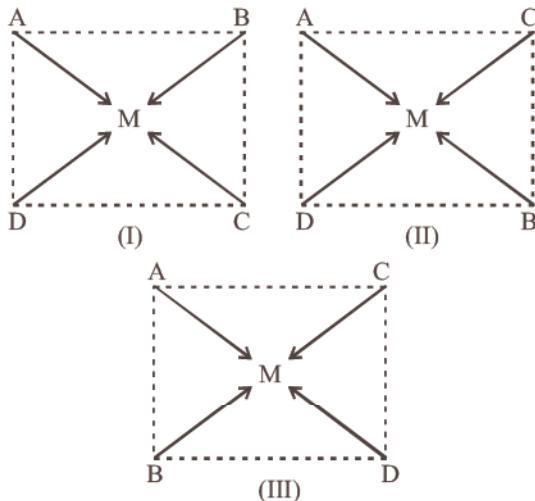
10. (c)

Interchange of ligand between the complexes give isomers e.g.



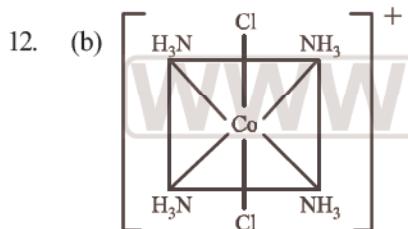
**NOTES** Coordination isomerism occurs when cationic and anionic complexes of different metal ions are present in a salt.

11. (a) Complexes of the type  $\text{M}_{\text{ABCD}}$  may exist in three isomeric forms.

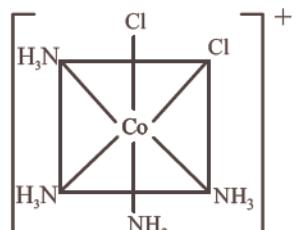


Similarly,  $[\text{Pt}(\text{Py})(\text{NH}_3)\text{BrCl}]$  may exist in three isomeric form in which

M = Pt, A = Py, B = NH<sub>3</sub>, C = Br, D = Cl.



*trans* (violet)



*cis* (green)

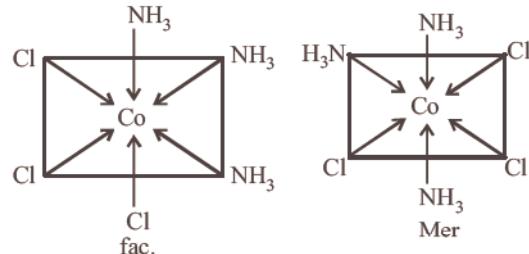
13. (d) In  $[\text{Ni}(\text{NH}_3)_2 \text{Cl}_2]$ ,  $\text{Ni}^{2+}$  is in  $sp^3$  hybridisation, thus tetrahedral in shape. Hence, the four ligands are not different to exhibit optical isomerism.  $\therefore$  Correct choice : (d)

(ii)  $[\text{Mabcd}]$  does not have a plane of symmetry, thus it will show optical isomerism. Whereas,  $[\text{Ma}_2\text{b}_2]$  has a plane of symmetry, thus it will show optical isomerism also.

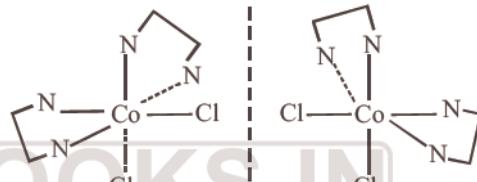
NOTES

Tetrahedral complexes are symmetrical in all directions. Thus, cannot show geometrical isomerism.

14. (a) The octahedral coordination compounds of the type  $MA_3B_3$  exhibit fac-mer isomerism.



15. (b) Non superimposable mirror images are called optical isomers and may be described as 'chiral'. They are also called enantiomers and rotate plane polarised light in opposite directions.



16. (a) The given compound may have linkage isomerism due to presence of  $\text{NO}_2$  group which may be in the form  $-\text{NO}_2$  or  $-\text{ONO}$ .

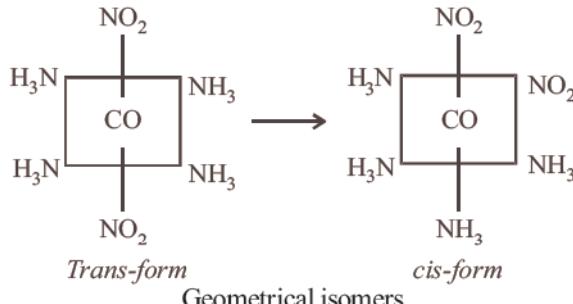
It may have ionisation isomerism due to presence of two ionisable group  $\text{--NO}_2$  &  $\text{--Cl}$ . It may have geometrical isomerism in the form of *cis-trans* form as follows :

[Co(NH<sub>3</sub>)<sub>4</sub>Cl(NO<sub>2</sub>)]NO<sub>3</sub>, &

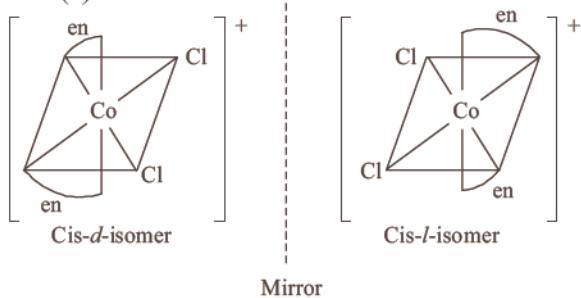
### [Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl — ionisation isomers.

[Co(NH<sub>3</sub>)<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl & [Co(NH<sub>3</sub>)<sub>4</sub>(ONO)<sub>2</sub>]Cl

### — Linkage isomers

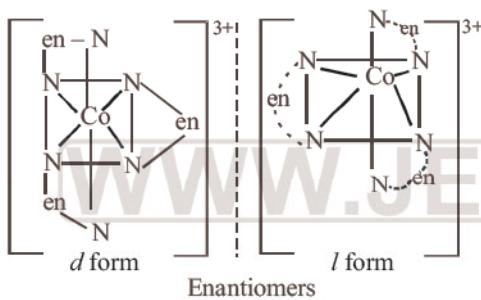


17. (c)



Trans-form of  $[M(AA)_2 a_2]^{n\pm}$  does not show optical isomerism.

18. (c) Diaminodichloroplatinum (II) commonly known as *cis*-platin is found to have anticancer property.  
19. (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.

20. (a)  $MA_3 B_3$  – 2 geometrical isomers  
 $MA_2 B_4$  – 2 geometrical isomers  
 $MA_4 B_2$  – 2 geometrical isomers

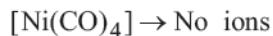


**NOTE** The complexes of general formula  $Ma_6$  and  $Ma_5b$  octahedral geometry do not show geometrical isomerism.

21. (a) IUPAC name of sodium nitroprusside  $Na_2[Fe(CN)_5NO]$  is sodium pentacyanonitrosoyl ferrate (III) because in it NO is neutral ligand. Hence  
 $2 \times O.N. of Na + O.N. of Fe + 5 \times O.N. of CN - 1 \times O.N. of NO = 0$   
 $2 \times (+1) + O.N. of Fe + 5 \times (-1) + 1 \times 0 = 0$   
 $O.N. of Fe = 5 - 2 = +3$ , Hence, ferrate (III)  
22. (a) Chloridodiaquatriammine cobalt (III) chloride is  $[CoCl(NH_3)_3(H_2O)_2]Cl_2$

23. (c)  $[Cr(SCN)_2(NH_3)_4]^+$  shows linkage and geometrical isomerism. Hence, produces maximum no. of isomers.

24. (a) The complex ion which give maximum ions in solution exhibit maximum ionic conductivity.

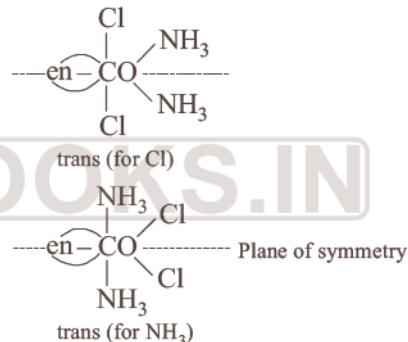


25. (c) O.N. of Ni in  $[Ni(C_2O_4)_3]^{4-}$

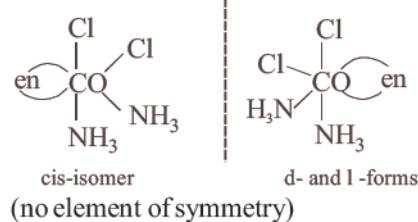
$$= x + 3(-2) = -4 \Rightarrow x = -4 + 6 = 2$$

26. (b) Complex  $[Co(en)(NH_3)_2Cl_2]Cl$  will have four different isomers.

- (i) Geometrical isomers



- (ii) Optical isomers



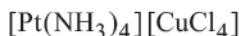
Hence, the compound has 4 different isomers

27. (d) In  $[Fe(CO)_5]$  iron exist in zero oxidation state.  
28. (d) The total number of isomers for the complex compound



These four isomers are



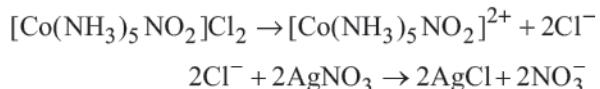


The isomer  $[\text{Cu}(\text{NH}_3)_2\text{Cl}_2][\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  does not exist as both the parts are neutral.



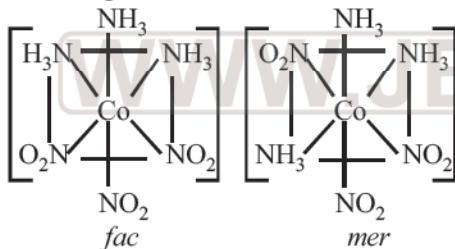
**NOTES** For writing all combination of structural isomers, we have to keep the same value of primary valence and secondary valence of central atom/ion for all the isomers.

29. (c) We know that IUPAC name of  $[\text{Pt}(\text{NH}_3)_3(\text{Br})(\text{NO}_2)\text{Cl}]\text{Cl}$  is triamminebromochloronitroplatinum (IV) chloride.  
 30. (c) As it forms two moles of silver chloride thus it has two moles of ionisable Cl.



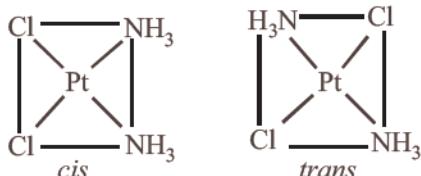
31. (c)  $[\text{CuCl}_2\{\text{O}=\text{C}(\text{NH}_2)_2\}_2]$   
 32. (a)  $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$

Possible geometrical isomers

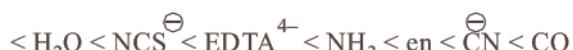


Total geometrical isomers = 2

33. (b)  $\text{CuF}_2$  is both paramagnetic and coloured due to unpaired electron in  $d$ -orbital ( $3d^94s^0$ ).  
 34. (a)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  is a disubstituted complex and shows only *cis*-& *trans*-isomers



35. (b) IUPAC name is potassium trioxalatoaluminate(III).  
 36. (b) It is optically active when two Cl atoms are in *cis* position.  
 37. (d) Potash alum  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  is a double salt.  
 38. (d) According to spectrochemical series, the order of ligand field strength is



So, correct order is



**NOTES** Strong and weak field ligands affect the electronic configuration of elements of first transition series. Second and third transition series electrons pair up irrespective of nature of ligand provided pairing of electrons is allowed.

39. (a) Electronic configuration of  $\text{Cr}^{2+}$  –  $[\text{Ar}]3d^4$



$$\mu_n = \sqrt{n(n+2)}$$

$$\therefore \mu_n = \sqrt{4(4+2)} = \sqrt{24} \text{ BM} = 4.9 \text{ BM}$$

$$40. \text{ (a) } \because \Delta_t = \frac{4}{9} \Delta_0$$

$$\Delta_t = \frac{4}{9} \times 18000 \text{ cm}^{-1} = 8000 \text{ cm}^{-1}$$

41. (b)

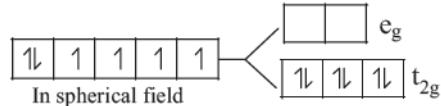


$$x - 6 = -4$$

$$x = +2$$

$$\text{Fe: } 4s^2 3d^6$$

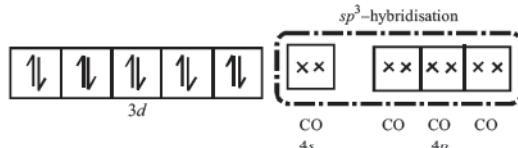
$$\text{Fe}^{2+}: 3d^6$$



**NOTES**  $\text{CN}^-$  is a strong field ligand and causes pairing of electrons.

42. (b)  $\text{Ni}(28): [\text{Ar}]3d^8 4s^2$

∴ CO is a strong field ligand, so unpaired electrons get paired. Hence, configuration would be:



For, four 'CO' ligands hybridisation would be  $sp^3$  and thus the complex would be diamagnetic and of tetrahedral geometry.

## Coordination Compounds

43. (a)  $\text{Co}^{3+} = [\text{Ar}] 3d^6$ , unpaired  $e^- (n) = 4$   
Spin magnetic moment

$$= \sqrt{4(4+2)} = \sqrt{24} \text{ B.M.}$$

$\text{Cr}^{3+} = [\text{Ar}] 3d^3$ , unpaired  $e^- (n) = 3$   
Spin magnetic moment

$$= \sqrt{3(3+2)} = \sqrt{15} \text{ B.M.}$$

$\text{Fe}^{3+} = [\text{Ar}] 3d^5$ , unpaired  $e^- (n) = 5$   
Spin magnetic moment

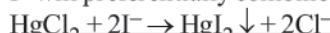
$$= \sqrt{5(5+2)} = \sqrt{35} \text{ B.M.}$$

$\text{Ni}^{2+} = [\text{Ar}] 3d^8$ , unpaired  $e^- (n) = 2$   
Spin magnetic moment

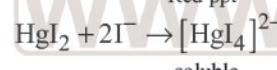
$$= \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.}$$

44. (b) In a solution containing  $\text{HgCl}_2$ ,  $\text{I}_2$  and  $\text{I}^-$ , both  $\text{HgCl}_2$  and  $\text{I}_2$  compete for  $\text{I}^-$ . Since formation constant of  $[\text{HgI}_4]^{2-}$  is very large ( $1.9 \times 10^{30}$ ) as compared with  $\text{I}_3^-$  ( $K_f = 700$ ).

$\therefore \text{I}^-$  will preferentially combine with  $\text{HgCl}_2$ .

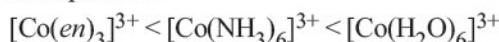


Red ppt



45. (d) The order of strength of ligand is  $\text{en} > \text{NH}_3 > \text{H}_2\text{O}$   
For strong ligand, the value of  $\Delta_0$  for the complex is higher.

Hence, the increasing order of wavelengths of absorption is:



**NOTES** Higher value of  $\Delta_0$  means higher stability, which means it will absorb high energy photons. High energy photons have low value of wavelength.

46. (b) In the complex  $[\text{Mn}(\text{CN})_6]^{3-}$ , O.S. of Mn is +3  
E.C. of  $\text{Mn}^{+3} \rightarrow 3d^4$

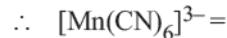
$3d$	$4s$	$4p$
1 1 1 1		

The presence of a strong field ligand  $\text{CN}^-$  causes pairing of electrons.

$\Rightarrow$	$1 1 1$		$4s$	$4p$
	$3d$			

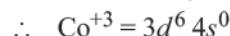
$d^2sp^3$

As, coordination number of Mn = 6, so it will form an octahedral complex.



$[\text{Ar}]$	1 1 1	$\boxed{\text{xx xx}}$	$\boxed{\text{xx}}$	$\boxed{\text{xx xx xx}}$
		$3d$	$4s$	$4p$
				$d^2sp^3$

47. (d) In  $[\text{Co}(\text{CN})_6]^{3-}$ , O.N. of Co is +3



$\text{CN}^-$  is a strong field ligand

$\therefore$  Pairing of electrons occurs so in this complex no unpaired electron is present and it is low spin complex.

48. (b) Due to  $d^5$  configuration CFSE is zero.

49. (b) cis-platin

50. (d)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  hybridisation  $dsp^2$   
 $\text{Cu}^{+2} - 3d^9$  has one unpaired  $e^-$

1 1	1 1	1 1	1 1	1
-----	-----	-----	-----	---

So, magnetic moment

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)}$$

$$= \sqrt{3} = 1.73$$

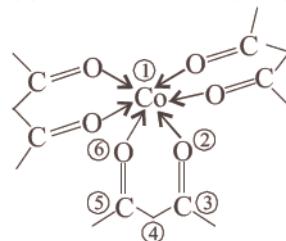
51. (c)  $\text{Ni}^{+2} \rightarrow 3d^8 =$ 

1 1	1 1	1 1	1	1
-----	-----	-----	---	---

$\text{CN}^-$  is a strong ligand and causes pairing of  $3d$  electrons of  $\text{Ni}^{+2}$ .

$\therefore$  It is diamagnetic.

52. (d) Structure of  $\text{Co}(\text{acac})_3$ :



Hence, the rings of chelate are six membered ring.

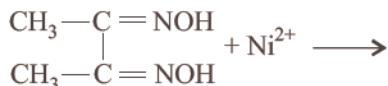
53. (d)  $\text{Co}^{+2} \Rightarrow [\text{Ar}] 3d^7 4s^0$ , here,  $\text{Br}^-$  is a weak field ligand so will not cause pairing of  $d$ -electrons in  $\text{Co}^{+2}$ .

$\therefore [\text{CoBr}_4]^{2-}$  will exhibit paramagnetic behaviour due to unpaired electrons.

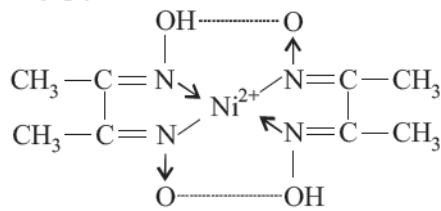
54. (a)  $[\text{Ni}(\text{NH}_3)_6]^{2+}$

$\text{Ni}^{2+} = 3d^8$ , according to CFT  $= t_{2g}^6 e_g^2$  therefore, hybridisation is  $sp^3d^2$  & complex is paramagnetic and outer orbital.

55. (c) Nickel ions are frequently detected by the formation of red precipitate of the complex of nickel dimethylglyoxime, when heated with dimethylglyoxime.



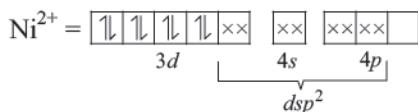
Dimethylglyoxime



Nickel dimethylglyoxime



dmg is a strong field ligand, so electrons will rearrange as:



Thus, the complex is square planar geometry.

56. (b) for  $d^6$ ,  $t_{2g}^6 e_g^0$  (in low spin)

$$\text{C.F.S.E} = -0.4 \times 6\Delta_0 + 3P$$

$$= -\frac{12}{5} \Delta_0 + 3P$$

[P is pairing energy for one electron]

57. (b)  $\text{Ni}^{2+} = 3d^8 4s^0$



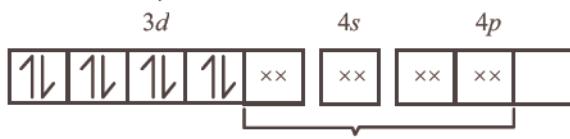
Since, the coordination number of Ni in this complex is 4, the configuration of  $\text{Ni}^{2+}$  at first sight shows that the complex is paramagnetic with two unpaired electron. However, experiments show that the complex is diamagnetic. This is possible when the  $3d$  electrons rearrange against the Hund's rule as shown below. This is in

accordance with the fact that the ligand involved here is strong i.e.,  $\text{CN}^-$  ion.

$\text{Ni}^{2+}$  (after rearrangement)



Hence, now  $dsp^2$  hybridization involving one  $3d$ , one  $4s$  and two  $4p$  orbitals, takes place leading to four  $dsp^2$  hybrid orbitals, each of which accepts four electron pairs from  $\text{CN}^-$  ion forming  $[\text{Ni}(\text{CN})_4]^{2-}$  ion.



four  $dsp^2$  hybrid bonds

Thus, the complex is diamagnetic as it has no unpaired electron.

58. (c)  $\text{Cr}^{2+}, d^4$   $\boxed{1} \boxed{1} \boxed{1} \boxed{1} \boxed{\phantom{1}}$

4 unpaired  $e^-$ s



5 unpaired  $e^-$ s

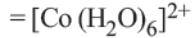


4 unpaired  $e^-$ s



3 unpaired  $e^-$ s

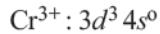
Minimum paramagnetic behaviour



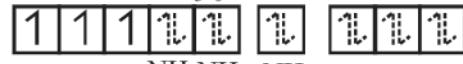
59. (b)

(a)  $[\text{Ti}(\text{NH}_3)_6]^{3+}$  :  $3d^1$  configuration and thus has one unpaired electron.

(b)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  : In this complex Cr is in +3 oxidation state.



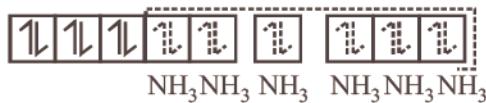
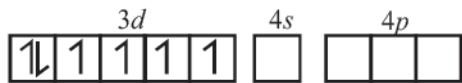
$\text{Cr}^{3+}$  ion  $[\text{Cr}(\text{NH}_3)_6]^{3+}$



$\text{NH}_3\text{NH}_3 \quad \text{NH}_3 \quad \text{NH}_3\text{NH}_3\text{NH}_3$

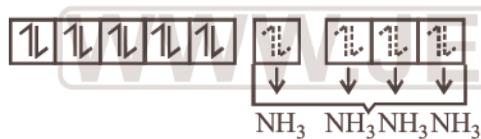
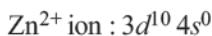
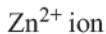
Thus, the complex is paramagnetic.

(c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$ : In this complex, cobalt ion is in +3 oxidation state with  $3d^6$  configuration.



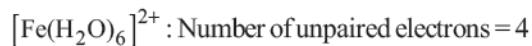
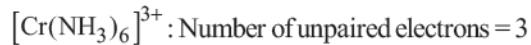
(inner orbital or  $d^2sp^3$  hybrid orbital low spin complex) diamagnetic

(d) In this complex Zn exists as

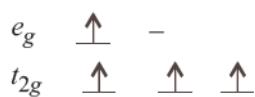


Due to presence of paired electrons, complex is diamagnetic in nature.

60. (a)  $[\text{Ni}(\text{CN})_4]^{2-}$ : Number of unpaired electrons = 0

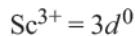
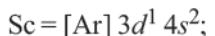
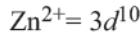
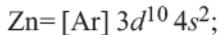


61. (d)  $d^4$  in high spin octahedral complex

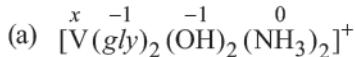


$$\text{CFSE} = [0.6 \times 1] + [-0.4 \times 3] = -0.6 \Delta_o$$

62. (b) Since Cr<sup>3+</sup> in the complex has unpaired electrons in the d orbital, hence will be coloured

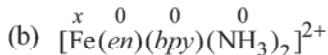
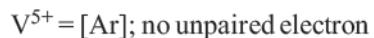


63. (c) More the number of unpaired electrons present in a complex more is its paramagnetic behaviour.



$$x + 2(-1) + 2(-1) + 2(0) = +1$$

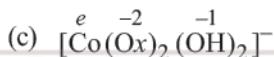
$$\Rightarrow x = +5$$



$$x = +2$$

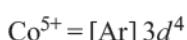


But due to presence of strong field ligands, en, bpy and NH<sub>3</sub>; the electrons will try to pair up. Thus, the complex will contain no unpaired electron.



$$x + 2(-2) + 2(-1) = -1$$

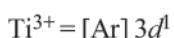
$$\Rightarrow x = +5$$



Thus, 4 unpaired electrons.



$$x = +3$$



Thus, 1 unpaired electron.

Hence, option (c) is the correct answer.



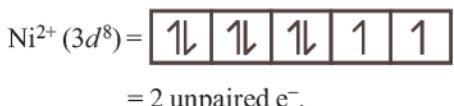
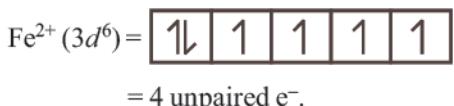
To find unpaired electrons let us calculate the oxidation states of elements in each complex and then write the electronic configuration for that oxidation state to find the number of unpaired electrons in it.

64. (c) Out of the given ligands water, ammonia, cyanide and oxalate, maximum splitting will occur in case of cyanide (CN<sup>-</sup>) i.e. the magnitude of  $\Delta_o$  will be maximum in case of  $[\text{Co}(\text{CN})_6]^{3-}$ .



In octahedral field the crystal field splitting of  $d$ -orbitals of a metal ion depends upon the field produced by the ligands.

65. (b) Lesser is the number of unpaired electrons smaller will be the paramagnetic behaviour. As  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  &  $\text{Ni}^{2+}$  contains.



As  $\text{Ni}^{2+}$  has minimum no. of unpaired  $e^-$  thus this is least paramagnetic.

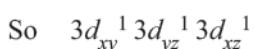
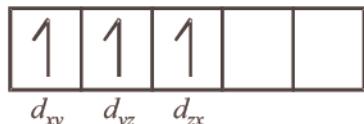
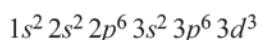
66. (b)  $\mu = \sqrt{n(n+2)}$

$$3.83 = \sqrt{n(n+2)}$$

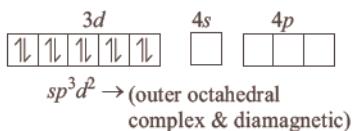
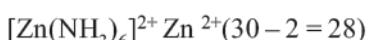
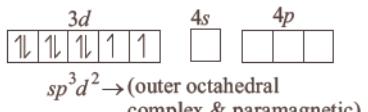
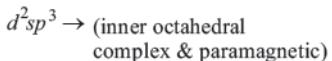
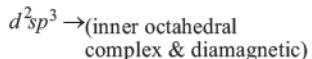
on solving  $n = 3$

As per magnetic moment, it has three unpaired electron.

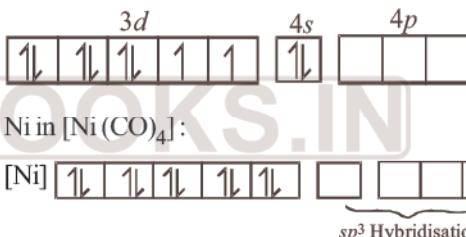
$\text{Cr}^{3+}$  will have configuration as =



67. (c)  $[\text{Co}(\text{NH}_3)_6]^{3+}$   $\text{Co}^{3+}(27-3=24)$



68. (b)  ${}_{28}\text{Ni}$ :

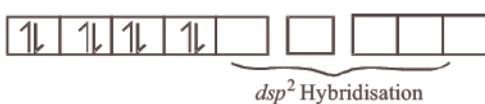


Remember CO is a strong ligand

$\text{Ni}^{2+}$ :

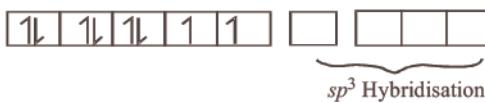


$\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$



Remember  $\text{CN}^-$  is also a strong ligand

$\text{Ni}^{2+}$  in  $[\text{NiCl}_4]^{2-}$



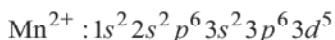
$\text{Cl}^-$  is a weak ligand, hence no pairing of electrons takes place

69. (b)  $\text{CN}^-$  is a strong field ligand as it is a psuedohalide ion.



Psuedohalide ions are strong coordinating ligands and hence have the tendency to form  $\sigma$ -bond (from the pseudo halide to the metal) and  $\pi$ -bond (from the metal to pseudo halide).

70. (b) Since  $\text{H}_2\text{O}$  is a weak ligand, it will not cause pairing of electrons in the metal ion  $\text{Mn}^{2+}$ . Thus electronic configuration of the metal ( $\text{Mn}^{2+}$ ) in the complex will be



i.e. 5 unpaired electrons.

71. (d) Co here is in +3 oxidation state

Co	<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	<table border="1"><tr><td><math>\uparrow\downarrow</math></td></tr></table>	$\uparrow\downarrow$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$				
$\uparrow\downarrow$								
$\text{Co}^{3+}$	<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td><td><math>\uparrow</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	<table border="1"><tr><td> </td></tr></table>	
$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$				

Unpaired electrons = 4 and  $sp^3d^2$  hybridisation and octahedral shape.

72. (d)  $\text{Cr}^{3+}$  has  $4s^0 3d^3$  electronic configuration with 3 unpaired electrons, hence paramagnetic. In other cases, pairing of  $d$ -electrons take place in presence of strong field ligands such as CO or  $\text{CN}^-$ .

In  $\text{Cr}(\text{CO})_6$  molecule 12 electrons are contributed by CO group and it contain no odd electron



<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$	<table border="1"><tr><td><math>\times</math></td></tr></table>	$\times$	<table border="1"><tr><td><math>\times</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\times$	$\times$	$\times$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$							
$\times$											
$\times$	$\times$	$\times$									
$3d$	$4s$	$4p$									

— diamagnetic



<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\times</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	<table border="1"><tr><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\times$	$\times$	<table border="1"><tr><td><math>\times</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\times$	$\times$	$\times$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$								
$\times$	$\times$											
$\times$	$\times$	$\times$										
$3d$	$4s$	$4p$										

— diamagnetic



<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$	<table border="1"><tr><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\times$	$\times$	$3d$	$4s$	$4p$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$							
$\times$	$\times$										

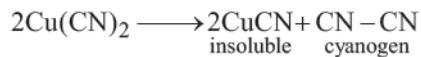
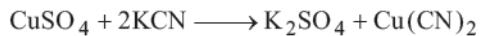
— diamagnetic



<table border="1"><tr><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\uparrow\downarrow</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$	<table border="1"><tr><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$\times$	$\times$	$3d$	$4s$	$4p$
$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\times$	$\times$							
$\times$	$\times$										

— Paramagnetic

73. (b) Copper sulphate react with KCN to give white ppt of  $\text{Cu}(\text{CN})_2$  and cyanogen gas. The insoluble copper cyanide dissolve in excess of KCN and give soluble potassium cuprocyanide



74. (a) (CO) carbonyl group being a strong ligand paired all electrons present in  $d$  orbital of Ni.

In  $[\text{Ni}(\text{CO})_4]$  complex, Ni will have  $3d^{10}$  configuration. It has tetrahedral geometry but diamagnetic as there are no unpaired electrons.

75. (b) As in  $[\text{NiCl}_4]^{2-}$ , chloride ion being a weak ligand is not able to pair up the  $d-e^-$ s.

76. (d) In  $[\text{Cr}(\text{NH}_3)_6]\text{Br}_3$ , Cr is in +3 oxidation state etc.

$24$	<table border="1"><tr><td><math>1</math></td><td><math>1</math></td><td><math>1</math></td><td><math>1</math></td><td><math>1</math></td></tr></table>	$1$	$1$	$1$	$1$	$1$	$3d$	$4s$	$4p$
$1$	$1$	$1$	$1$	$1$					

$\text{Cr}^{+3}$	<table border="1"><tr><td><math>1</math></td><td><math>1</math></td><td><math>1</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$1$	$1$	$1$	$\times$	$\times$	$3d$	$4s$	$4p$
$1$	$1$	$1$	$\times$	$\times$					

$d^2sp^3$  hybridized

$\text{Cr}^{+3}$	<table border="1"><tr><td><math>1</math></td><td><math>1</math></td><td><math>1</math></td><td><math>\times</math></td><td><math>\times</math></td></tr></table>	$1$	$1$	$1$	$\times$	$\times$	$3d$	$4s$	$4p$
$1$	$1$	$1$	$\times$	$\times$					

Its ion is octahedral in nature. Due to the presence of three unpaired electrons it is paramagnetic.

77. (b)

Atom/Ion Complex	Configuration				No. of unpaired electrons	Magnetic nature
$\text{Ni}^{2+} (d^8)$ $[\text{NiCl}_4]^{2-}$	$3d$	$4s$	$4p$		2	Paramagnetic
					2	Paramagnetic
$[\text{Ni}(\text{CN})_4]^{2-}$			$sp^3$	$dsp^2$	0	Diamagnetic
$\text{Ni} (d^8 s^2)$ $[\text{Ni}(\text{CO})_4]$			$1\downarrow$	$sp^3$	2	Paramagnetic
					0	Diamagnetic

78. (d) In the formation of a coordinate bond, the ligands donate a pair of electrons to the metal atom. Further nitrogen and oxygen has great tendency to donate the pair of electrons in most of the compounds. Therefore, both nitrogen and oxygen are common donor atoms in ligands.
79. (a) According to VSEPR theory, a molecule with six bond pairs must be octahedral.

80. (b)  $[\text{Fe}(\text{CO})_5]$

$$\text{EAN} = \text{Z} - \text{O.N.} + 2(\text{C.N.})$$

$$= 26 - 0 + 2(5)$$

$$= 26 + 10$$

$$= 36$$

Only one central metal atom/ion is present and it follows EAN rule, so it is mononuclear.

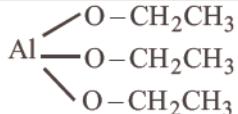
81. (a) Grignard's reagent ( $\text{RMgX}$ ) is a  $\sigma$ -bonded organometallic compound.

82. (c)  $[\text{Fe}(\text{CO})_4]^{2-}$

Since metal atom is carrying maximum  $-ve$  charge therefore, it would show maximum synergic bonding as a resultant C—O bond length would be maximum.

83. (a) As  $+ve$  charge on the central metal atom increases, the less readily the metal can donate electron density into the  $\pi^*$  orbitals of CO ligand to weaken the C—O bond. Hence, the C—O bond would be strongest in  $[\text{Mn}(\text{CO})_6]^+$ .

84. (a) Triethoxyaluminium has no Al—C linkage



85. (a) The number of carbon atom found in  $\pi$  bonded organometallic compounds is indicated by the greek latter ' $\eta$ ' with a number. The prefixes  $\eta^2$ ,  $\eta^5$  and  $\eta^6$  indicate that 2, 5 and 6 carbon atom are bound to the metal in the compound.  $(\text{CH}_3)_4\text{Sn}$  does not involve any pi ( $\pi$ ) bond formation.  $(\text{CH}_3)_4\text{Sn}$  is a  $\sigma$  bonded organometallic compound.

86. (d) In metal carbonyl complexes,  $\sigma$  and  $\pi$  both bonds are present because of synergic bonding. Thus,  $[\text{Co}(\text{CO})_5(\text{NH}_3)]^{2+}$  has  $\sigma$  and  $\pi$  bonding.

87. (a) Organometallic compounds are those compounds in which there is a bond which involve metal-carbon bond. In  $[\text{Ni}(\text{CO})_4]$  there are bond involving Ni—C.

In chlorophyll, there are 4 bonds between Mg—N.



M—C  $\pi$  bond in metal carbonyl which is formed by the donation of an electron pair from a filled  $d$ -orbital of metal into the vacant anti bonding  $\pi$ -orbital of CO, strengthens the M—C  $\sigma$  bond. This is called synergic effect.

# 24

## Haloalkanes and Haloarenes



Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Preparation and properties of haloalkanes	elimination/dehydration reaction	1	A								
	Wurtz reaction	1	A								
Preparation and properties of haloarenes	conversion(halogenation/reduction)					1	A				
	elimination/substitution/addition									1	A
	optical activity in biphenyls									1	D

LOD - Level of Difficulty

E - Easy

A - Average

D - Difficult

Qns - No. of Questions

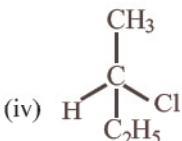
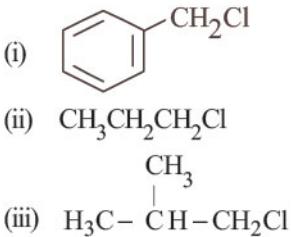
### Topic 1: Preparation and Properties of Haloalkanes

- Elimination reaction of 2-Bromo-pentane to form pent-2-ene is: *[2020]*
  - $\beta$ -Elimination reaction
  - Follows Zaitsev rule
  - Dehydrohalogenation reaction
  - Dehydration reaction
  - (A), (C), (D)
  - (B), (C), (D)
  - (A), (B), (D)
  - (A), (B), (C)
- Which of the following alkane cannot be made in good yield by Wurtz reaction? *[2020]*
  - 2,3-Dimethylbutane
  - n-Heptane
  - n-Butane
  - n-Hexane
- In an S<sub>N</sub>1 reaction on chiral centres there is : *[2015 RS]*
  - 100 % racemization
  - inversion more than retention leading to partial racemization
  - 100 % retention
  - 100 % inversion

4. Two possible stereo-structures of CH<sub>3</sub>CHOH.COOH, which are optically active, are called. *[2015 RS]*

- (a) Diastereomers      (b) Atropisomers  
 (c) Enantiomers      (d) Mesomers

5. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses? *[2014]*

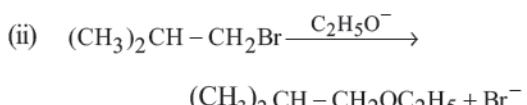
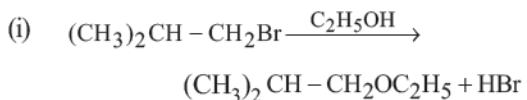


- (a) (i) and (ii)      (b) (ii) and (iv)  
 (c) (iii) and (iv)      (d) (i) and (iv)

6. Which of the following acids does not exhibit optical isomerism ? *[2012]*

(a) Maleic acid      (b)  $\alpha$ -amino acids  
 (c) Lactic acid      (d) Tartaric acid

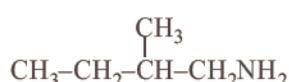
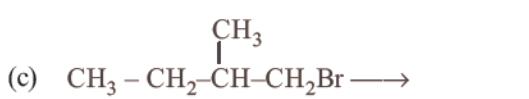
7. Consider the reactions : *[2011 M]*



The mechanisms of reactions (i) and (ii) are respectively :

- (a)  $S_N1$  and  $S_N2$       (b)  $S_N1$  and  $S_N1$   
 (c)  $S_N2$  and  $S_N2$       (d)  $S_N2$  and  $S_N1$

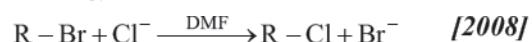
8. Which one is a nucleophilic substitution reaction among the following ? *[2011]*



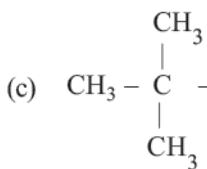
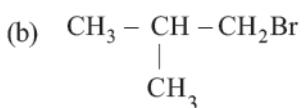
9. Which of the following reactions is an example of nucleophilic substitution reaction? *[2009]*

- (a)  $2RX + 2Na \rightarrow R - R + 2NaX$   
 (b)  $RX + H_2 \rightarrow RH + HX$   
 (c)  $RX + Mg \rightarrow RMgX$   
 (d)  $RX + KOH \rightarrow ROH + KX$

10. In an  $S_N2$  substitution reaction of the type



which one of the following has the highest reactivity rate?



11. How many stereoisomers does this molecule have? *[2008]*

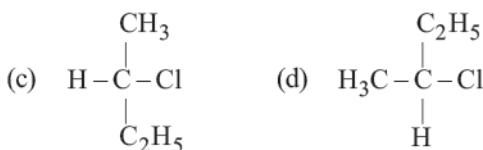
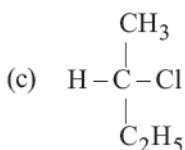
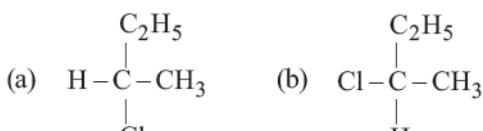
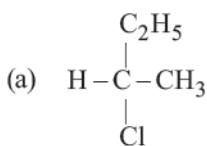


- (a) 4      (b) 6  
 (c) 8      (d) 2

12. If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that *[2007]*

- (a) the compound is certainly meso  
 (b) there is no compound in the solvent  
 (c) the compound may be a racemic mixture  
 (d) the compound is certainly achiral.

13.  $CH_3 - CHCl - CH_2 - CH_3$  has a chiral centre. Which one of the following represents its R-configuration? *[2007]*



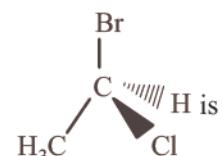
14. For (i)  $I^-$ , (ii)  $Cl^-$ , (iii)  $Br^-$ , the increasing order of nucleophilicity would be *[2007]*

- (a)  $Cl^- < Br^- < I^-$       (b)  $I^- < Cl^- < Br^-$   
 (c)  $Br^- < Cl^- < I^-$       (d)  $I^- < Br^- < Cl^-$

15. Which of the following is *not* chiral? [2006]

- (a) 2, 3-Dibromopentane
- (b) 3-Bromopentane
- (c) 2-Hydroxypropanoic acid
- (d) 2-Butanol

16. The chirality of the compound [2005]



- (a) R
- (b) S
- (c) E
- (d) Z

17. Which of the following undergoes nucleophilic substitution exclusively by  $S_N1$  mechanism? [2005]

- (a) Ethyl chloride
- (b) Isopropyl chloride
- (c) Chlorobenzene
- (d) Benzyl chloride

18. The molecular formula of diphenylmethane,



How many structural isomers are possible when one of the hydrogens is replaced by a chlorine atom? [2004]

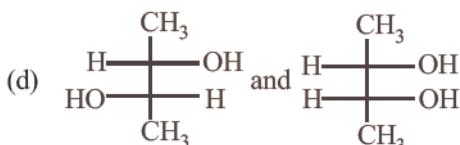
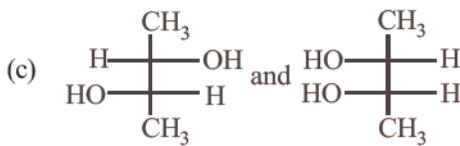
- (a) 6
- (b) 4
- (c) 8
- (d) 7

19. Which of the following is least reactive in a nucleophilic substitution reaction. [2004]

- (a)  $(CH_3)_3C - Cl$
- (b)  $CH_2 = CHCl$
- (c)  $CH_3CH_2Cl$
- (d)  $CH_2 = CHCH_2Cl$

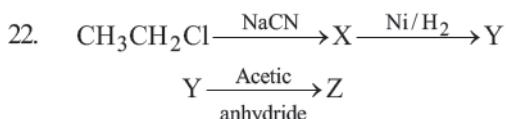
20. Which of the following pairs of compounds are enantiomers? [2003]

- (a) and
- (b) and



21. Reactivity order of halides for dehydrohalogenation is [2002]

- (a)  $R - F > R - Cl > R - Br > R - I$
- (b)  $R - I > R - Br > R - Cl > R - F$
- (c)  $R - I > R - Cl > R - Br > R - F$
- (d)  $R - F > R - I > R - Br > R - Cl$

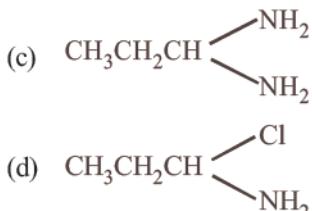


Z in the above reaction sequence is [2002]

- (a)  $CH_3CH_2CH_2NHCOCH_3$
- (b)  $CH_3CH_2CH_2NH_2$
- (c)  $CH_3CH_2CH_2CONHCH_3$
- (d)  $CH_3CH_2CH_2CONHCOCH_3$

23. When  $CH_3CH_2CHCl_2$  is treated with  $NaNH_2$ , the product formed is [2002]

- (a)  $CH_3 - CH = CH_2$
- (b)  $CH_3 - C \equiv CH$



24. An organic compound A ( $C_4H_9Cl$ ) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then A is [2001]

- (a) tert-butyl chloride
- (b) sec-butyl chloride
- (c) isobutyl chloride
- (d) n-butyl chloride

- |     |   |        |     |   |
|-----|---|--------|-----|---|
| 25. | $\text{CH}_3 - \text{CH}_2 - \underset{\text{Cl}}{\overset{ }{\text{C}}} - \text{CH}_3$ obtained by chlorination<br>of n-butane, will be  | [2001] | 33. | An important chemical method to resolve a racemic mixture makes use of the formation of [1994]<br>(a) a meso compound (b) enantiomers<br>(c) diasteromers (d) racemates         |
|     | (a) l-form (b) d-form<br>(c) Meso form (d) Racemic mixture  |        | 34. | The process of separation of a racemic modification into d and l-enantiomers is called [1994]<br>(a) Resolution<br>(b) Dehydration<br>(c) Revolution<br>(d) Dehydrohalogenation |
| 26. | Which is a chiral molecule?   | [1999] | 35. | When chlorine is passed through propene at 400°C, which of the following is formed? [1993]<br>(a) PVC<br>(b) Allyl chloride<br>(c) Alkyl chloride<br>(d) 1, 2-Dichloroethane    |
| 27. | 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is  | [1998] | 36. | Which of the following is an optically active compound? [1988]<br>(a) 1-Butanol (b) 1-Propanol<br>(c) 2-Chlorobutane (d) 4-Hydroxyheptane                                       |
| 28. | Which of the following compounds is not chiral?   | [1998] |     | Topic 2: Preparation and Properties of Haloarenes   |
|     | (a) $\text{DCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (b) $\text{CH}_3\text{CH}_2\text{CHDCl}$<br>(c) $\text{CH}_3\text{CHDCH}_2\text{Cl}$ (d) $\text{CH}_3\text{CHClCH}_2\text{D}$   |        | 37. | The hydrolysis reaction that takes place at the slowest rate, among the following is [NEET Odisha 2019]<br>(a)  |
| 29. | Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions?  | [1998] |     | $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{aq. NaOH}} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$   |
|     | (a) Methyl acetate (b) Acetonitrile<br>(c) Diethyl ether (d) Acetamide  |        | (b) | $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{aq. NaOH}} \text{C}_6\text{H}_5\text{CH}_2^+$  |
| 30. | The reaction:   |        |     | (c) $\text{H}_3\text{C}-\text{CH}_2-\text{Cl} \xrightarrow{\text{aq. NaOH}} \text{H}_3\text{C}-\text{CH}_2-\text{OH}$   |
|     | $\text{CH}_3(\text{CH}_2)_5 \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Br} \end{array} \xrightarrow{\text{OH}^-} \text{HO} \begin{array}{c} \text{H} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} (\text{CH}_2)_5\text{CH}_3$ |        |     | (d) $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{Cl} \xrightarrow{\text{aq. NaOH}} \text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$   |
|     | is described as   | [1997] |     |   |
| 31. | Which of the following will exhibit chirality?  | [1996] |     |   |
|     | (a) 2-Methylhexane (b) 3-Methylhexane<br>(c) Neopentane (d) Isopentane  |        |     |   |
| 32. | Zerevitinov's determination of active hydrogen in a compound is based upon its reaction with  | [1994] |     |   |
|     | (a) Na (b) $\text{CH}_3\text{MgI}$<br>(c) Zn (d) Al.  |        |     |   |

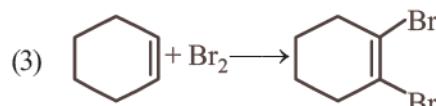
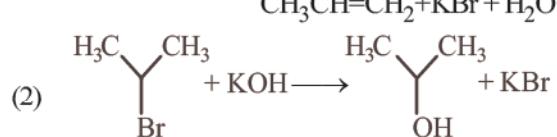
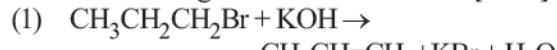
38. The compound  $C_7H_8$  undergoes the following reactions:  
[2018]



The product 'C' is

- (a) *m*-bromotoluene
- (b) *o*-bromotoluene
- (c) *p*-bromotoluene
- (d) 3-bromo-2,4,6-trichlorotoluene

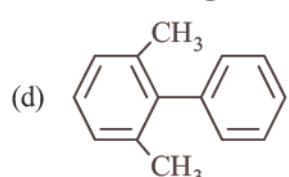
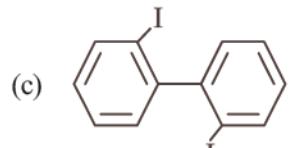
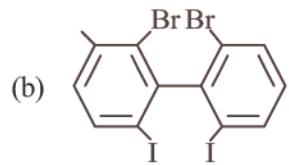
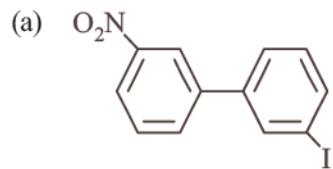
39. For the following reactions : [2016]



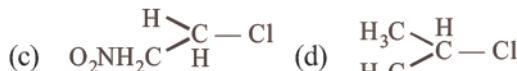
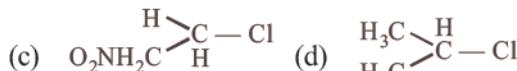
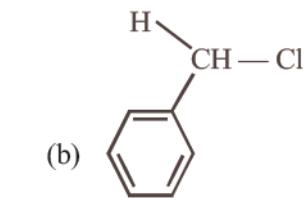
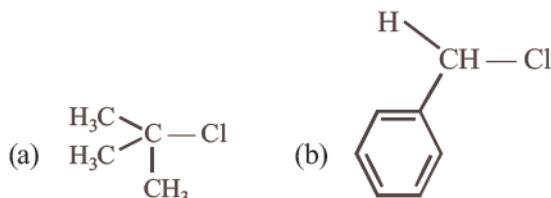
Which of the following statements is correct ?

- (a) (1) and (2) are elimination reactions and (3) is addition reaction
- (b) (1) is elimination, (2) is substitution and (3) is addition reaction
- (c) (1) is elimination, (2) and (3) are substitution reactions
- (d) (1) is substitution, (2) and (3) are addition reactions

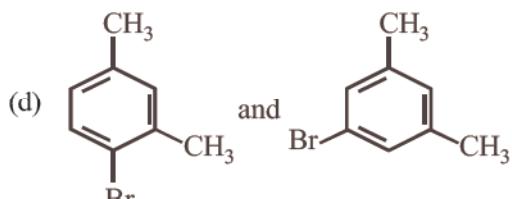
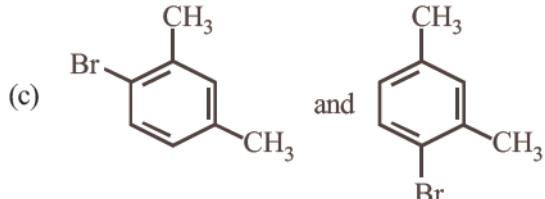
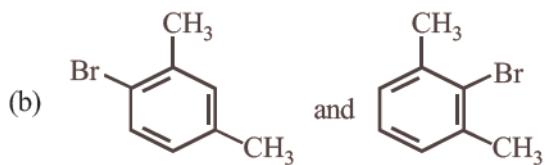
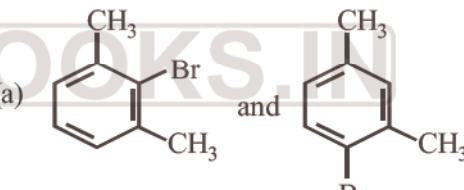
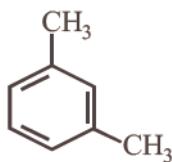
40. Which of the following biphenyls is optically active ? [2016]



41. In which of the following compounds, the C - Cl bond ionisation shall give most stable carbonium ion? [2015]

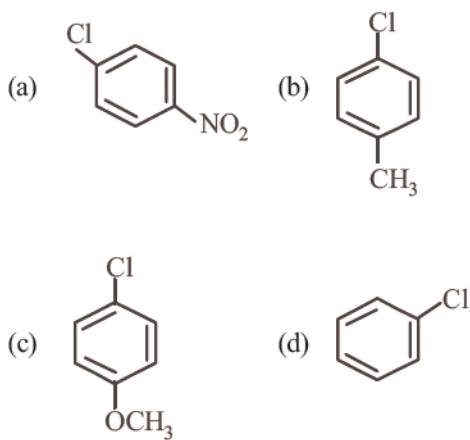


42. What products are formed when the following compounds is treated with  $Br_2$  in the presence of  $FeBr_3$ ? [2014]



43. Which of the following compounds undergoes nucleophilic substitution reaction most easily?

[2011 M]



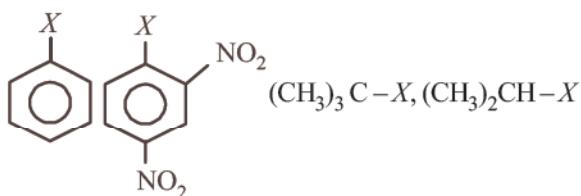
44. The reaction of toluene with  $\text{Cl}_2$  in presence of  $\text{FeCl}_3$  gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are : [2010]

- (a) X = Benzal chloride, Y = *o*-Chlorotoluene
- (b) X = *m*-Chlorotoluene, Y = *p*-Chlorotoluene
- (c) X = *o*-and *p*-Chlorotoluene,  
Y = Trichloromethyl – benzene
- (d) X = Benzyl chloride, Y = *m*-Chlorotoluene

45. Which one is most reactive towards  $\text{S}_{\text{N}}1$  reaction?

- (a)  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$  [2010]
- (b)  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$
- (c)  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Br}$
- (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$

46. The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is: [2010]



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

47. Benzene reacts with  $\text{CH}_3\text{Cl}$  in the presence of anhydrous  $\text{AlCl}_3$  to form: [2009]

- (a) chlorobenzene
- (b) benzylchloride
- (c) xylene
- (d) toluene

48. The replacement of chlorine of chlorobenzene to give phenol requires drastic conditions, but the chlorine of 2,4-dinitrochlorobenzene is readily replaced since, [1997]

- (a) nitro groups make the aromatic ring electron rich at ortho/para positions
- (b) nitro groups withdraw electrons from the meta position of the aromatic ring
- (c) nitro groups donate electrons at meta position
- (d) nitro groups withdraw electrons from ortho/para positions of the aromatic ring

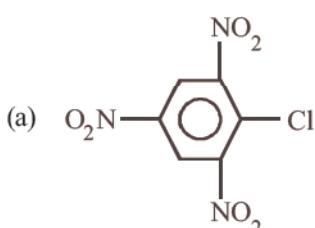
49. Benzene reacts with *n*-propyl chloride in the presence of anhydrous  $\text{AlCl}_3$  to give [1993]

- (a) 3 – Propyl – 1 – chlorobenzene
- (b) *n*-Propylbenzene
- (c) No reaction
- (d) Isopropylbenzene.

50. Chlorobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield [1993]

- (a) Phenol
- (b) Benzene
- (c) Ethylbenzene
- (d) Phenyl ether.

51. Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative? [1989]

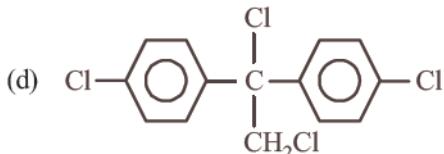


- (b)
- (c)
- (d)

### Topic 3: Some Important Polyhalogen Compounds

52. Trichloroacetaldehyde,  $\text{CCl}_3\text{CHO}$  reacts with chlorobenzene in presence of sulphuric acid and produces: [2009]

- (a)
- (b)
- (c)



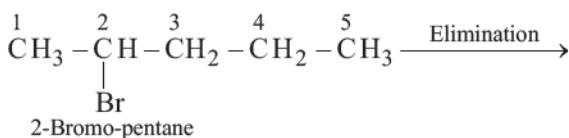
53. Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere? [2004]
- (a) Polyhalogens      (b) Ferrocene  
 (c) Fullerenes      (d) Freons
54. Chloropicrin is obtained by the reaction of [2004]
- (a) steam on carbon tetrachloride  
 (b) nitric acid on chlorobenzene  
 (c) chlorine on picric acid  
 (d) nitric acid on chloroform
55. Industrial preparation of chloroform employs acetone and [1993]
- (a) Phosgene  
 (b) Calcium hypochlorite  
 (c) Chlorine gas  
 (d) Sodium chloride.
56. Phosgene is a common name for [1988]
- (a) phosphoryl chloride  
 (b) Thionyl chloride  
 (c) Carbon dioxide and phosphine  
 (d) Carbonyl chloride.

### ANSWER KEY

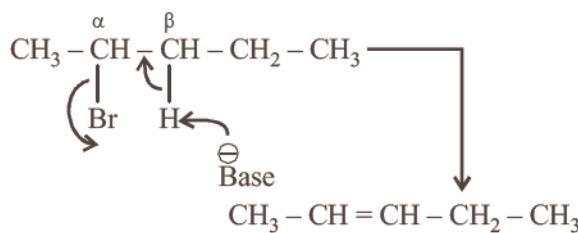
1	(d)	7	(a)	13	(b)	19	(b)	25	(d)	31	(b)	37	(b)	43	(a)	49	(d)	55	(b)
2	(b)	8	(c)	14	(a)	20	(b)	26	(c)	32	(b)	38	(a)	44	(c)	50	(b)	56	(d)
3	(b)	9	(d)	15	(b)	21	(b)	27	(c)	33	(c)	39	(b)	45	(c)	51	(a)		
4	(c)	10	(d)	16	(a)	22	(a)	28	(a)	34	(a)	40	(b)	46	(a)	52	(c)		
5	(N)	11	(a)	17	(d)	23	(b)	29	(c)	35	(b)	41	(b)	47	(d)	53	(d)		
6	(a)	12	(a)	18	(b)	24	(a)	30	(d)	36	(c)	42	(c)	48	(d)	54	(d)		

# Hints & Solutions

1. (d)



Mechanism :

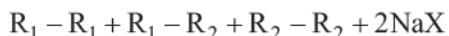
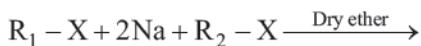


It is an  $\beta$  elimination reaction as  $\beta$  hydrogen is abstracted and results more substituted alkene, which follows Zaitsev's rule.  
Since 'H' and 'Br' are removed, it is dehydrohalogenation.

2. (b) Wurtz reaction is used to prepare symmetrical alkanes like  $R_1 - R_1$ , as

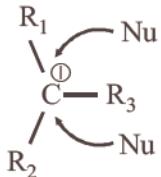


If  $R_1$  and  $R_2$  are different, then mixture of alkanes may be obtained as



Hence,  $n$ -heptane cannot be made in good yield using Wurtz reaction, since it is unsymmetrical alkene.

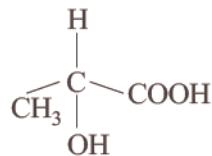
3. (b) In  $S_N1$  reaction, carbocation a planar species as intermediate is formed.



So attack from below or above the plane can take place.

If 50% attack below and above the plane of carbocation take place than 100% racemization occurs but it may not be highly probable.  
*i.e.* if inversion occurs more than retention leading to partial racemization.

4. (c)

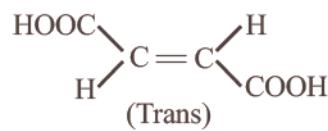
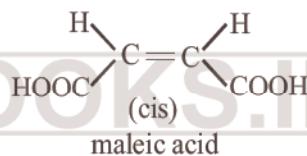


Four different Substituent, only one chiral centre.  
Hence only enantiomers are possible.

5.

(N) The compound in option (iv) will undergo  $S_N1$  reaction with KOH solution. Hence, only this compound will undergo partial racemisation. Compounds given in other options are not chiral.

6. (a)



It shows geometrical isomerism but does not show optical isomerism.

7.

(a) First reaction is  $S_N1$  reaction because  $C_2H_5OH$  is used as solvent which is a weak nucleophile.

Second reaction is  $S_N2$  reaction because  $C_2H_5O^-$  is a strong nucleophile.



A strong nucleophile favours the  $S_N2$  reaction and a weak nucleophile favours the  $S_N1$  reaction.

8.

(c) Nucleophilic substitution reactions are the most common reactions of alkyl halides.

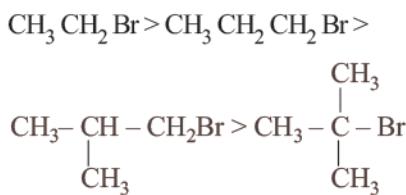


Because of high electronegativities of the halogen atom, the carbon halogen ( $C - X$ ) is highly polarised covalent bond. Thus, the carbon atom of the  $C - X$  bond becomes a good site for attack by nucleophiles (electron rich species).

9. (d) In nucleophilic substitution, a nucleophile provides an electron pair to the substrate and the leaving group departs with an electron pair.

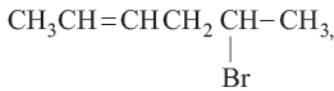


10. (d)  $S_N2$  mechanism is followed in case of primary and secondary halides i.e.,  $S_N2$  reaction is favoured by small groups on the carbon atom attached to halogens so reactivity order is:



i.e. option (d) is correct.

11. (a) In the molecule



the number of stereoisomers is given by sum of geometrical isomers (because of presence of  $\text{C}=\text{C}$ ) and optical isomers (because of presence of chiral carbon atom).

Number of geometrical isomers = 2 (one  $\text{C}=\text{C}$  is present).

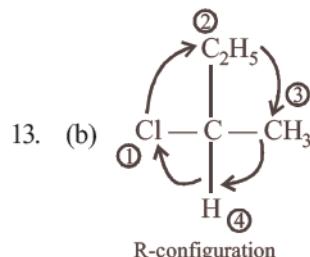
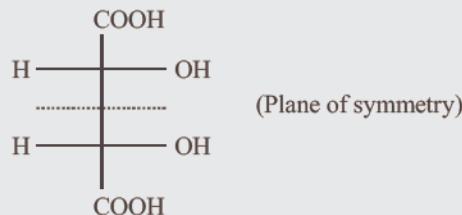
Number of optical isomers = 2 (one chiral carbon atom).

Total number of stereoisomers =  $2 + 2 = 4$

12. (a) Compounds which do not show optical activity inspite of the presence of chiral carbon atoms are called *meso*-compounds.



The absence of optical activity in these compound is due to the presence of a plane of symmetry in their molecules. e.g. meso-tartaric acid is optically inactive.



14. (a) Nucleophilicity increases down the periodic table :  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

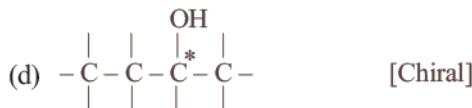
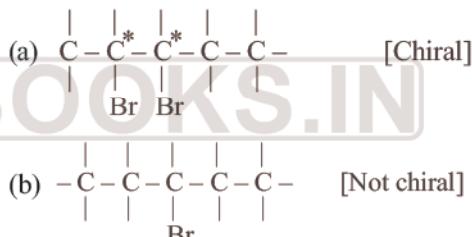


Nucleophilicity governs the kinetics of a reaction while basicity determines its thermodynamics.

Since, electronegativity decreases down the group (or electropositivity increases), nucleophilicity also increases down the group. But the order of basicity is:

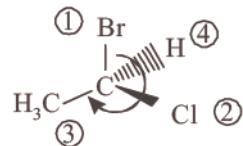


15. (b)



\* marked are chiral carbons.

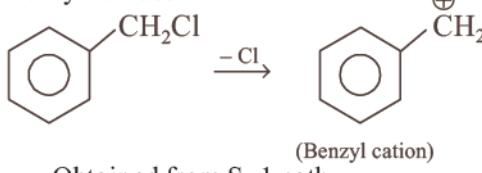
16. (a) Clockwise rotation.



Hence configuration is R.

If the eye travel in a clockwise direction, the configuration is (R) as the order of priority is  $\text{Br} > \text{Cl} > \text{CH}_3 > \text{H}$ .

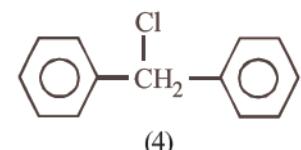
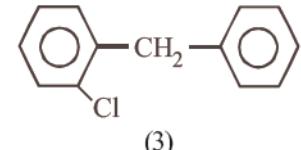
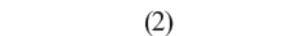
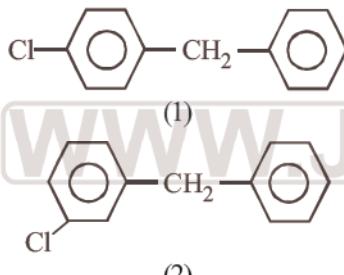
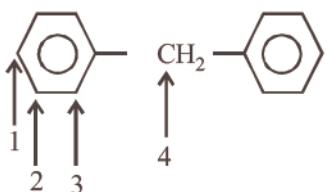
17. (d)  $S_N1$  reaction is favoured by heavy groups on the carbon atom attached to halogen i.e Benzyl > allyl > tertiary > secondary > primary > alkyl halides



Obtained from  $S_N1$  path.

This molecule is resonance stabilised.

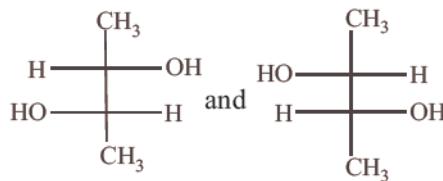
18. (b) In diphenylmethane monochlorination at following positions will produce structured isomers



19. (b)  $H_2C = CHCl$  is capable of showing resonance which develops a partial double bond, character to C–Cl bond, thereby making it less reactive towards nucleophilic substitution.



20. (b) Compound which are mirror image of each other and are not superimposable are termed as enantiomers.



21. (b) The order of atomic size of halogens decrease in the order I > Br > Cl > F

i.e on moving down a group atomic size increases. Further the bond length of C-X bond decreases in the order

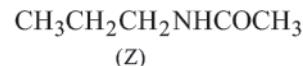
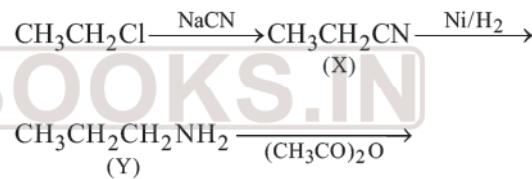


and hence the bond dissociation energy decreases in the order

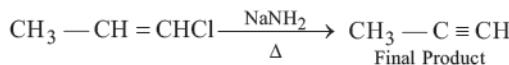


hence R – I being a weakest bond break most easily. Hence R – I is most reactive.

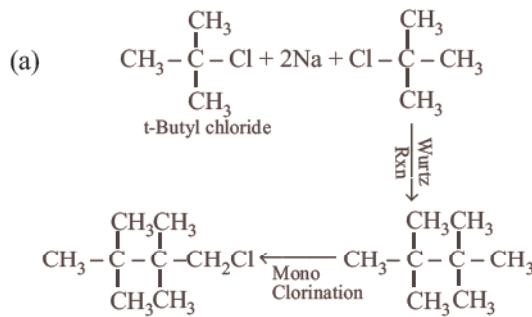
22. (a)

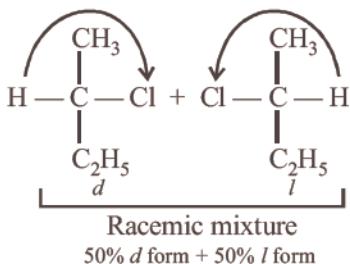
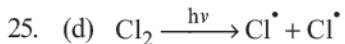


23. (b)  $CH_3-CH_2-CHCl_2 \xrightarrow[\Delta]{NaNH_2}$



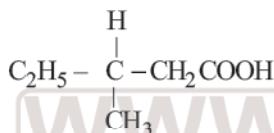
24. (a)



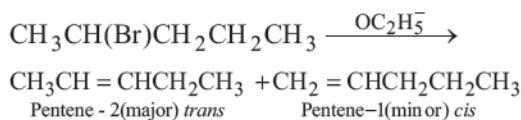


Chlorination of alkane takes place via free radical formation.  $\text{Cl}^\bullet$  may attack on either side and gives a racemic mixture.

26. (c) Chiral molecules are those molecules which have atleast one asymmetric carbon atom (a carbon atom attached to 4 different groups). This is true in case of 3-methylpentanoic acid.

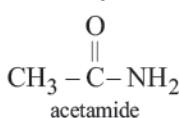
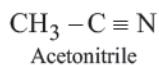
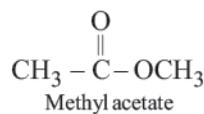
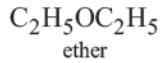


27. (c) Potassium ethoxide is a strong base, and 2-bromopentane is a 2° bromide, so elimination reaction predominates

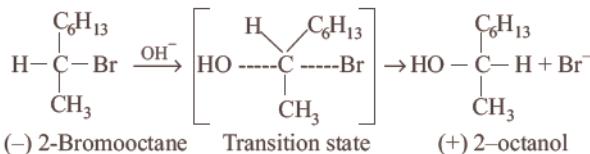


Since, *trans*- alkene is more stable than *cis*, thus *trans*-pentene -2 is the main product.

28. (a) Due to absence of a chiral C-atom. D — CH<sub>2</sub> — CH<sub>2</sub> — CH<sub>2</sub>Cl molecule is not a chiral molecule.
29. (c) The compound is diethyl ether ( $\text{CH}_3\text{CH}_2\text{OCH}_3$ ) which is resistant to nucleophilic attack by hydroxyl ion due to absence of double or triple bond, whereas all other compounds given are unsaturated.



30. (d) When (-) 2-bromooctane is allowed to react with sodium hydroxide under given conditions, where second order kinetics is followed, the product obtained is (+) 2-octanol.

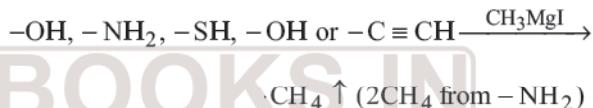


In this reaction Walden Inversion takes place so it is an example of  $S_N2$ -reaction.

31. (b)  $\text{H}_3\text{C} - \text{CH}_2 - \overset{*}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$   
3-Methylhexane

Due to presence of four different groups on carbon, ( $\text{C}^*$ ) it is chiral

32. (b) Number of active hydrogen in a compound corresponds to the number of moles of  $\text{CH}_4$  evolved per mole of the compound.



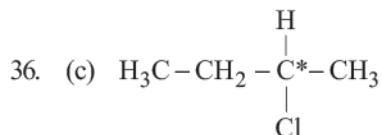
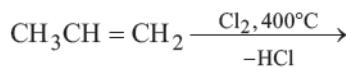
33. (c) Racemic mixtures are resolved by the formation of Diastereomers.



Enantiomers have same physical and chemical properties except rotation of plane polarized light. Diasteromers have different physical and chemical properties.

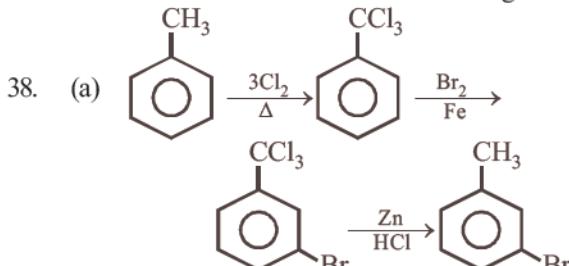
34. (a) Resolution.

35. (b) At high temp. i.e., 400°C substitution occurs in preference to addition.



The compound containing a chiral carbon atom i.e., (a carbon atom which is attached to four different substituents is known as a chiral carbon atom) is optically active.

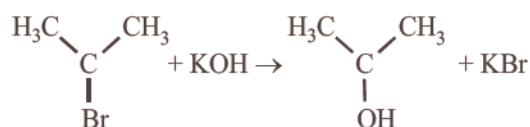
37. (b) Aryl halides do not give substitution reactions due to partial double bond character between carbon and halogen.



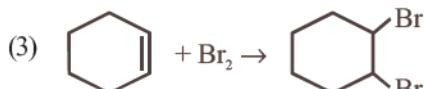
39. (b) (1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KOH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$

This is dehydrohalogenation reaction which is an example of elimination reaction.

(2)



Replacement of  $\text{Br}^-$  by  $\text{OH}^-$  is substitution reaction thus, it is a nucleophilic substitution reaction.



Above reaction involves addition of  $\text{Br}_2$  across double bond. Thus, it is called addition reaction.

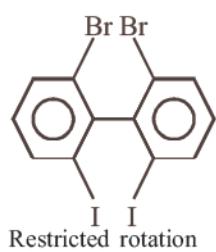
40. (b)

In option (a), there is no chiral carbon.

In option (c), there exist a center of symmetry.

In option (d), there exist a plane of symmetry.

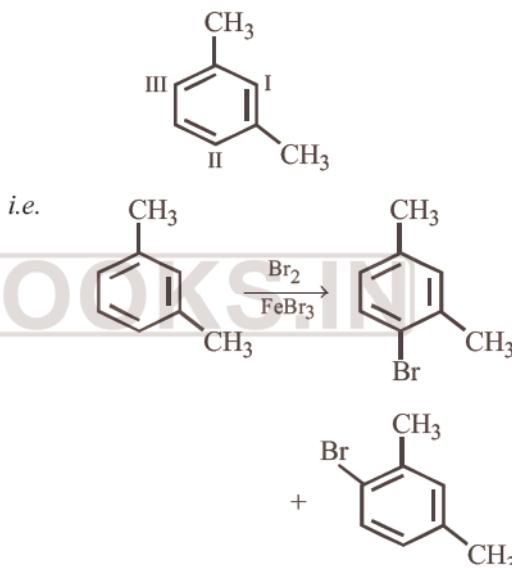
In option (d), both the rings are not in the same plane and the rotation is restricted around the single bond.



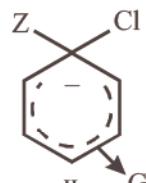
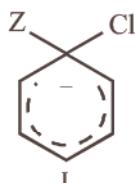
Biphenyl compounds are devoid of individual chiral carbon atoms, but *o*-substituted biphenyl show optical isomerism. This is due to the fact that, both the rings are not in the same plane because of steric hindrance of the groups present in *o*-position. Also, these groups restrict the rotation around the single bond and hence they must exist in two non-super imposable mirror images of each other.

41. (b)

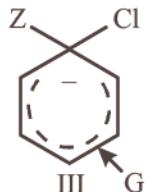
42. (c) Methyl group is ortho para directing but due to steric hindrance effect, generated by two  $\text{CH}_3$  groups substitution will not take place on position (I). Hence, only two products are possible.



43. (a) To compare the rates of substitution, in chlorobenzene, electron-withdrawing group, and chlorobenzene having electron-releasing group, we compare the structures carbanion I (from chlorobenzene), II (from chlorobenzene containing electron-withdrawing group) and III (from chlorobenzene containing electron-releasing group).



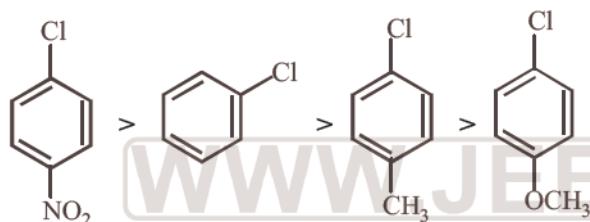
G withdraws electrons, neutralises (disperses) –ve charge of the ring, stabilises carbanion, facilitates  $S_N$  reaction (**activation effect**)



G releases electrons, intensifies –ve charge, destabilizes carbanion, retards  $S_N$  reaction (**deactivation**)

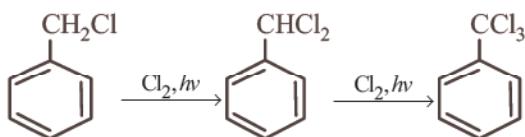
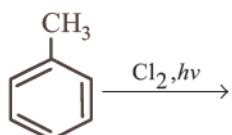
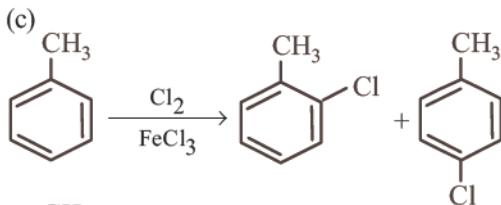
$\text{NO}_2$  is activating group and  $\text{CH}_3$  and  $\text{OCH}_3$  are deactivating group.

Hence, the correct order of nucleophilic substitution reaction is :



In  $S_N$  reactions, a carbanion is formed as an intermediate, so any substituent that increases the stability of carbanion and hence the transition state leading to its formation will enhance the  $S_N$  reactions.

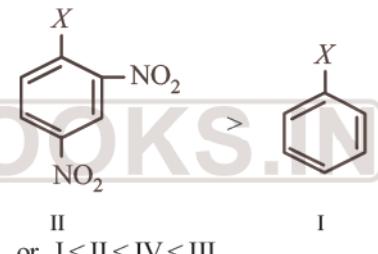
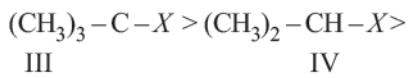
44.



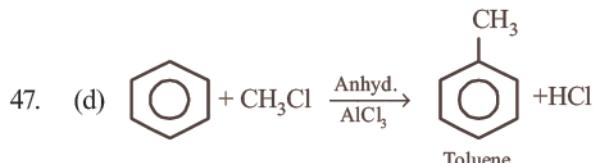
45. (c)  $S_N1$  reactions involve the formation of carbocations, hence higher the stability of intermediate carbocation, more will be reactivity of the parent alkyl halide. The tertiary carbocation formed from (c) is stabilized by two phenyl groups and one methyl group, hence most stable.

46. (a) Tertiary alkyl halide is most reactive towards nucleophilic substitution because the corresponding carbocation ( $3^\circ$ ) is most stable. Aryl halide is least reactive due to partial double bond character of the C – Cl bond.

Presence of —  $\text{NO}_2$  groups in *ortho* and *para* positions increases the reactivity of the – Cl towards nucleophiles.

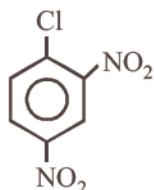


II  
or I < II < IV < III



Friedel Craft's reaction

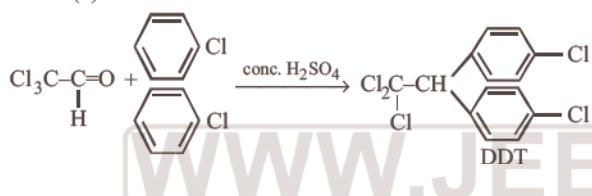
48. (d) —  $\text{NO}_2$  group is electron attracting group, so it is able to deactivate the benzene ring.



Hence, withdrawal of electrons from *ortho* & *para* position cause easy removal of –Cl atom due to development of +ve charge on *o*- and *p*-positions.

51. (a) Cl in 2, 4, 6-trinitrochlorobenzene is activated by three  $\text{NO}_2$  groups at *o*- and *p*-positions and hence, undergoes hydrolysis most readily.

52. (c)



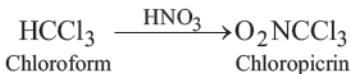
53. (d) Chlorofluorocarbons, e.g.  $\text{CF}_2\text{Cl}_2$ ,  $\text{CHF}_2\text{Cl}_2$ ,  $\text{HCF}_2\text{CHCl}_2$ . These are non-inflammable, colourless and stable upto  $550^\circ\text{C}$ . These are emitted as propellants in aerosol spray, refrigerators, fire fighting reagents etc. They absorb UV-rays in the stratosphere and

produce free atomic chlorine which results in decomposition of ozone.

 NOTES

Chlorofluorocarbons are chemically inert and hence do not react with any substance with which they come in contact and therefore, float through the atmosphere and as a result enter the stratosphere.

54. (d) Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with  $\text{HNO}_3$ .

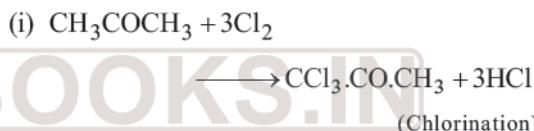


Chloropicrin is poisonous and used as an insecticide and a war gas.

55. (b) By distilling ethanol or acetone with a paste of bleaching powder (*laboratory and commercial method*).



$\text{Cl}_2$ , so obtained acts as a mild oxidising as well as chlorinating agent



56. (d) Carbonyl chloride ( $\text{COCl}_2$ ).

25

# Alcohols, Phenols and Ethers



## Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Preparation and properties of alcohols	conversion reaction with Na/PCl <sub>5</sub> /ether formation					1	A				
Preparation and properties of phenols	preparation of phenols			1	A						
	Reimer- Tieman reaction					1	A				
	haloform reaction					1	A				
	conversion(reaction with AlCl <sub>3</sub> /ozonolysis)					1	D				
	cis trans diol									1	A
	acidity order							1	D		
Preparation and properties of ether	cleavage with HI	1	A					1	A		
	protonation of ether			1	A						
	Williamson synthesis									1	A
	substitution reactions							1	D		

## **Topic 1: Preparation and Properties of Alcohols**

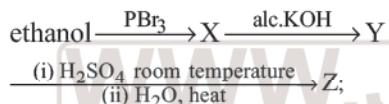


$B \xrightarrow[\text{ether}]{\text{LiAlH}_4} C$ , the end product (C) is :

7. When glycerol is treated with excess of HI, it produces: **[2010]**

(a) glycerol triiodide (b) 2-iodopropane  
(c) allyl iodide (d) propene

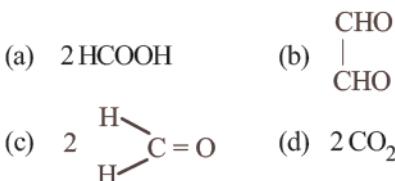
8. Consider the following reaction. **[2009]**



the product Z is:

- (a)  $\text{CH}_3\text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3$   
 (b)  $\text{CH}_3 - \text{CH}_2 - \text{O} - \text{SO}_3\text{H}$   
 (c)  $\text{CH}_3\text{CH}_2\text{OH}$   
 (d)  $\text{CH}_2 = \text{CH}_2$

9.  $\text{H}_2\text{COH} \cdot \text{CH}_2\text{OH}$  on heating with periodic acid gives: [2009]



10. Ethylene oxide when treated with Grignard reagent yields [2006]

  - (a) Tertiary alcohol
  - (b) Cyclopropyl alcohol
  - (c) Primary alcohol
  - (d) Secondary alcohol

11. Which of the following will **not** form a yellow precipitate on heating with an alkaline solution of iodine? [2004]

- (a)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$   
 (c)  $\text{CH}_3\text{OH}$   
 (d)  $\text{CH}_3\text{CH}_2\text{OH}$

12. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent? [2002]  
 (a)  $\text{PCl}_5$   
 (b) Reduction  
 (c) Oxidation with potassium dichromate  
 (d) Ozonolysis

13. Which of the following is correct? [2001]  
 (a) On reduction of any aldehyde, secondary alcohol is formed  
 (b) Reaction of vegetable oil with  $\text{H}_2\text{SO}_4$  gives glycerine  
 (c) Sucrose on reaction with  $\text{NaCl}$  gives invert sugar  
 (d) Alcoholic iodine gives iodoform with  $\text{NaOH}$

14. Propan - 1 - ol may be prepared by the reaction of propene with [2000]  
 (a)  $\text{H}_3\text{BO}_3$   
 (b)  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$   
 (c)  $\text{B}_2\text{H}_6, \text{NaOH}-\text{H}_2\text{O}_2$   
 (d)  $\text{CH}_3\text{C}=\overset{\text{O}}{\underset{\parallel}{\text{O}}}\text{-O-}\text{H}$

15. Reaction of  $\begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{O} \\ \diagup \\ \text{CH}_2 \end{array}$  with  $\text{RMgX}$  leads to formation of [1998]  
 (a)  $\text{RCHOHR}$       (b)  $\text{RCHOHCH}_3$   
 (c)  $\text{RCH}_2\text{CH}_2\text{OH}$       (d)  $\begin{array}{c} \text{R} \\ \diagup \\ \text{R}-\text{C}-\text{CH}_2\text{OH} \\ \diagdown \\ \text{R} \end{array}$

16. The stablest among the following is [1994]  
 (a)  $\text{CH}_3\text{CH}(\text{OH})_2$       (b)  $\text{ClCH}_2\text{CH}(\text{OH})_2$   
 (c)  $(\text{CH}_3)_2\text{C}(\text{OH})_2$       (d)  $\text{CCl}_3\text{CH}(\text{OH})_2$

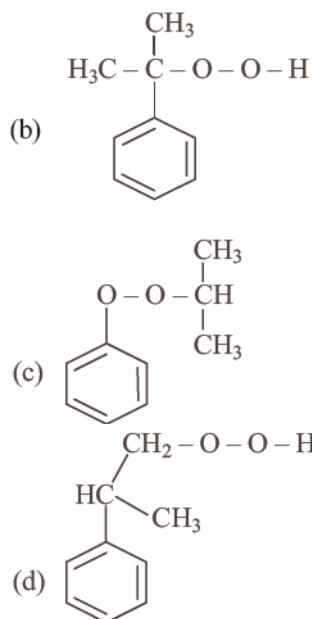
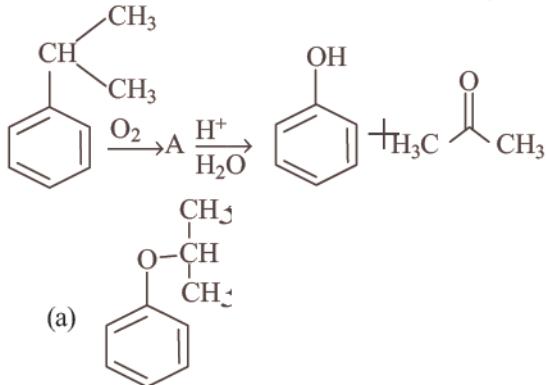
17. Which one of the following on oxidation gives a ketone? [1993]  
 (a) Primary alcohol      (b) Secondary alcohol  
 (c) Tertiary alcohol      (d) All of these

18. What is formed when a primary alcohol undergoes catalytic dehydrogenation? [1993]  
 (a) Aldehyde      (b) Ketone  
 (c) Alkene      (d) Acid

19. Methanol is industrially prepared by [1992]  
 (a) Oxidation of  $\text{CH}_4$  by steam at  $900^\circ\text{C}$   
 (b) Reduction of  $\text{HCHO}$  using  $\text{LiAlH}_4$   
 (c) Reaction  $\text{HCHO}$  with a solution of  $\text{NaOH}$   
 (d) Reduction of  $\text{CO}$  using  $\text{H}_2$  and  $\text{ZnO} - \text{Cr}_2\text{O}_3$ .
20.  $\text{HBr}$  reacts fastest with [1992]  
 (a) 2-Methylpropan-1-ol  
 (b) 2-Methylpropan-2-ol  
 (c) propan-2-ol  
 (d) propan-1-ol.
21. The compound which reacts fastest with Lucas reagent at room temperature is [1989]  
 (a) Butan-1-ol  
 (b) Butan-2-ol  
 (c) 2-Methyl propan-1-ol  
 (d) 2-Methylpropan-2-ol
22. Propene,  $\text{CH}_3\text{CH} = \text{CH}_2$  can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal to effect the above conversion ? [1989]  
 (a)  $\text{KMnO}_4$  (alkaline)  
 (b) Osmium tetroxide ( $\text{OsO}_4/\text{CH}_2\text{Cl}_2$ )  
 (c)  $\text{B}_2\text{H}_6$  and alk.  $\text{H}_2\text{O}_2$   
 (d)  $\text{O}_3/\text{Zn}$
23. Lucas reagent is [1988]  
 (a) Conc.  $\text{HCl}$  and anhydrous  $\text{ZnCl}_2$   
 (b) Conc.  $\text{HNO}_3$  and hydrous  $\text{ZnCl}_2$   
 (c) Conc.  $\text{HCl}$  and hydrous  $\text{ZnCl}_2$   
 (d) Conc.  $\text{HNO}_3$  and anhydrous  $\text{ZnCl}_2$

### Topic 2: Preparation and Properties of Phenols

24. The structure of intermediate A in the following reaction, is: [2019]



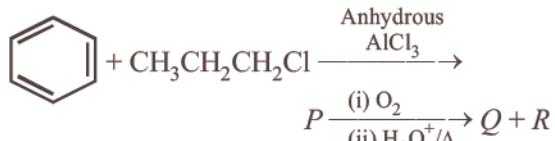
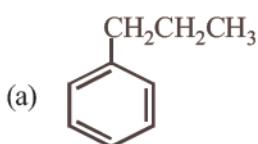
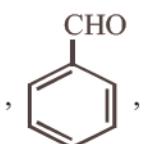
25. In the reaction [2018]
- $\text{C}_6\text{H}_5\text{OH} + \text{CHCl}_3 + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{O}^-\text{Na}^+ + \text{CHO}$
- The electrophile involved is

- (a) Dichloromethyl cation ( $\overset{\oplus}{\text{CHCl}}_2$ )  
 (b) Formyl cation ( $\overset{\oplus}{\text{CHO}}$ )  
 (c) Dichlorocarbene ( $: \text{CCl}_2$ )  
 (d) Dichloromethyl anion ( $\overset{\ominus}{\text{CHCl}}_2$ )

26. Compound  $A$ ,  $\text{C}_8\text{H}_{10}\text{O}$ , is found to react with  $\text{NaOI}$  (produced by reacting  $Y$  with  $\text{NaOH}$ ) and yields a yellow precipitate with characteristic smell.  
 $A$  and  $Y$  are respectively [2018]

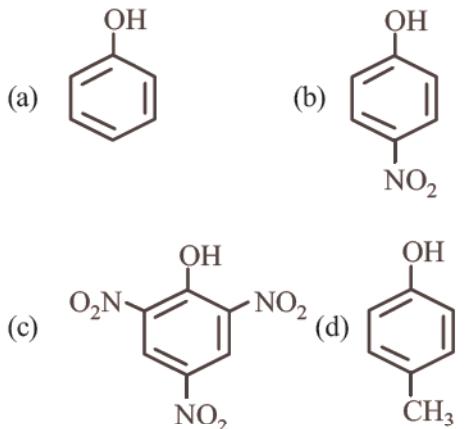
- (a)  $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$  and  $\text{I}_2$   
 (b)  $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{OH}$  and  $\text{I}_2$   
 (c)  $\text{CH}_3-\text{C}_6\text{H}_4-\text{CH}_3$  and  $\text{I}_2$   
 (d)  $\text{C}_6\text{H}_5-\text{CH}(\text{OH})-\text{CH}_3$  and  $\text{I}_2$

27. Identify the major products *P*, *Q* and *R* in the following sequence of reactions: [2018]

*P**Q**R*

- (a) Benzene ring, , Benzene ring,  
 (b) Benzene ring, , Benzene ring, , Benzene ring  
 (c) Benzene ring, , Benzene ring, , Benzene ring  
 (d) Benzene ring, , Benzene ring, , Benzene ring

28. Which one is the most acidic compound? [2017]



29. Which of the following reagents would distinguish cis-cyclopentane-1,2-diol from the trans-isomer? [2016]

- (a) Acetone

- (b) Ozone

- (c) MnO<sub>2</sub>

- (d) Aluminium isopropoxide

30. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group? [2015 RS]

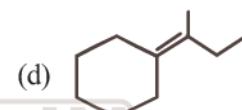
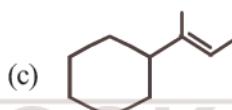
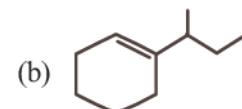
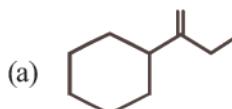
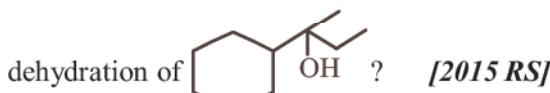
- (a) -CH<sub>2</sub>Cl

- (b) -COOH

- (c) -CHCl<sub>2</sub>

- (d) -CHO

31. Which of the following is not the product of



32. Among the following sets of reactants which one produces anisole? [2014]

- (a) CH<sub>3</sub>CHO; RMgX

- (b) C<sub>6</sub>H<sub>5</sub>OH; NaOH; CH<sub>3</sub>I

- (c) C<sub>6</sub>H<sub>5</sub>OH; neutral FeCl<sub>3</sub>

- (d) C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>; CH<sub>3</sub>COCl; AlCl<sub>3</sub>

33. Which of the following will not be soluble in sodium hydrogen carbonate? [2014]

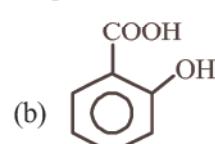
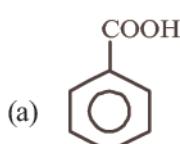
- (a) 2, 4, 6-trinitrophenol

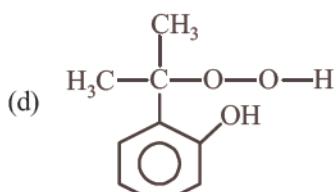
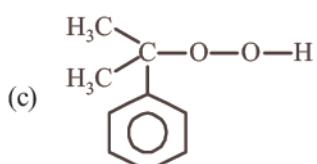
- (b) Benzoic acid

- (c) *o*-Nitrophenol

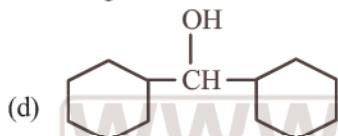
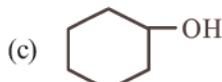
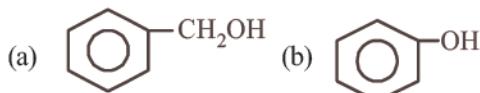
- (d) Benzenesulphonic acid

34. Phenol is distilled with Zn dust followed by Friedel Crafts alkylation with propyl chloride in the presence of AlCl<sub>3</sub> to give a compound (B). (B) is oxidised in the presence of air to form the compound (C). The structural formula of (C) is [NEET Kar. 2013]



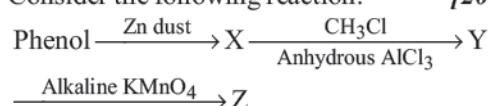


35. Which one of the following compounds has the most acidic nature? **[2010]**



36. Among the following four compounds [2010]  
 (i) phenol                   (ii) methylphenol  
 (iii) meta-nitrophenol   (iv) para-nitrophenol  
 the acidity order is :  
 (a) ii > i > iii > iv       (b) iv > iii > i > ii  
 (c) iii > iv > i > ii      (d) i > iv > iii > ii

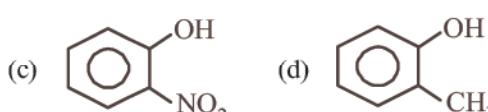
Consider the following reaction: [2009]



The product Z is:

- (a) benzaldehyde      (b) benzoic acid  
 (c) benzene            (d) toluene

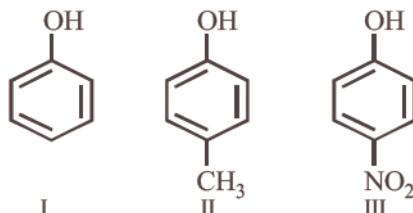
38. Which one of the following compounds is most acidic? [2005]



39. When phenol is treated with  $\text{CHCl}_3$  and  $\text{NaOH}$ , the product formed is **[2002]**

- (a) Benzaldehyde
  - (b) Salicylaldehyde
  - (c) Salicylic acid
  - (d) Benzoic acid

40. The correct order of acidic strength for following compounds will be [2001]

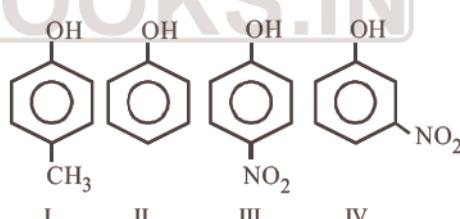


- (a) III > I > II      (b) I > III > II  
 (c) II > III > I      (d) I > II > III

41. The ionization constant of phenol is higher than that of ethanol because : **[2000]**

- (a) Phenoxide ion is bulkier than ethoxide
  - (b) Phenoxide ion is stronger base than ethoxide
  - (c) Phenoxide ion is stabilized through delocalization
  - (d) Phenoxide ion is less stable than ethoxide

42. Consider the following phenols :



The decreasing order of acidity of the above phenols is [1999]

- (a) III > IV > II > I      (b) II > I > IV > III  
 (c) I > IV > II > III      (d) III > IV > I > II

43. 1-Phenylethanol can be prepared by the reaction  
of phenylmagnesium bromide with

- of benzaldehyde with 119

  - (a) Ethyl iodide and magnesium
  - (b) Methyl iodide and magnesium
  - (c) Methyl bromide and aluminium bromide
  - (d) Methyl bromide

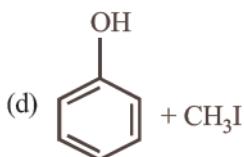
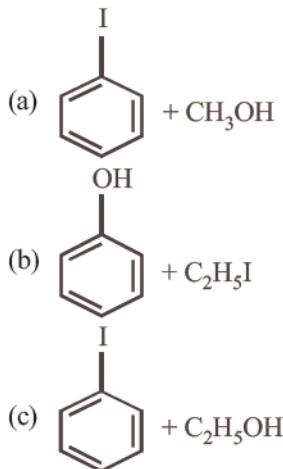
44. Correct increasing order of acidity is as follows:

- (a)  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{CO}_3$ , Phenol
  - (b)  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}_3$ , Phenol
  - (c) Phenol,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$
  - (d)  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{O}$ , Phenol,  $\text{H}_2\text{CO}_3$

45. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is **[1993]**
- p*-Nitrophenol, *p*-Methoxyphenol, *p*-Methylphenol
  - p*-Methylphenol, *p*-Methoxyphenol, *p*-Nitrophenol
  - p*-Nitrophenol, *p*-Methylphenol, *p*-Methoxyphenol.
  - p*-Methoxyphenol, *p*-Methylphenol, *p*-Nitrophenol
46. When phenol is treated with excess bromine water. It gives **[1992]**
- m*-Bromophenol
  - o*-and *p*-Bromophenols
  - 2,4-Dibromophenol
  - 2,4,6-Tribromophenol.
47. Which one of the following compounds will be most readily attacked by an electrophile? **[1989]**
- Chlorobenzene
  - Benzene
  - Phenol
  - Toluene
48. When phenol is heated with  $\text{CHCl}_3$  and aqueous KOH then salicylaldehyde is produced. This reaction is known as **[1988, 89]**
- Rosenmund's reaction
  - Reimer-Tiemann reaction
  - Friedel-Crafts reaction
  - Sommelet reaction

### Topic 3: Preparation and Properties of Ethers

49. Anisole on cleavage with HI gives **[2020]**



50. The major products C and D formed in the following reaction respectively are

**[NEET Odisha 2019]**



- $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{OH}$  and  $\text{HO}-\text{C}(\text{CH}_3)_3$
- $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{I}$  and  $\text{I}-\text{C}(\text{CH}_3)_3$
- $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{OH}$  and  $\text{I}-\text{C}(\text{CH}_3)_3$
- $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{I}$  and  $\text{HO}-\text{C}(\text{CH}_3)_3$

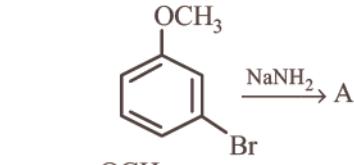
51. The compound that is most difficult to protonate is: **[2019]**

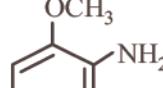


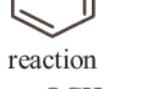
52. The heating of phenyl-methyl ethers with HI produces **[2017]**

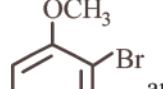
- Iodobenzene
- Phenol
- Benzene
- Ethyl chlorides

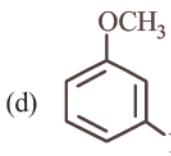
53. Identify A and predict the type of reaction **[2017]**



- (a)  and elimination addition

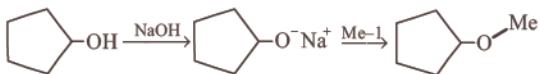
- reaction  
(b)  and cine substitution reaction

- (c)  and cine substitution reaction



and substitution reaction

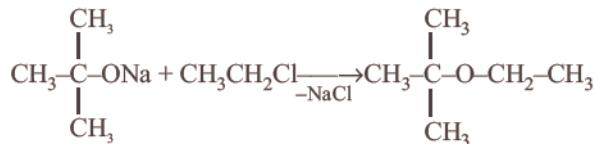
54. The reaction



Can be classified as :- [2016]

- (a) Williamson ether synthesis reaction
- (b) Alcohol formation reaction
- (c) Dehydration reaction
- (d) Williamson alcohol synthesis reaction

55. The reaction

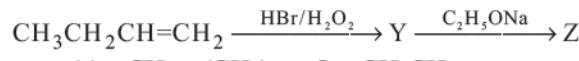


is called : [2015]

- (a) Williamson continuous etherification process
- (b) Etard reaction
- (c) Gatterman - Koch reaction
- (d) Williamson Synthesis

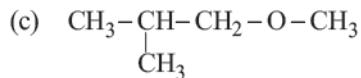
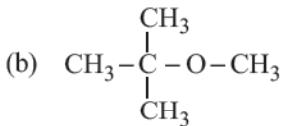
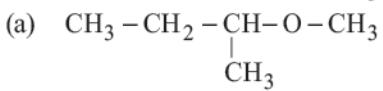
56. Identify Z in the sequence of reactions:

[2014]

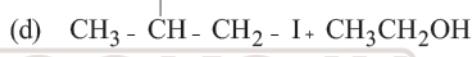
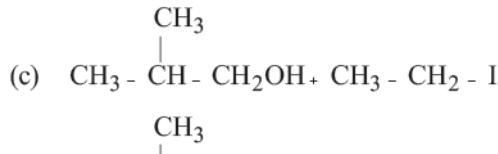
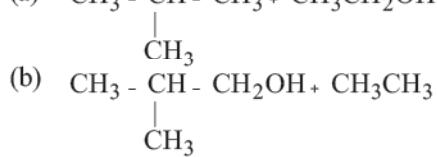
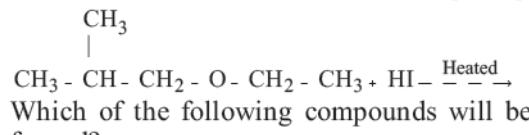


- (a)  $\text{CH}_3 - (\text{CH}_2)_3 - \text{O} - \text{CH}_2\text{CH}_3$
- (b)  $(\text{CH}_3)_2\text{CH}_2 - \text{O} - \text{CH}_2\text{CH}_3$
- (c)  $\text{CH}_3(\text{CH}_2)_4 - \text{O} - \text{CH}_3$
- (d)  $\text{CH}_3\text{CH}_2 - \text{CH}(\text{CH}_3) - \text{O} - \text{CH}_2\text{CH}_3$

57. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI? [NEET 2013]

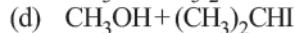
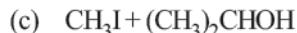
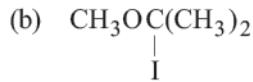


58. In the reaction: [2007]



59. The major organic product in the reaction,  $\text{CH}_3 - \text{O} - \text{CH}(\text{CH}_3)_2 + \text{HI} \rightarrow$  Product is

[2006]



60. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of [1993]

- (a) H-bonding in ethanol
- (b) H-bonding in dimethyl ether
- (c)  $\text{CH}_3$  group in ethanol
- (d)  $\text{CH}_3$  group in dimethyl ether

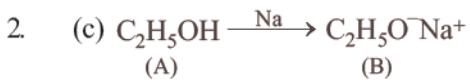
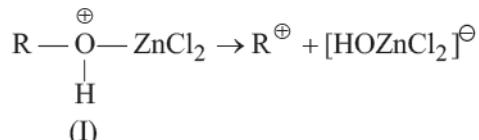
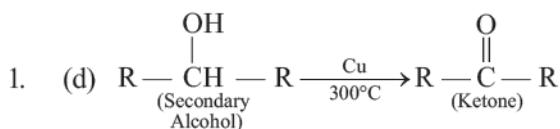
61. Which one is formed when sodium phenoxide is heated with ethyl iodide ? [1988]

- (a) Phenetole
- (b) Ethyl phenyl alcohol
- (c) Phenol
- (d) None of these

## ANSWER KEY

1	(d)	8	(c)	15	(c)	22	(c)	29	(a)	36	(b)	43	(b)	50	(b)	57	(b)
2	(c)	9	(c)	16	(d)	23	(a)	30	(d)	37	(b)	44	(d)	51	(d)	58	(c)
3	(b)	10	(c)	17	(b)	24	(b)	31	(b)	38	(c)	45	(d)	52	(b)	59	(c)
4	(a)	11	(c)	18	(a)	25	(c)	32	(b)	39	(b)	46	(d)	53	(d)	60	(a)
5	(c)	12	(c)	19	(d)	26	(d)	33	(c)	40	(a)	47	(c)	54	(a)	61	(a)
6	(d)	13	(d)	20	(b)	27	(c)	34	(c)	41	(c)	48	(b)	55	(d)		
7	(b)	14	(c)	21	(d)	28	(c)	35	(b)	42	(a)	49	(d)	56	(a)		

## Hints &amp; Solutions

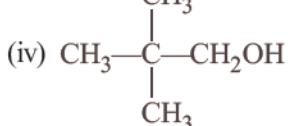
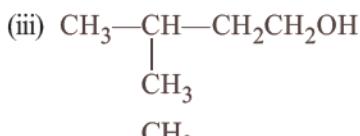
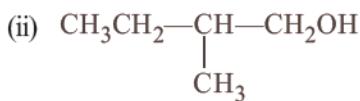


Carbocation is formed as intermediate in the  $\text{S}_{\text{N}}1$  mechanism which these reaction undergoes.  
(III) Tertiary carbocation easily formed due to the stability.

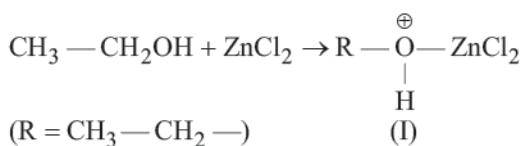


So, the correct option is (c)

3. (b) Four primary alcohols of  $\text{C}_5\text{H}_{11}\text{OH}$  are possible. These are:



4. (a)

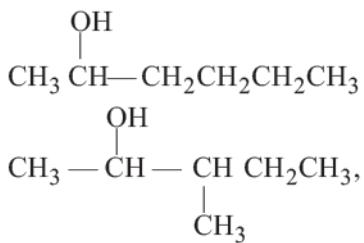


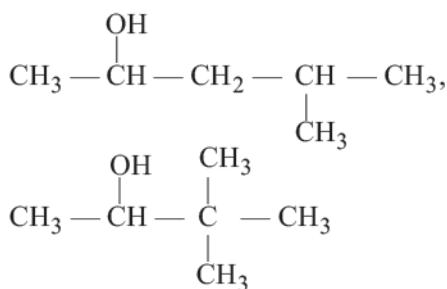
(IV) In the presence of  $\text{ZnCl}_2$ ,  $2^\circ$  carbocation is formed from  $(\text{CH}_3)_2-\underset{\substack{| \\ \text{H}}}{\text{C}}-\text{OH}$   
i.e.,  $\text{CH}_3-\underset{\substack{\oplus \\ |}}{\text{CH}}-\text{CH}_3$



$\text{ZnCl}_2$  is a lewis acid and interact with alcohol. In the absence of  $\text{ZnCl}_2$  formation of primary carbocation is difficult.

5. (c) Compound containing  $\text{CH}_3\text{CH}(\text{OH})$  or  $\text{CH}_3\text{CO}-$ group give positive iodoform test.





6. (d)  $\text{CH}_3 - \text{Br} \xrightarrow[\text{(A)}]{\text{KCN}} \text{CH}_3 - \text{CN} \xrightarrow{\text{H}_3\text{O}^+}$

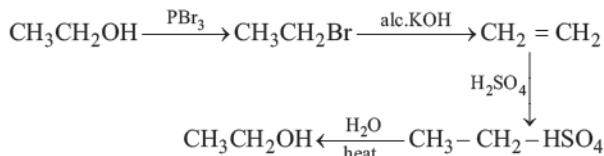
$\text{CH}_3 - \text{COOH} \xrightarrow[\text{(B)}]{\text{LiAlH}_4} \text{CH}_3 - \text{CH}_2 - \text{OH} \quad \text{(C)}$   
Ethyl alcohol

7. (b) Glycerol when treated with excess HI produces 2-iodopropane

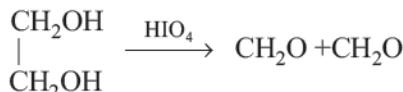
$$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CHOH} + 3\text{HI} \longrightarrow \end{array} \begin{array}{c} \text{CH}_2\text{I} \\ | \\ \text{CHI} - \text{CH}_2\text{I} \\ | \\ \text{CH}_2\text{I} \end{array} \xrightarrow{-\text{I}_2} \begin{array}{c} \text{CH}_2 \\ \parallel \\ \text{CH} \\ | \\ \text{CH}_2\text{I} \end{array}$$

$$\xrightarrow{+\text{HI}} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CHI} \\ | \\ \text{CH}_2\text{I} \end{array} \xrightarrow{-\text{I}_2} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} \\ \parallel \\ \text{CH}_2 \end{array} \xrightarrow{+\text{HI}} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CHI} \\ | \\ \text{CH}_2 \end{array}$$

∴ Correct choice : (b)  
(c)

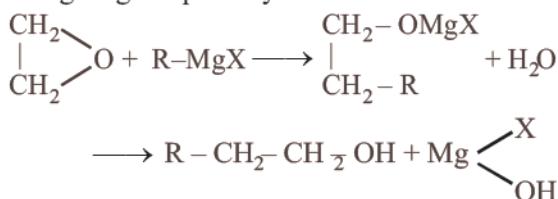


9. (c) 1, 2 - Diols, when treated with an aqueous solution of periodic acid give aldehyde or ketones

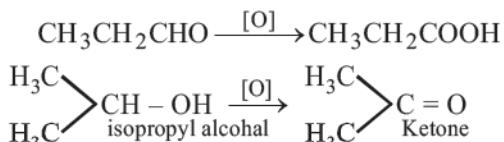


A 1° alcohol on reaction with periodic acid gives  $\text{CH}_2\text{O}$ . Since in glycol, both the OH groups are primary hence, 2 molecules of  $\text{CH}_2\text{O}$  is formed as product.

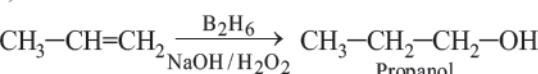
10. (c) Ethylene oxide when treated with Grignard Reagent gives primary alcohol.



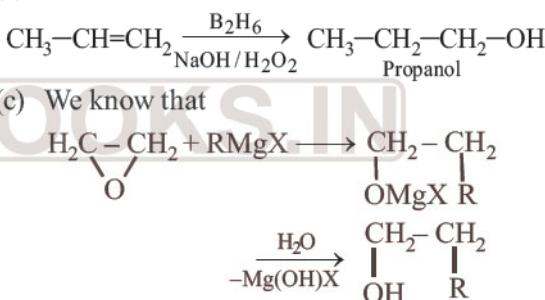
11. (c)  $\text{CH}_3\text{OH}$  does not have  $-\text{CH}(\text{OH})\text{CH}_3$  group hence it will not form yellow precipitate with an alkaline solution of iodine (haloform reaction).
  12. (c) Primary alcohol on oxidation give aldehyde which on further oxidation give carboxylic acid whereas secondary alcohols give ketone.



13. (d)  $\text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + 6\text{NaOH} \longrightarrow$   
 $\text{CHI}_3 \downarrow + \text{HCOONa} + 5\text{NaI} + 5\text{H}_2\text{O}$   
 Iodoform

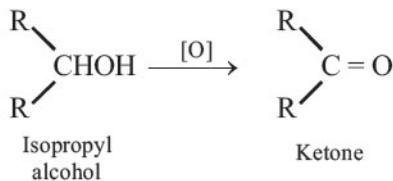


14. (c)



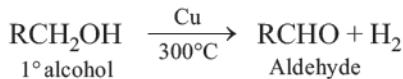
16. (d) Due to  $-I$ -effect of the three C–Cl-bonding between Cl and C-atom of the OH group,  $\text{CCl}_3\text{CH}(\text{OH})_2$  is most stable.

17. (b) Secondary alcohols on oxidation give ketones.

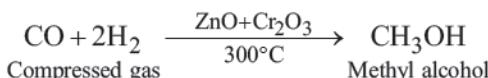


Primary alcohols form aldehydes.

18. (a)  $1^\circ$  Alcohols on catalytic dehydrogenation give aldehydes.



19. (d) Water gas is mixed with half of its volume of hydrogen. The mixture is compressed to approximately 200 – 300 atmospheres. It is then passed over a catalyst ( $ZnO + Cr_2O_3$ ) at 300°C. Methyl alcohol vapours are formed which are condensed.



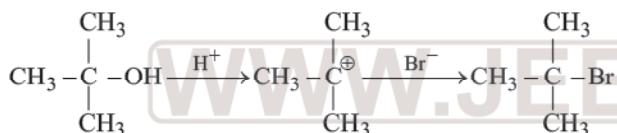
20. (b) Since 2-methylpropan-2-ol generates  $3^\circ$  carbocation, therefore, it reacts fastest with HBr.

**NOTE** Greater the stability of the intermediate carbocation, more reactive is the alcohol.

21. (d) The rates of reaction of different alcohols with Lucas reagent follows the order.

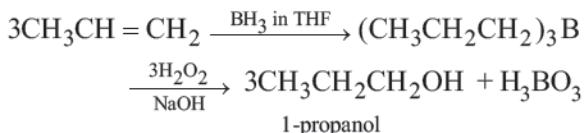
$3^\circ$  alcohol  $\geq 2^\circ$  alcohol  $\geq 1^\circ$  alcohol

Since carbocations are formed as intermediate, more stable the carbocation, higher will be the reactivity of the parent compound (alcohol). 2-Methylpropan-2-ol generates a  $3^\circ$  carbocation, so it will react fastest; other three generates either  $1^\circ$  or  $2^\circ$  carbocations.

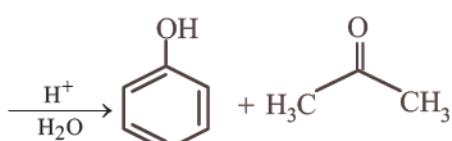
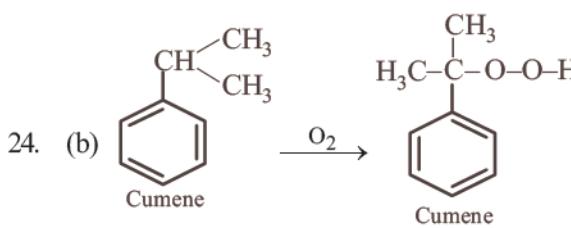


## 2-Methylpropan-2-ol

22. (c)  $\text{KMnO}_4$  (alkaline) and  $\text{OsO}_4 / \text{CH}_2\text{Cl}_2$  are used for hydroxylation of double bond while  $\text{O}_3 / \text{Zn}$  is used for ozonolysis. Therefore, the right option is (c), i.e.,

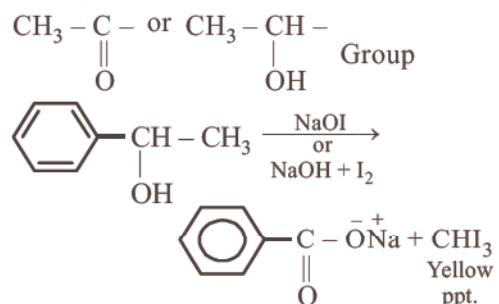


23. (a) Lucas reagent is conc. HCl + anhyd. ZnCl<sub>2</sub>.

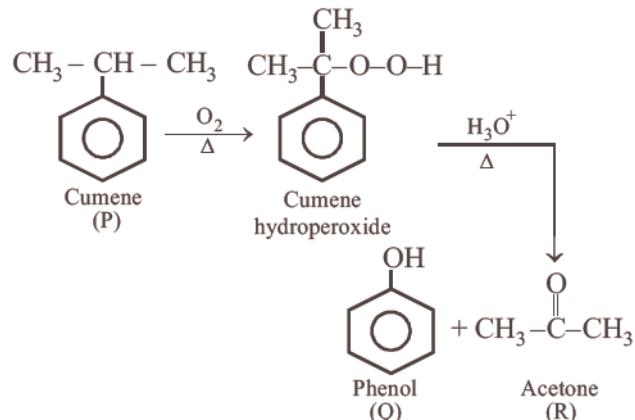
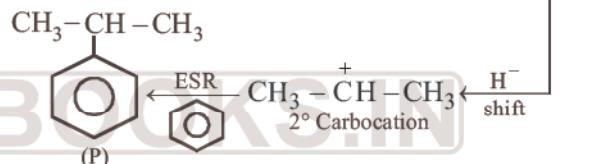
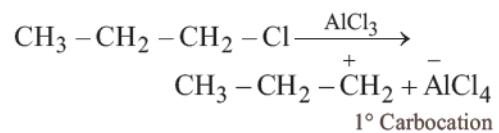


25. (c)  $\text{CHCl}_3 + \text{NaOH} \longrightarrow \text{CCl}_3 + \text{H}_2\text{O}$   
 $\qquad\qquad\qquad\downarrow -\text{Cl} (\alpha\text{-elimination})$   
 $\qquad\qquad\qquad : \text{CCl}_2 \text{ dichlorocarbene}$   
 $\qquad\qquad\qquad \text{(electrophile)}$

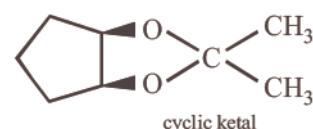
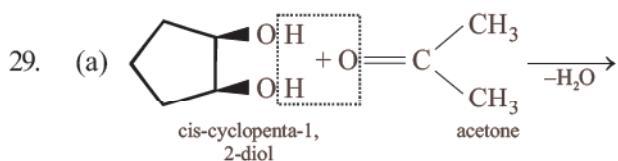
26. (d) Haloform reaction is shown by compound having



27. (c) Mechanism:

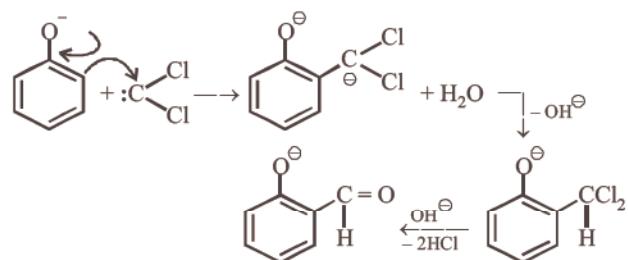
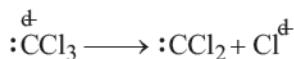
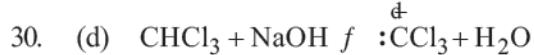


28. (c) Electron withdrawing  $\text{NO}_2$  group has very strong  $-I$  and  $-R$  effects so, compound 3 will be most acidic.

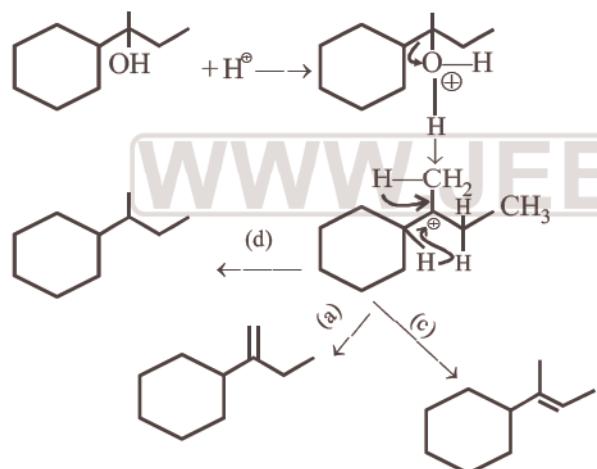




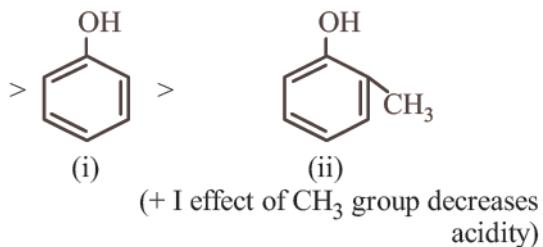
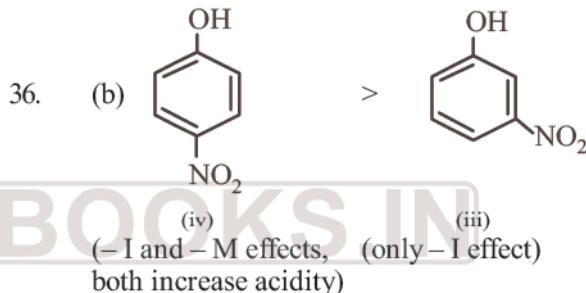
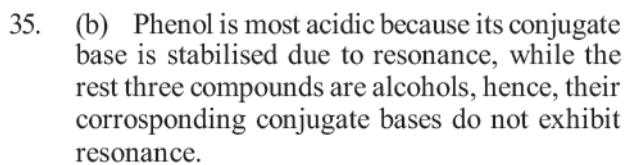
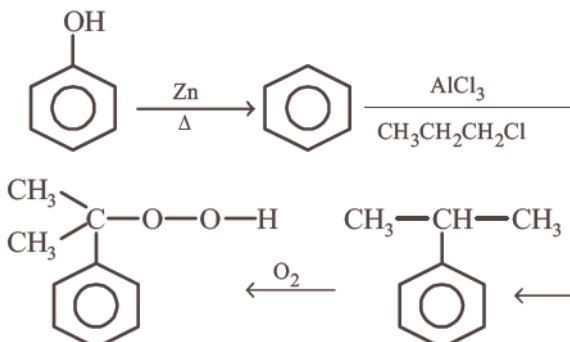
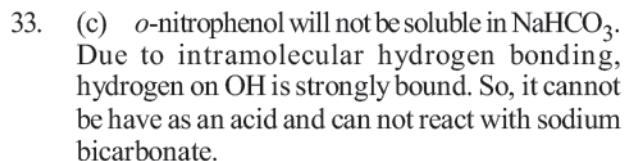
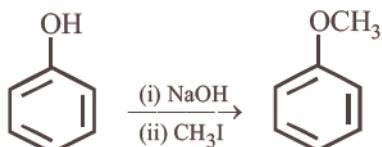
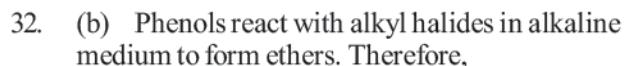
Trans isomer can not react with acetone to form cyclic ketal.



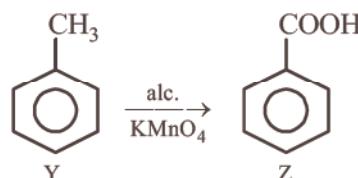
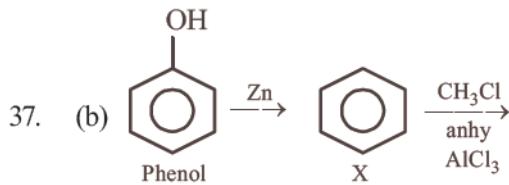
Therefore, functional group  $-\text{CHO}$  is introduced.



The intermediate is a  $3^\circ$  carbocation, which is very stable. Hence, rearrangement will not take place and product mentioned in option (b) will not form.

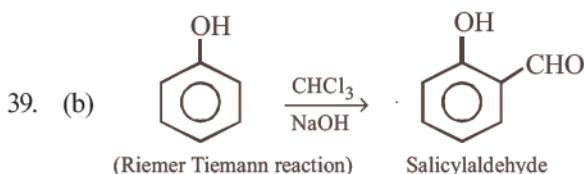


$\therefore$  Correct choice : (b)



38. (c) Phenols are more acidic than alcohols as they are resonance stabilised whereas alcohols are not.

Further  $\text{--NO}_2$  is an electron withdrawing group which increases acidic character and facilitates release of proton, whereas  $\text{--CH}_3$  is an electron donating group which decreases acidic character, thus removal of  $\text{H}^+$  becomes difficult.



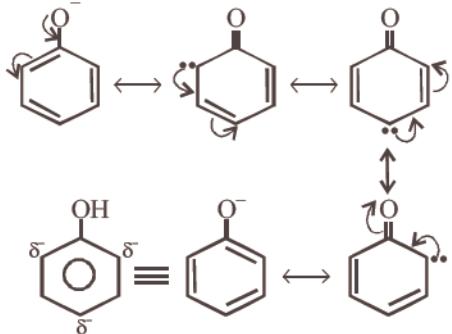
If  $\text{CCl}_4$  is used in place of  $\text{CHCl}_3$ , then the product is salicylic acid.

40. (a) Electron releasing group ( $-CH_3$ ) decreases acidity while electron withdrawing group ( $-NO_2$ ) increases acidity.

41. (c) The acidic nature of phenol is due to the formation of stable phenoxide ion in solution



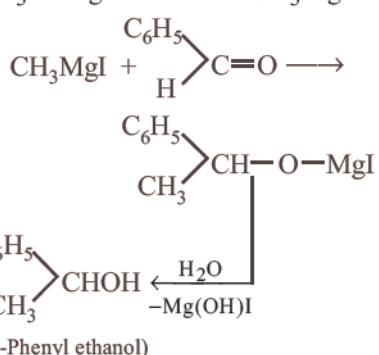
The phenoxide ion is stable due to resonance.



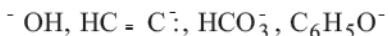
The negative charge is delocalized in the benzene ring which is a stabilizing factor in the phenoxide ion and increase acidity of phenol, whereas no resonance is possible in alkoxide ions ( $\text{RO}^-$ ) derived from alcohol. The negative charge is localized on oxygen atom. Thus, alcohols are less acidic.

42. (a) Electron withdrawing group ( $-NO_2$ ) increases the acidity while electron releasing group ( $-CH_3$ ,  $-H$ ) decreases acidity. Also effect will be more if functional group is present at para position than ortho and meta position.

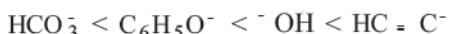
43. (b)  $\text{CH}_3\text{I} + \text{Mg} \xrightarrow{\text{Dry ether}} \text{CH}_3\text{MgI}$



44. (d) Such questions can be solved by considering the relative basic character of their conjugated bases which for  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{CO}_3$  and  $\text{C}_6\text{H}_5\text{OH}$  are



More the possibility for the dispersal of the negative charge, weaker will be the base. Thus the relative basic character of the four bases is



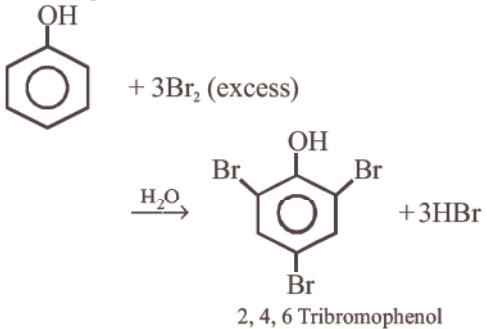
Equivalent Non-equivalent Oxygen can accommodate  
resonating structures (-) charge easily

Due to resonance  
Thus, the acidic character of the four corresponding acids will be



45. (d) Electron-donating groups ( $-\text{OCH}_3$ ,  $-\text{CH}_3$  etc.) tend to decrease and electron withdrawing groups ( $-\text{NO}_2$ ) tend to increase the acidic character of phenols. Since  $-\text{OCH}_3$  is a more powerful electron-donating group than  $-\text{CH}_3$  group, therefore, *p*-methylphenol is slightly more acidic than *p*-methoxyphenol while *p*-nitrophenol is the strongest acid. Thus, option (d), i.e. *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol is correct.

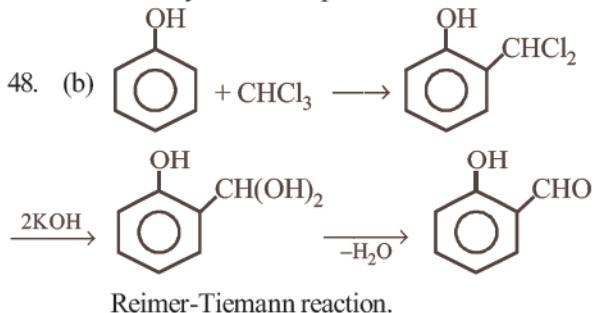
46. (d) With  $\text{Br}_2$  water, phenol gives 2, 4, 6-tribromophenol.



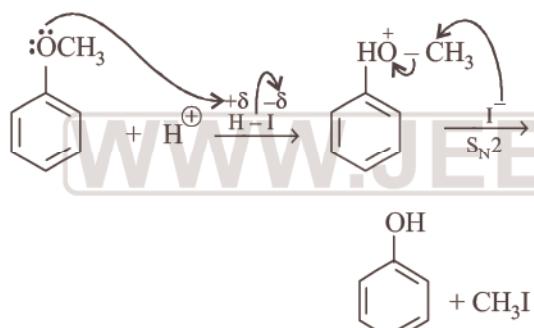


When phenol is treated  $\text{Br}_2/\text{CS}_2$  monobromination takes place.

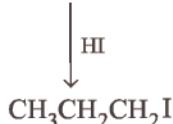
47. (c) Due to strong electron-donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and hence phenol is readily attacked by the electrophile.



49. (d)



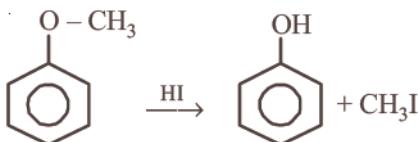
50. (b)  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(\text{CH}_3)_3 \xrightarrow[\Delta]{\text{HI}} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH} + (\text{CH}_3)_3\text{C}-\text{I}$



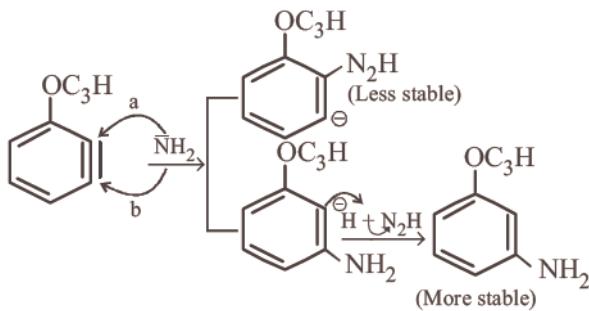
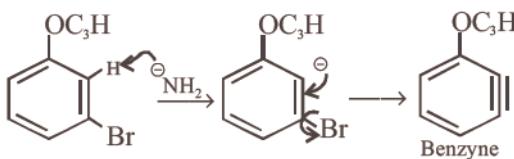
51. (d) In
- lone pair of e<sup>-</sup>s present on

oxygen atom is involved in delocalisation. Therefore, it is most difficult to protonate the phenol amongst the given compounds, due to less availability of e<sup>-</sup>s.

52. (b) When Ar – O – R ethers are reacted with HI, they are cleaved at weaker O – R bond to give phenol and alkyl iodide.



53. (d)



More stable as -ve charge is close to electron withdrawing group.

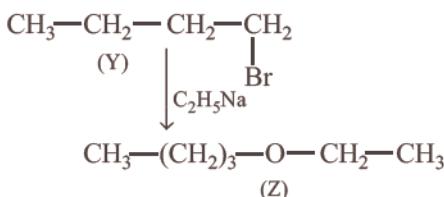
Also, incoming nucleophile gets attached on same 'C' on which 'Br' (Leaving group) was present.

$\therefore$  not a cine substitution reaction.

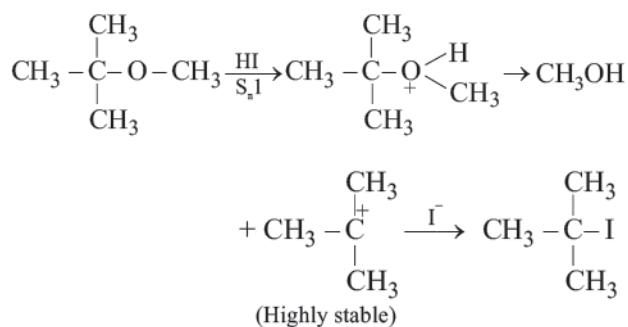
54. (a) This is an example of Williamson ether synthesis reaction in which sodium alkoxide reacts with alkyl halide and gives ether.

55. (d) Williamson synthesis is one of the best methods for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

56. (a)

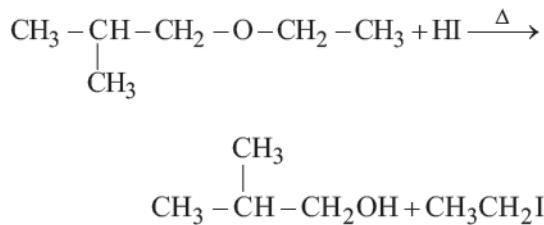


57. (b) The reaction will proceed via  $S_N1$  mechanism because alkyl group attached is  $3^\circ$ .

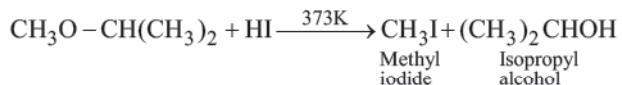


When tertiary alkyl group is attached then it forms alkyl iodide because of the stability of tertiary carbocation.

58. (c) In the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide that form depend on the nature of alkyl group. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide therefore

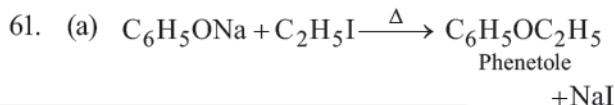


59. (c) In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl group e.g.,



The alkyl halide is always formed from the smaller alkyl group.

60. (a) Due to H-bonding, the boiling point of ethanol is much higher than that of the isomeric diethyl ether.



# 26

# Aldehydes, Ketones, and Carboxylic Acids



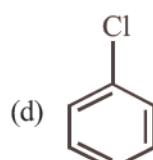
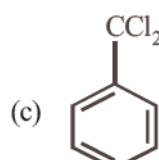
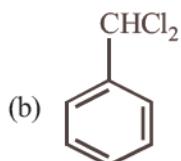
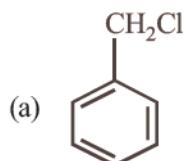
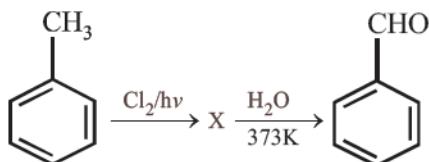
Trend Analysis with Important Topics & Sub-Topics



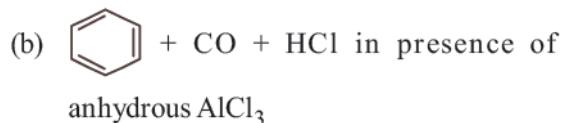
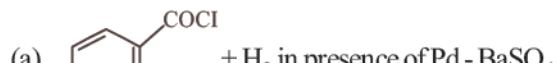
		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Methods of preparation of	preparation of benzaldehyde	1	D								
Properties of carbonyl compounds	reaction with Grignard reagent	1	A								
	cross aldol /aldol condensation	1	A					1	D		
	conversion(semicarbazone/aldol condensation)							1	D		
	keto enol tautomerism									1	A
	reaction with amine									1	E
Preparation and properties of carboxylic acids	reaction with ammonia			1	A						
	physical properties					1	A				
LOD - Level of Difficulty		E - Easy		A - Average		D - Difficult		Qns - No. of Questions			

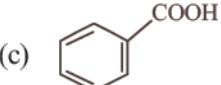
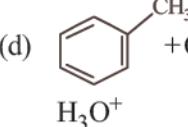
## Topic 1: Methods of Preparation of Carbonyl Compounds

1. Identify compound X in the following sequence of reactions [2020]



2. Reaction by which Benzaldehyde cannot be prepared : [NEET 2013]



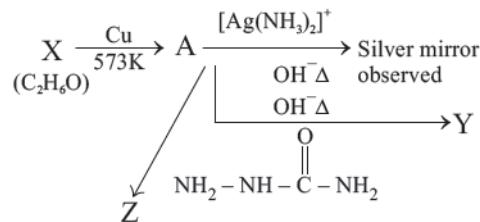
- (c)  + Zn/Hg and conc. HCl
- (d)  + CrO2Cl2 in CS2 followed by H3O+
3. Consider the following reaction :
- 
- The product 'A' is : *[2012 M]*
- (a) C6H5CHO      (b) C6H5OH  
 (c) C6H5COCH3    (d) C6H5Cl
4. Which of the following reactions will not result in the formation of carbon-carbon bonds? *[2010]*
- (a) Reimer-Tiemann reaction  
 (b) Cannizaro reaction  
 (c) Wurtz reaction  
 (d) Friedel-Crafts acylation
5. Which one of the following can be oxidised to the corresponding carbonyl compound? *[2004]*
- (a) 2-hydroxypropane  
 (b) Ortho-nitrophenol  
 (c) Phenol  
 (d) 2-methyl-2 hydroxypropane
6. In the following reaction, product 'P' is *[2002]*
- $$\text{R}-\underset{\text{O}}{\overset{||}{\text{C}}}-\text{Cl} \xrightarrow[\text{Pd-BaSO}_4]{\text{H}_2} \text{P}$$
- (a) RCH2OH      (b) RCOOH  
 (c) RCHO        (d) RCH3
7. The catalyst used in Rosenmund's reduction is *[2000]*
- (a) HgSO4      (b) Pd/BaSO4  
 (c) anhydrous AlCl3    (d) anhydrous ZnCl2
8. Ketones  
 [ R — C — R1, where R = R1 = alkyl groups]  
 can be obtained in one step by *[1998]*

- (a) oxidation of primary alcohols  
 (b) hydrolysis of esters  
 (c) oxidation of tertiary alcohols  
 (d) reaction of acid halides with alcohols
9. Pinacolone is *[1994]*
- (a) 2, 3-Dimethyl-2, 3-butanediol  
 (b) 3, 3-Dimethyl-2-butanone  
 (c) 1-Phenyl-2-Propanone  
 (d) 1,1-Diphenyl-2-ethanol.

### Topic 2: Properties of Carbonyl Compounds

10. Reaction between acetone and methyl-magnesium chloride followed by hydrolysis will give : *[2020]*
- (a) Sec. butyl alcohol (b) Tert. butyl alcohol  
 (c) Isobutyl alcohol (d) Isopropyl alcohol
11. Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as *[2020]*
- (a) Cannizzaro's reaction  
 (b) Cross Cannizzaro's reaction  
 (c) Cross Aldol condensation  
 (d) Aldol condensation

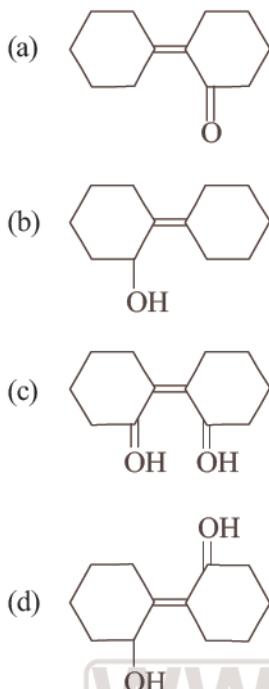
12. Consider the reactions :- *[2017]*



Identify A, X, Y and Z

- (a) A-Methoxymethane, X-Ethanol, Y-Ethanoic acid, Z-Semicarbazide.  
 (b) A - Ethanal, X-Ethanol, Y - But - 2-enal, Z-Semicarbazone  
 (c) A-Ethanol, X-Acetaldehyde, Y - Butanone, Z-Hydrazone  
 (d) A-Methoxymethane, X-Ethanoic acid, Y-Acetate ion, Z-hydrazine.

13. Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? [2017]



14. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is : [2016]

- (a) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol.
- (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.
- (c) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation.
- (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism.

15. The product formed by the reaction of an aldehyde with a primary amine is [2016]

- (a) Schiff base      (b) Ketone  
 (c) Carboxylic acid      (d) Aromatic acid

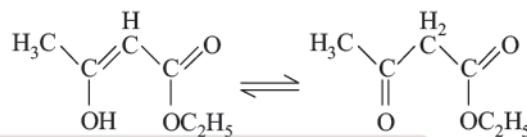
16. An organic compound 'X' having molecular formula  $C_5H_{10}O$  yields phenyl hydrazone and gives negative response to the Iodoform test and Tollen's test. It produces n-pentane on reduction. 'X' could be :- [2015]

- (a) 2-pentanone      (b) 3-pentanone  
 (c) n-amyl alcohol      (d) pentanal

17. Treatment of cyclopentanone  with methyl lithium gives which of the following species? [2015]

- (a) Cyclopentanonyl cation  
 (b) Cyclopentanonyl radical  
 (c) Cyclopentanonyl biradical  
 (d) Cyclopentanonyl anion

18. The enolic form of ethyl acetoacetate as below has: [2015]

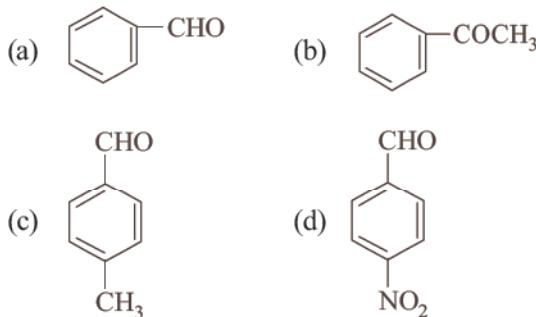


- (a) 16 sigma bonds and 1 pi - bond  
 (b) 9 sigma bonds and 2 pi - bonds  
 (c) 9 sigma bonds and 1 pi - bond  
 (d) 18 sigma bonds and 2 pi - bonds

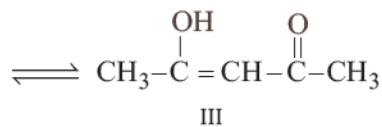
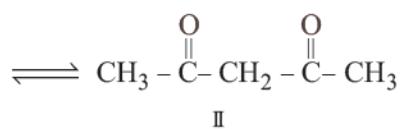
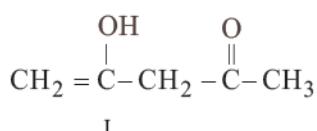
19. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is : [2015 RS]

- (a) a Grignard reagent  
 (b) hydrazine in presence of feebly acidic solution  
 (c) hydrocyanic acid  
 (d) sodium hydrogen sulphite

20. Which one is most reactive towards Nucleophilic addition reaction? [2014]

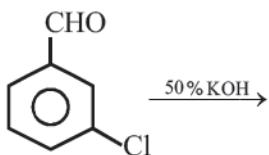


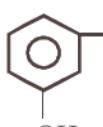
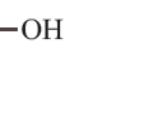
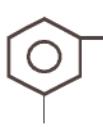
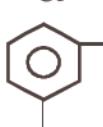
21. The order of stability of the following tautomeric compounds is : *[NEET 2013]*



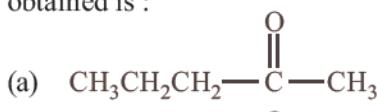
- (a) III > II > I      (b) II > I > III  
 (c) II > III > I      (d) I > II > III

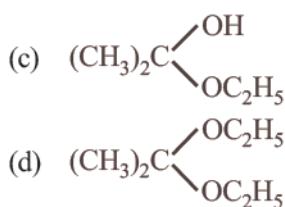
22. Predict the product in the given reaction. *[2012]*



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

23. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is : *[2012]*

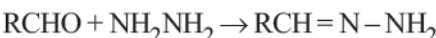
- (a)   
 (b) 



24.  $\text{CH}_3\text{CHO}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$  can be distinguished chemically by : *[2012]*

- (a) Benedict test      (b) Iodoform test  
 (c) Tollen's reagent test      (d) Fehling solution test

25. Consider the reaction :



What sort of reaction is it ? *[2012 M]*

- (a) Electrophilic addition – elimination reaction  
 (b) Free radical addition – elimination reaction  
 (c) Electrophilic substitution – elimination reaction  
 (d) Nucleophilic addition – elimination reaction

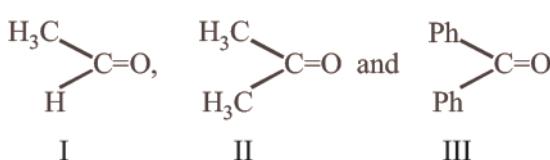
26. Which of the following compounds will give a yellow precipitate with iodine and alkali? *[2012 M]*

- (a) Acetophenone      (c) Methyl acetate  
 (b) Acetamide      (d) 2-Hydroxypropane

27. Clemmensen reduction of a ketone is carried out in the presence of which of the following? *[2011]*

- (a) Glycol with KOH  
 (b) Zn-Hg with HCl  
 (c)  $\text{Li Al H}_4$   
 (d)  $\text{H}_2$  and Pt as catalyst

28. The order of reactivity of phenyl magnesium bromide ( $\text{PhMgBr}$ ) with the following compounds *[2011 M]*



- (a) III > II > I      (b) II > I > III  
 (c) I > III > II      (d) I > II > III

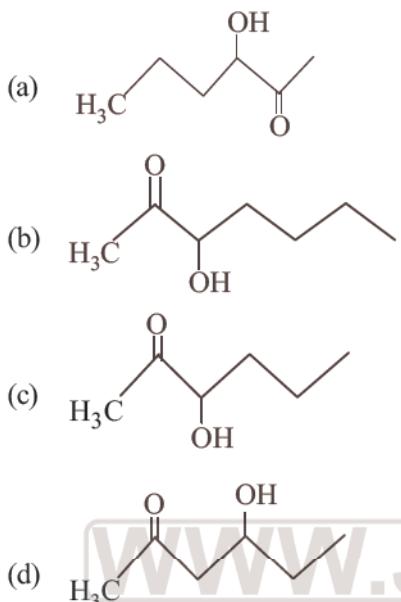
29. Following compounds are given:

- (1)  $\text{CH}_3\text{CH}_2\text{OH}$       (2)  $\text{CH}_3\text{COCH}_3$   
 (3)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CHOH}}$       (4)  $\text{CH}_3\text{OH}$

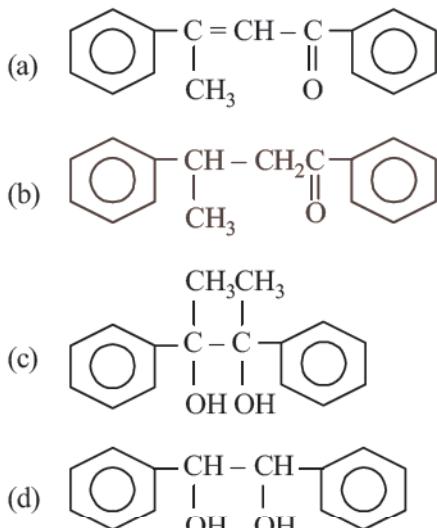
Which of the above compound(s), on being warmed with iodine solution and NaOH, will give iodoform? [2010]

- (a) (1) and (2)      (b) (1), (3) and (4)  
 (c) only (2)      (d) (1), (2) and (3)

30. Which one of the following compounds will be most readily dehydrated? [2010]



31. Acetophenone when reacted with a base,  $C_2H_5ONa$ , yields a stable compound which has the structure. [2008]



32. A strong base can abstract an  $\alpha$ -hydrogen from: [2008]

- (a) alkene      (b) amine  
 (c) ketone      (d) alkane

33. Reduction of aldehydes and ketones into hydrocarbons using zinc amalgam and conc. HCl is called [2007]

- (a) Cope reduction  
 (b) Dow reduction  
 (c) Wolff-Kishner reduction  
 (d) Clemmensen reduction.

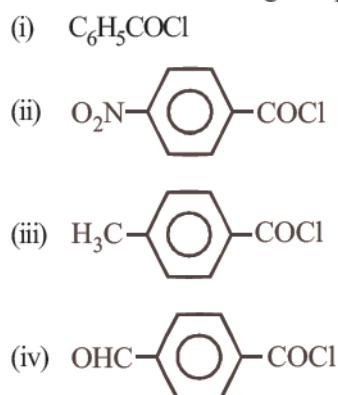
34. Which one of the following on treatment with 50% aqueous sodium hydroxide yields the corresponding alcohol and acid? [2007]

- (a)  $C_6H_5CHO$       (b)  $CH_3CH_2CH_2CHO$
- (c)
- (d)  $C_6H_5CH_2CHO$

35. The product formed in Aldol condensation is [2007]

- (a) A beta-hydroxy aldehyde or a beta-hydroxy ketone  
 (b) An alpha-hydroxy aldehyde or ketone  
 (c) An alpha, beta unsaturated ester  
 (d) A beta-hydroxy acid

36. Consider the following compounds. [2007]



The correct decreasing order of their reactivity towards hydrolysis is

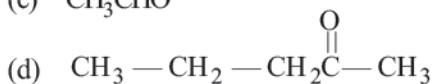
- (a) (i)>(ii)>(iii)>(iv) (b) (iv)>(ii)>(i)>(iii)  
 (c) (ii)>(iv)>(i)>(iii) (d) (ii)>(iv)>(iii)>(i)

37. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of  $\alpha$ -hydroxy acid. The carbonyl compound is [2006]

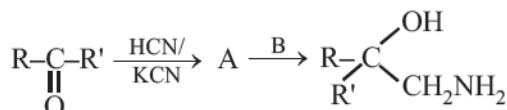
- (a) Acetone      (b) Diethyl ketone  
 (c) Formaldehyde      (d) Acetaldehyde

38. Nucleophilic addition reaction will be most favoured in [2006]

- (a)  $(CH_3)_2C=O$   
 (b)  $CH_3CH_2CHO$   
 (c)  $CH_3CHO$



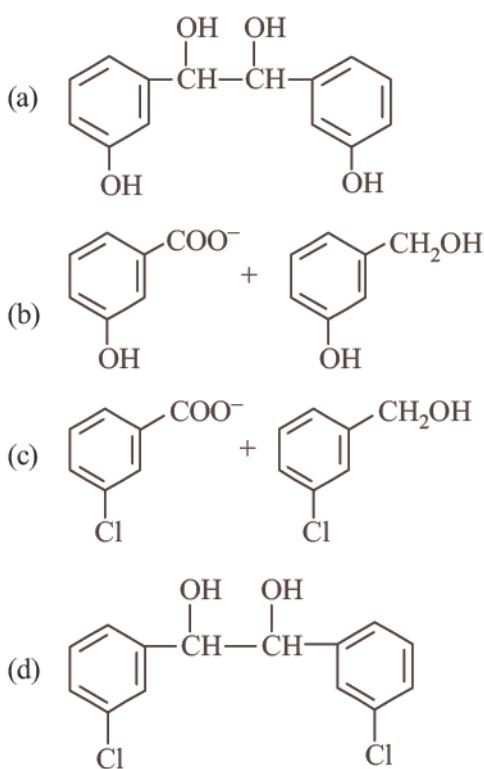
39. A and B in the following reactions are [2003]



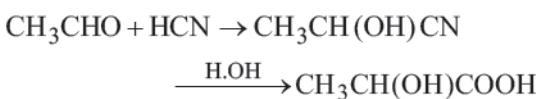
- (a)  $A = RR'C(OH)_2$ ,  $B = LiAlH_4$   
 (b)  $A = RR'C(OH)_2COOH$ ,  $B = NH_3$   
 (c)  $A = RR'C(OH)CN$ ,  $B = H_3O^+$   
 (d)  $A = RR'CH_2CN$ ,  $B = NaOH$

40. When *m*-chlorobenzaldehyde is treated with 50% KOH solution, the product(s) obtained is (are)

[2003]



41. In the reaction



an asymmetric centre is generated. The acid obtained would be [2003]

- (a) 20 % D + 80 % L-isomer  
 (b) D-isomer  
 (c) L-isomer  
 (d) 50% D + 50% L-isomer

42. Which of the following is correct? [2001]

- (a) Diastase is an enzyme  
 (b) Acetophenone is an ether  
 (c) Cycloheptane is an aromatic compound  
 (d) All the above

43. Which of the following is incorrect? [2001]

- (a)  $NaHSO_3$  is used in detection of carbonyl compound  
 (b)  $FeCl_3$  is used in detection of phenolic group  
 (c) Tollens' reagent is used in detection of unsaturation  
 (d) Fehling solution is used in detection of glucose

44. Polarization of electrons in acrolein may be written as: [2000]

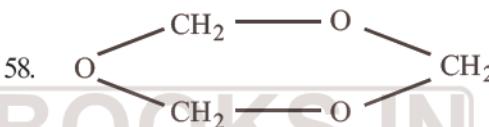
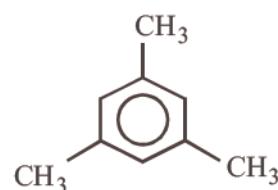
- (a)  $\delta^- CH_2=CH - \overset{\delta+}{CH=O}$   
 (b)  $\overset{\delta+}{CH_2}=CH - \overset{\delta-}{CH=O}$   
 (c)  $\overset{\delta+}{CH_2}=CH - \overset{\delta-}{CH=O}$   
 (d)  $\overset{\delta-}{CH_2} = \overset{\delta+}{CH} - \overset{\delta+}{CH=O}$

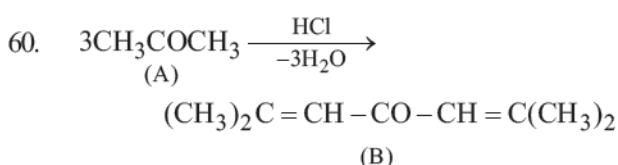
45. During reduction of aldehydes with hydrazine and potassium hydroxide, the first is the formation of: [2000]

- (a)  $R-CH=N-NH_2$   
 (b)  $R-C\equiv N$   
 (c)  $R-\overset{\parallel}{C}-NH_2$   
 (d)  $R-CH=NH$

46. Iodoform test is not given by [1999]

- (a) 2-Pentanone      (b) Ethanol  
 (c) Ethanal           (d) 3-Pentanone

47. Reaction of phenylacetylene with dil.  $H_2SO_4$  and  $HgSO_4$  gives [1999]  
 (a) Acetophenone (b) 2-Phenylethanol  
 (c) Phenylacetaldehyde (d) Phenylacetic acid
48. The cyanohydrin of a compound on hydrolysis gives an optically active  $\alpha$ -hydroxy acid. The compound is [1999]  
 (a) Diethyl ketone (b) Formaldehyde  
 (c) Acetaldehyde (d) Acetone
49. Phenylmethyl ketone can be converted into ethylbenzene in one step by which of the following reagents? [1999]  
 (a)  $LiAlH_4$  (b)  $Zn-Hg/HCl$   
 (c)  $NaBH_4$  (d)  $CH_3MgI$
50.  $(CH_3)_3C-CHO$  does not undergo Aldol condensation due to [1996]  
 (a) three electron donating methyl groups  
 (b) cleavage taking place between  $-C-CHO$  bond  
 (c) absence of alpha hydrogen atom in the molecule  
 (d) bulky  $(CH_3)_3C-$  group
51. Decreasing order of reactivity towards nucleophilic addition to carbonyl group among cyclopentanone, 3-pentanone and n-pentanal is [1996]  
 (a) 3-pentanone, cyclopentanone, n-pentanal  
 (b) n-pentanal, 3-pentanone, cyclopentanone  
 (c) n-pentanal, cyclopentanone, 3-pentanone  
 (d) cyclopentanone, 3-pentanone, n-pentanal
52. Acetone reacts with iodine ( $I_2$ ) to form iodoform in the presence of [1995]  
 (a)  $CaCO_3$  (b)  $NaOH$   
 (c)  $KOH$  (d)  $MgCO_3$
53. Benzaldehyde reacts with ethanoic KCN to give [1994]  
 (a)  $C_6H_5CHOHCN$   
 (b)  $C_6H_5CHOHCOC_6H_5$   
 (c)  $C_6H_5CHOHCOOH$   
 (d)  $C_6H_5CHOHCHOHC_6H_5$
54. Aldehydes and ketones will not form crystalline derivatives with [1994]  
 (a) Sodium bisulphite  
 (b) Phenylhydrazine  
 (c) Semicarbazide hydrochloride  
 (d) Dihydrogen sodium phosphate.
55. Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali? [1994]  
 (a)  $CH_2=CH-CHO$  (b)  $CH=C-CHO$   
 (c)  $C_6H_5CHO$  (d)  $CH_3CH_2CHO$ .
56. Acetaldehyde reacts with [1991]  
 (a) Electrophiles only  
 (b) Nucleophiles only  
 (c) Free radicals only  
 (d) Both electrophiles and nucleophiles.
57. The reagent(s) which can be used to distinguish acetophenone from benzophenone is (are)  
 (a) 2,4-Dinitrophenylhydrazine [1990]  
 (b) Aqueous solution of  $NaHSO_3$   
 (c) Benedict reagent  
 (d)  $I_2$  and  $NaOH$ .
58. 
- The above shown polymer is obtained when a carbonyl compound is allowed to stand. It is a white solid. The polymer is [1989]  
 (a) Trioxane (b) Formose  
 (c) Paraformaldehyde (d) Metaldehyde.
59. 
- The above compound describes a condensation polymer which can be obtained in two ways : either treating 3 molecules of acetone ( $CH_3COCH_3$ ) with conc.  $H_2SO_4$  or passing propyne ( $CH_3C \equiv CH$ ) through a red hot tube. The polymer is [1989]  
 (a) Phorone  
 (b) Mesityl oxide  
 (c) Deacetonyl alcohol  
 (d) Mesitylene.



This polymer (B) is obtained when acetone is saturated with hydrogen chloride gas, B can be

- (a) phorone      (b) formose [1989]  
(c) diacetone alcohol      (d) mesityl oxide.

61. If formaldehyde and KOH are heated, then we get [1988]

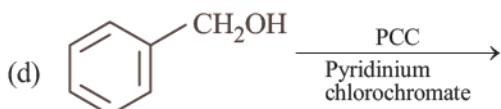
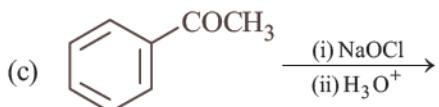
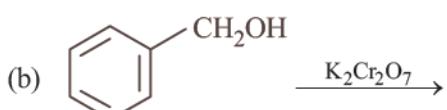
- (a) Methane      (b) Methyl alcohol  
(c) Ethyl formate      (d) Acetylene.

62. Formalin is an aqueous solution of [1988]

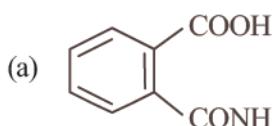
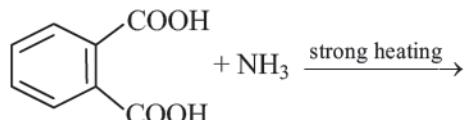
- (a) Fluorescein      (b) Formic acid  
(c) Formaldehyde      (d) Furfuraldehyde.

### Topic 3: Preparation and Properties of Carboxylic Acids

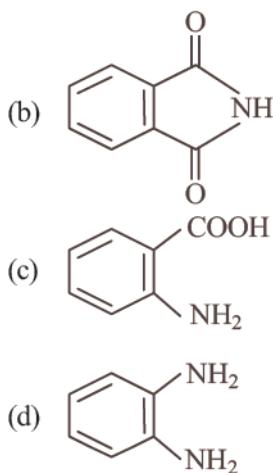
63. The reaction that does not give benzoic acid as the major product is [NEET Odisha 2019]



64. The major product of the following reaction is :



[2019]



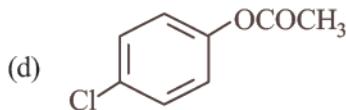
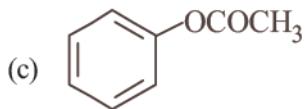
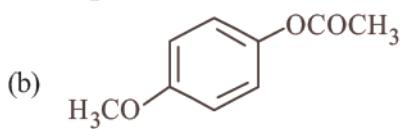
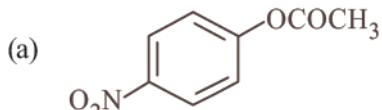
65. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their

[2018]

- (a) Formation of intramolecular H-bonding  
(b) Formation of carboxylate ion  
(c) Formation of intermolecular H-bonding  
(d) More extensive association of carboxylic acid via van der Waals force of attraction

66. Which one of the following esters gets hydrolysed most easily under alkaline conditions?

[2015 RS]



67. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is : [2012]

- (a) B > A > D > C      (b) B > D > C > A  
(c) A > B > C > D      (d) A > C > B > D

68. Match the compounds given in List-I with List-II and select the suitable option using the code given below : [2011 MJ]

**List I**

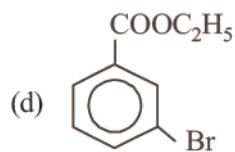
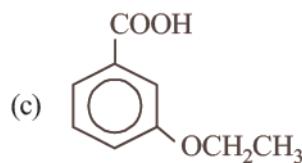
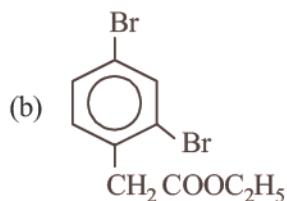
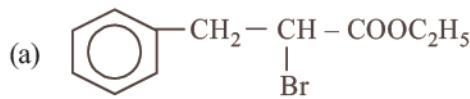
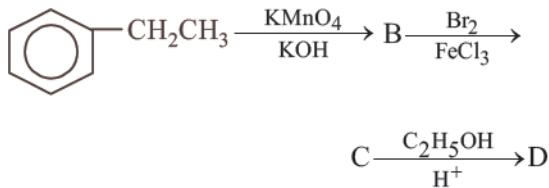
- |                        |                           |
|------------------------|---------------------------|
| (A) Benzaldehyde       | (i) Phenolphthalein       |
| (B) Phthalic anhydride | (ii) Benzoin condensation |
| (C) Phenyl benzoate    | (iii) Oil of wintergreen  |
| (D) Methyl salicylate  | (iv) Fries rearrangement  |

**List-II**

- |          |       |       |       |
|----------|-------|-------|-------|
| (A)      | (B)   | (C)   | (D)   |
| (a) (iv) | (i)   | (iii) | (ii)  |
| (b) (iv) | (ii)  | (iii) | (i)   |
| (c) (ii) | (iii) | (iv)  | (i)   |
| (d) (ii) | (i)   | (iv)  | (iii) |

69. An organic compound 'A' on treatment with  $\text{NH}_3$  gives 'B' which on heating gives 'C', 'C' when treated with  $\text{Br}_2$  in the presence of KOH produces ethylamine. Compound 'A' is: [2011 MJ]
- (a)  $\text{CH}_3\text{COOH}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
 (c)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}}\text{COOH}$   
 (d)  $\text{CH}_3\text{CH}_2\text{COOH}$

70. In a set of reactions, ethylbenzene yielded a product D. [2010]



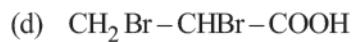
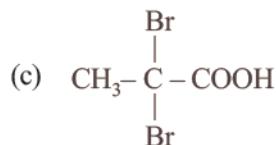
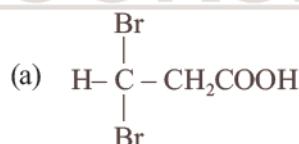
71. Given are cyclohexanol (I) acetic acid (II), 2, 4, 6 – trinitrophenol (III) and phenol (IV). In these, the order of decreasing acidic character will be: [2010]

- (a) III > II > IV > I      (b) II > III > I > IV  
 (c) II > III > IV > I      (d) III > IV > II > I

72. Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl group is: [2010]

- (a)  $\text{CH}_3\text{COOCH}_3$       (b)  $\text{CH}_3\text{CONH}_2$   
 (b)  $\text{CH}_3\text{COOCOCH}_3$       (d)  $\text{CH}_3\text{COCl}$

73. Propionic acid with  $\text{Br}_2/\text{P}$  yields a dibromo product. Its structure would be: [2009]



74. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of: [2008]

- (a) Acyl chloride > Acid anhydride > Ester > Amide  
 (b) Ester > Acyl chloride > Amide > Acid anhydride  
 (c) Acid anhydride > Amide > Ester > Acyl chloride  
 (d) Acyl chloride > Ester > Acid anhydride > Amide

75. Which of the following represents the correct order of the acidity in the given compounds?

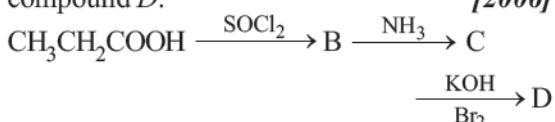
[2007]

- (a)  $\text{FCH}_2\text{COOH} > \text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH}$   
 $> \text{ClCH}_2\text{COOH}$
- (b)  $\text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{FCH}_2\text{COOH}$   
 $> \text{CH}_3\text{COOH}$
- (c)  $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH}$   
 $> \text{CH}_3\text{COOH}$
- (d)  $\text{CH}_3\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ClCH}_2\text{COOH}$   
 $> \text{FCH}_2\text{COOH}$

76. Self condensation of two moles of ethyl acetate in presence of sodium ethoxide yields [2006]

- (a) acetoacetic ester (b) methyl acetoacetate
- (c) ethyl propionate (d) ethyl butyrate

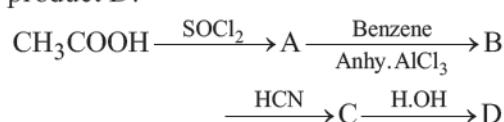
77. In a set of reactions propionic acid yielded a compound D. [2006]



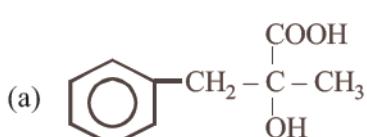
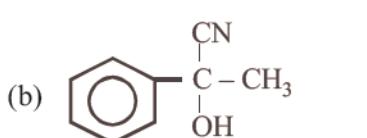
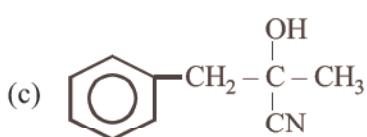
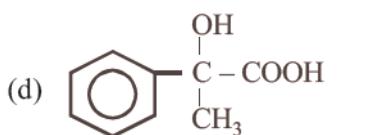
The structure of D would be

- (a)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  (b)  $\text{CH}_3\text{CH}_2\text{NHCH}_3$
- (c)  $\text{CH}_3\text{CH}_2\text{NH}_2$  (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

78. In a set of reactions acetic acid yielded a product D.



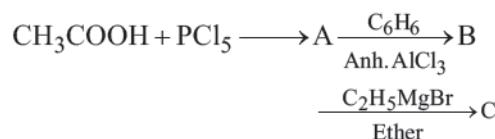
The structure of D would be: [2005]

- (a) 
- (b) 
- (c) 
- (d) 

79. The  $-\text{OH}$  group of an alcohol or the  $-\text{COOH}$  group of a carboxylic acid can be replaced by  $-\text{Cl}$  using [2004]

- (a) Phosphorus pentachloride
- (b) Hypochlorous acid
- (c) Chlorine
- (d) Hydrochloric acid

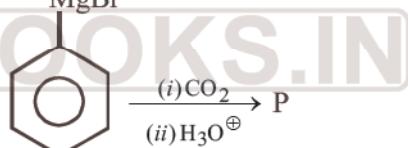
80. In a set of the given reactions, acetic acid yielded a product C.



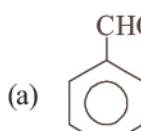
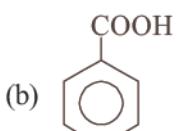
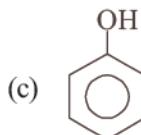
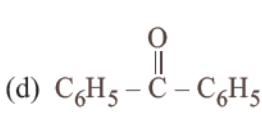
Product C would be - [2003]

- (a)  $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\overset{|}{\text{C}}}(\text{OH})\text{C}_6\text{H}_5$
- (b)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$
- (c)  $\text{CH}_3\text{COC}_6\text{H}_5$
- (d)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$

81.  $\text{MgBr}$



In the above reaction product 'P' is [2002]

- (a) 
- (b) 
- (c) 
- (d) 

82. Benzoic acid may be converted to ethyl benzoate by reaction with : [2000]

- (a) Sodium ethoxide (b) Ethyl chloride
- (c) Dry HCl— $\text{C}_2\text{H}_5\text{OH}$  (d) Ethanol

83. Acetaldehyde reacts with semicarbazide and forms semicarbazone. Its structure is [1999]

- (a)  $\text{CH}_3\text{CH}=\text{NNHCON}=\text{CHCH}_3$
- (b)  $\text{CH}_3\text{CH}=\text{NNHCONH}_2$
- (c)  $\text{CH}_3\text{CH}=\text{N}—\underset{\text{OH}}{\text{N}}—\text{CONH}_2$
- (d)  $\text{CH}_3\text{CH}=\text{N}—\text{CONHNH}_2$

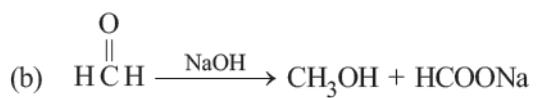
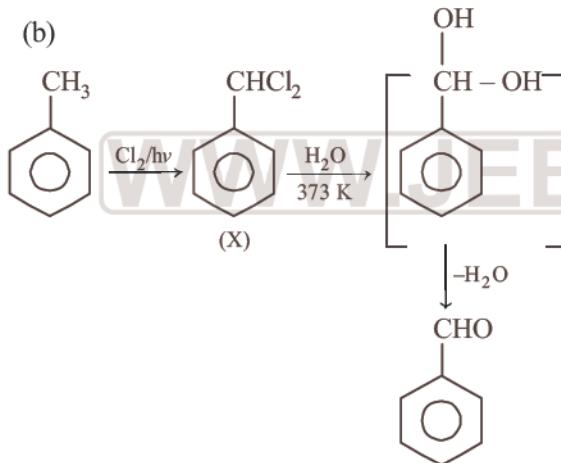
- |     |  |        |
|-----|--|--------|
| 84. | Aspirin is an acetylation product of<br>(a) <i>o</i> -Hydroxybenzoic acid<br>(b) <i>o</i> -Dihydroxybenzene<br>(c) <i>m</i> -Hydroxybenzoic acid<br>(d) <i>p</i> -Dihydroxybenzene   | [1998] |
| 85. | An ester (A) with molecular formula, $C_9H_{10}O_2$ 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 +ve iodoform test. The structure of (A) is [1998]<br>(a) $C_6H_5COOC_2H_5$<br>(b) $C_2H_5COOC_6H_5$<br>(c) $H_3COCH_2COC_6H_5$<br>(d) $p - H_3CO - C_6H_4 - COCH_3$ |        |
| 86. | Which one of the following esters cannot undergo Claisen self-condensation? [1998]<br>(a) $CH_3 - CH_2 - CH_2 - CH_2 - COOC_2H_5$<br>(b) $C_6H_5COOC_2H_5$<br>(c) $C_6H_5CH_2COOC_2H_5$<br>(d) $C_6H_{11}CH_2COOC_2H_5$  |        |
| 87. | Consider the following transformations :<br>$CH_3COOH \xrightarrow{CaCO_3} [A] \xrightarrow{heat} [B] \xrightarrow[I_2]{NaOH} [C]$   |        |
|     | The molecular formula of [C] is [1996]   |        |
|     | OH<br> <br>(a) $CH_3 - C - CH_3$ (b) $ICH_2 - COCH_3$<br> <br>I<br>(c) $CHI_3$ (d) $CH_3I$   |        |
| 88. | Formic acid is obtained when [1994]<br>(a) Calcium acetate is heated with conc. $H_2SO_4$<br>(b) Calcium formate is heated with calcium acetate<br>(c) Glycerol is heated with oxalic acid at 373 K<br>(d) Acetaldehyde is oxidised with $K_2Cr_2O_7$ and $H_2SO_4$ .  |        |
| 89. | The preparation of ethyl acetoacetate involves<br>(a) Wittig reaction [1994]<br>(b) Cannizzaro's reaction<br>(c) Reformatsky reaction<br>(d) Claisen condensation.   |        |
| 90. | Schotten-Baumann reaction is a reaction of phenols with [1994]<br>(a) Benzoyl chloride and sodium hydroxide<br>(b) Acetyl chloride and sodium hydroxide<br>(c) Salicylic acid and conc. $H_2SO_4$<br>(d) Acetyl chloride and conc $H_2SO_4$  |        |
| 91. | An ester is boiled with KOH. The product is cooled and acidified with concentrated HCl. A white crystalline acid separates. The ester is [1994]<br>(a) Methyl acetate      (b) Ethyl acetate<br>(c) Ethyl formate      (d) Ethyl benzoate  |        |
| 92. | Sodium formate on heating yields [1993]<br>(a) Oxalic acid and $H_2$<br>(b) Sodium oxalate and $H_2$<br>(c) $CO_2$ and NaOH<br>(d) Sodium oxalate.   |        |
| 93. | Among acetic acid, phenol and n-hexanol, which of the following compounds will react with $NaHCO_3$ solution to give sodium salt and carbon dioxide? [1993]<br>(a) Acetic acid<br>(b) n-Hexanol<br>(c) acetic acid and phenol<br>(d) Phenol.   |        |
| 94. | $(CH_3)_2C = CHCOCH_3$ can be oxidized to $(CH_3)_2C = CHCOOH$ by [1993]<br>(a) Chromic acid      (b) $NaOI$<br>(c) Cu at 300°C      (d) $KMnO_4$ .  |        |
| 95. | In which of the following, the number of carbon atoms does not remain same when carboxylic acid is obtained by oxidation [1992]<br>(a) $CH_3COCH_3$ (b) $CCl_3CH_2CHO$<br>(c) $CH_3CH_2CH_2OH$ (d) $CH_3CH_2CHO$ .   |        |
| 96. | Benzoic acid gives benzene on being heated with X and phenol gives benzene on being heated with Y. Therefore X and Y are respectively [1992]<br>(a) Soda-lime and copper<br>(b) Zn dust and NaOH<br>(c) Zn dust and soda-lime<br>(d) Soda-lime and zinc dust.  |        |
| 97. | The compound formed when malonic ester is heated with urea is [1989]<br>(a) Cinnamic acid      (b) Butyric acid<br>(c) Barbituric acid      (d) Crotonic acid.   |        |
| 98. | Which of the following is the correct decreasing order of acidic strength of [1988]<br>(i) methanoic acid      (ii) ethanoic acid<br>(iii) propanoic acid      (iv) butanoic acid.<br>(a) (i)>(ii)>(iii)>(iv)      (b) (ii)>(iii)>(ii)>(i)<br>(c) (i)>(iv)>(iii)>(ii)      (d) (iv)>(i)>(iii)>(ii)   |        |
| 99. | Among the following the strongest acid is [1988]<br>(a) $CH_3COOH$ (b) $CH_2ClCH_2COOH$<br>(c) $CH_2ClCOOH$ (d) $CH_3CH_2COOH$   |        |

## ANSWER KEY

1	(b)	11	(c)	21	(a)	31	(a)	41	(d)	51	(c)	61	(b)	71	(a)	81	(b)	91	(d)
2	(c)	12	(b)	22	(c)	32	(c)	42	(a)	52	(b)	62	(c)	72	(d)	82	(c)	92	(b)
3	(a)	13	(a)	23	(d)	33	(d)	43	(c)	53	(b)	63	(d)	73	(c)	83	(b)	93	(a)
4	(b)	14	(d)	24	(b)	34	(a)	44	(c)	54	(d)	64	(b)	74	(a)	84	(a)	94	(b)
5	(a)	15	(a)	25	(d)	35	(a)	45	(a)	55	(d)	65	(c)	75	(c)	85	(a)	95	(a)
6	(c)	16	(b)	26	(a, d)	36	(c)	46	(d)	56	(b)	66	(a)	76	(a)	86	(b)	96	(d)
7	(b)	17	(d)	27	(b)	37	(d)	47	(a)	57	(d)	67	(a)	77	(c)	87	(c)	97	(c)
8	(c)	18	(d)	28	(d)	38	(c)	48	(c)	58	(a)	68	(d)	78	(d)	88	(c)	98	(a)
9	(b)	19	(b)	29	(d)	39	(a)	49	(b)	59	(d)	69	(d)	79	(a)	89	(d)	99	(c)
10	(b)	20	(d)	30	(d)	40	(c)	50	(c)	60	(a)	70	(d)	80	(a)	90	(a)		

## Hints &amp; Solutions

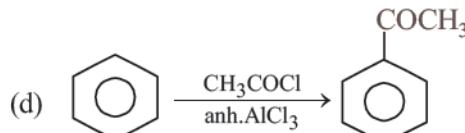
1. (b)



Cannizzaro reaction



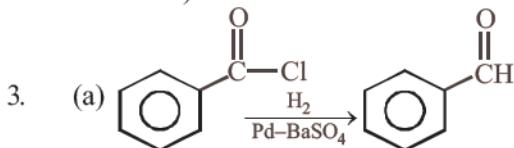
Wurtz reaction



Friedel-Craft acylation

**NOTES** In presence of sunlight chlorination takes place at the side chain by free radical mechanism.

2. (c) Zn/Hg and conc. HCl reduce carboxyl group to methylene group (Clemmensen reduction).



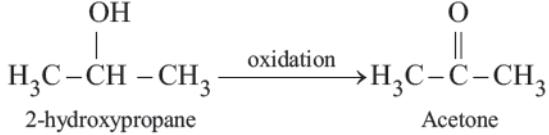
It is Rosenmund reaction.

4. (b)  $\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{NaOH}]{\text{CHCl}_3} \text{C}_6\text{H}_5\text{CHO}$
- (a)  $\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{NaOH}]{\text{CHCl}_3} \text{C}_6\text{H}_5\text{CHO}$

Riemer-Tiemann reaction

Note that, no new C–C bond is formed in Cannizzaro reaction.

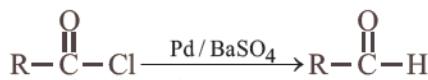
5. (a) Among the given options, only (a) can be oxidized to ketone.



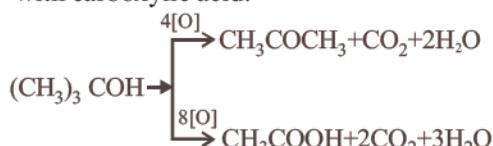
**NOTES** Carbonyl compounds (aldehydes and ketones) are obtained by the oxidation of 1° and 2° alcohols respectively.

6. (c)  $\text{R}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{Cl} \xrightarrow[\text{Pd-BaSO}_4]{\text{H}_2} \text{R}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{H} + \text{HCl}$
- 'P'

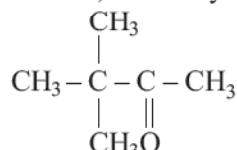
7. (b) Catalyst used in Rosenmund reduction is Pd/BaSO<sub>4</sub>. Rosenmund Reduction is used for reduction of acid chloride.



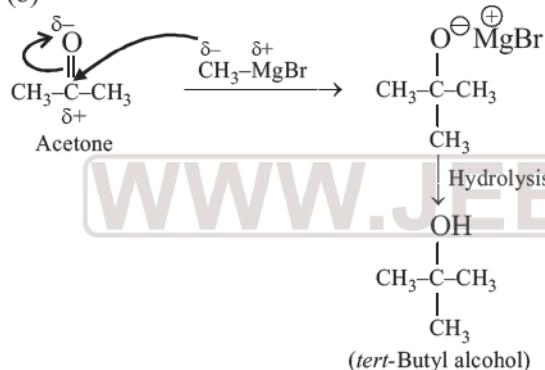
8. (c) By oxidation of tertiary alcohol with stronger oxidising agents ketones may be formed along with carboxylic acid.



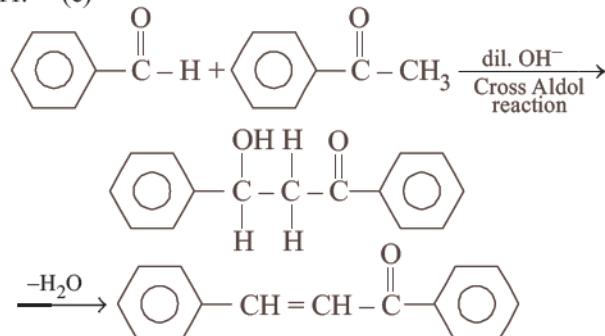
9. (b) Pinacolone is 3,3-dimethyl-2-butanone.



10. (b)

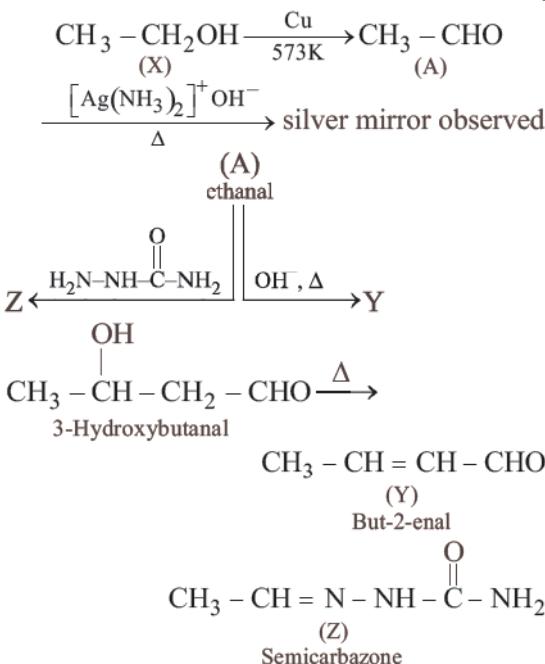


11. (c)

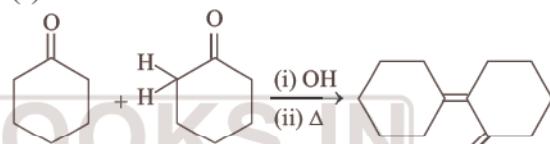


In the presence of dil. NaOH, C<sub>6</sub>H<sub>5</sub>CHO and C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub> will react to undergo cross-alcohol condensation.

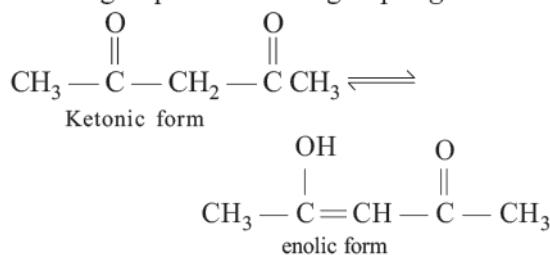
12. (b) Since 'A' gives positive silver mirror test therefore, it must be an aldehyde or α-Hydroxyketone. Also, reaction with OH<sup>-</sup> i.e., aldol condensation (by assuming alkali to be dilute) indicates that 'A' is aldehyde as aldol reaction of ketones is reversible and carried out in special apparatus. It indicates that 'A' is an aldehyde.



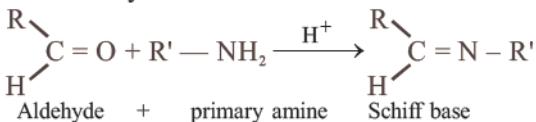
13. (a)



14. (d) Keto-enol tautomerism is possible only in those aldehydes and ketones which have at least one α-hydrogen atom, which can convert the ketonic group to the enolic group. e.g.



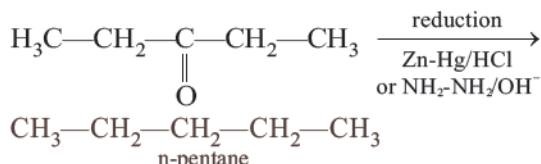
15. (a) Schiff base is formed when 1° amine reacts with aldehydes.



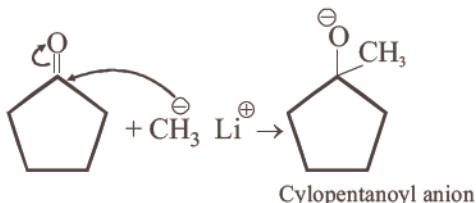
16. (b) H<sub>3</sub>C—CH<sub>2</sub>—C(=O)—CH<sub>2</sub>—CH<sub>3</sub>

does not give iodoform test due to absence of (CH<sub>3</sub>—C—) group. It also does not give Tollen's test.

On reduction, it gives n-pentane

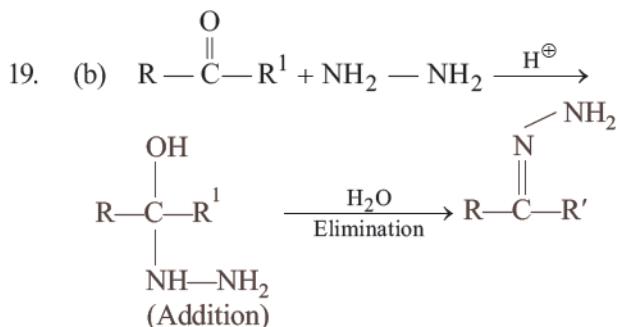
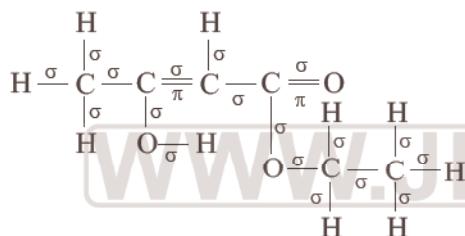


17. (d)



Reactions involving methyl lithium require anhydrous conditions, because the compound is highly reactive towards water. Methyl lithium is stable as a solution in ether.

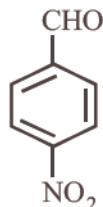
18. (d) Enolic form of ethyl acetoacetate has 18 sigma and 2 pi-bonds as shown below:



While in all other cases no elimination take place.

20. (d) Any substituent in the carbonyl compound that increases the positive charge on the carbonyl carbon will increase reactivity towards nucleophilic addition.

$-\text{NO}_2$  shows  $-M$  effect hence



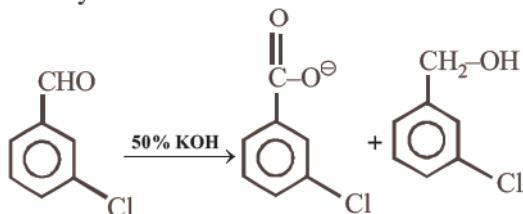
is most reactive towards nucleophilic addition reaction.

21. (a) Enolic form predominates in compounds containing two carbonyl groups separated by a  $-\text{CH}_2$  group. This is due to following two factors.

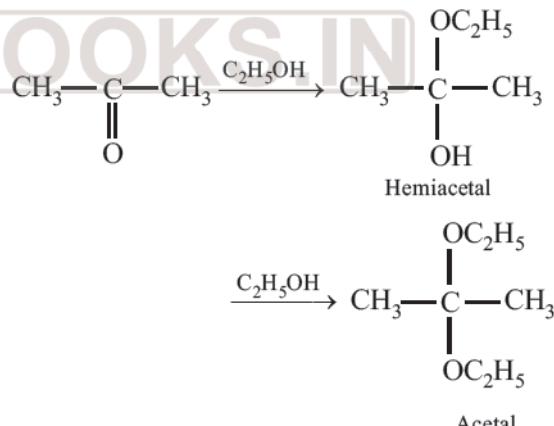
(i) Presence of conjugation which increases stability.

(ii) Formation of intramolecular hydrogen bond between enolic hydroxyl group and second carbonyl group which leads to stabilisation of the molecule. Hence, the correct answer is III > II > I.

22. (c) Cannizzaro reaction - when an aldehyde containing no  $\alpha$ -H undergo reaction in presence of 50% KOH. It disproportionates to form a molecule of carboxylic acid and a molecule of alcohol.



23. (d) Anhydrous alcohols add to the carbonyl group of aldehydes in the presence of anhydrous hydrogen chloride to form acetals via hemiacetals.

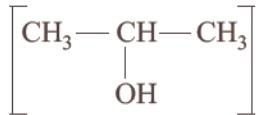
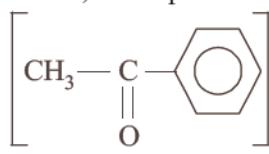


24. (b)  $\text{CH}_3\text{CHO}$  gives Iodoform test but  $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$  does not give Iodoform test due to absence of methyl group.

25. (d)  $\text{R}-\text{CH}=\text{O} + \text{H}_2\text{N}-\text{NH}_2 \rightarrow \text{R}-\text{CH}=\text{N}-\text{NH}_2$   
Such reactions take place in slightly acidic medium and involve nucleophilic addition of the ammonia derivative.

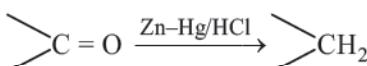
26. (a, d) The compounds with  $\text{CH}_3-\underset{\text{OH}}{\underset{|}{\text{C}}}-\text{group}$  or  $\text{CH}_3-\text{CH}-\text{group}$  give iodoform test.

Hence, Acetophenone

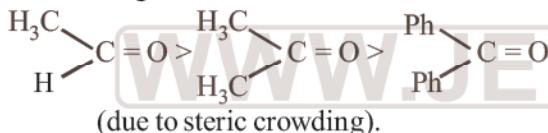


both give a yellow precipitate of  $\text{CHI}_3$  (iodoform) with iodine and alkali.

27. (b) Clemmensen reduction is

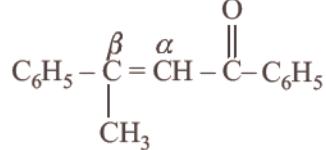
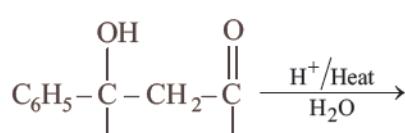
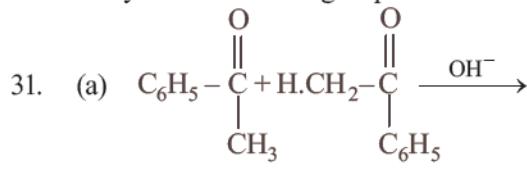


28. (d) The reactivity of the carbonyl group towards the nucleophilic addition reactions depend upon the magnitude of the positive charge on the carbonyl carbon atom (electronic factor) and also on the crowding around the carboxyl carbon atom in the transition state (steric factor). Both these factors predict the following order



29. (d) Among the given compounds only  $\text{CH}_3\text{OH}$  does not give iodoform reaction.

30. (d) The intermediate is carbocation which is destabilised by  $\text{C} = \text{O}$  group (present on  $\alpha$ -carbon to the  $-\text{OH}$  group) in the first three cases. In (d),  $\alpha$ -hydrogen is more acidic which can be removed as water. Moreover, the positive charge on the intermediate carbocation is relatively away from the  $\text{C} = \text{O}$  group.



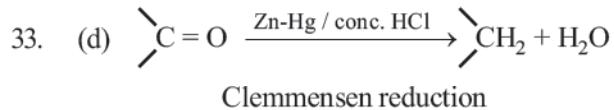
Thus, two molecules of acetophenone condense to form a  $\beta$ -hydroxy ketone which gets dehydrated in the presence of acid upon heating to form  $\alpha$ ,  $\beta$ -unsaturated compound.

i.e., option (a) is correct.

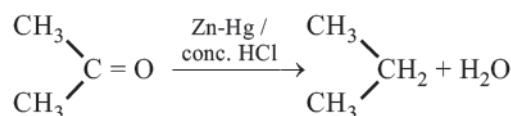
32. (c) A strong base ( $\text{OH}^-$ ) abstract an  $\alpha - \text{H}$  atom from ketone which is acidic in nature.



The acidity of  $\alpha$ -hydrogen atom in ketone is due to resonance stabilization of enolate anion.

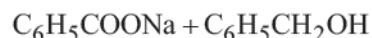


e.g.

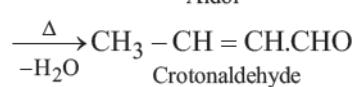
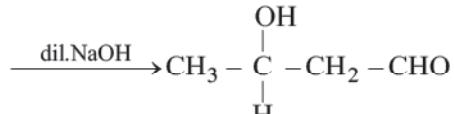
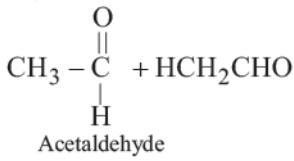


Clemmensen reduction is complementary to wolf-kishner reduction, which also convert aldehyde and ketones to hydrocarbons. Clemmensen reduction carried out in strongly acidic conditions and wolf-kishner reduction carried out in strongly basic conditions.

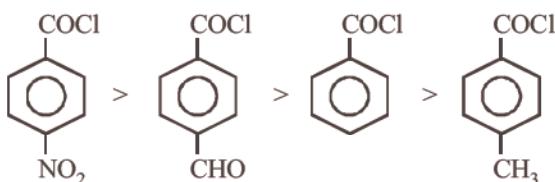
34. (a) Aldehydes containing no  $\alpha$ -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation-reduction known as Cannizzaro's reaction.



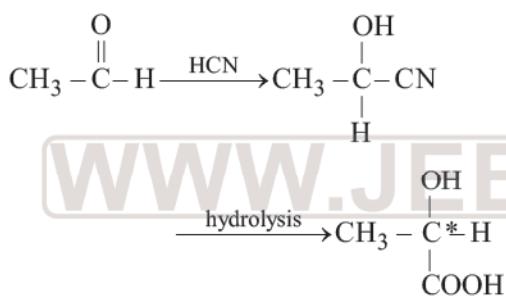
35. (a) Aldehydes and ketones having at least one  $\alpha$ -hydrogen atom in presence of dilute alkali give  $\beta$ -hydroxy aldehyde or  $\beta$ -hydroxy ketone.



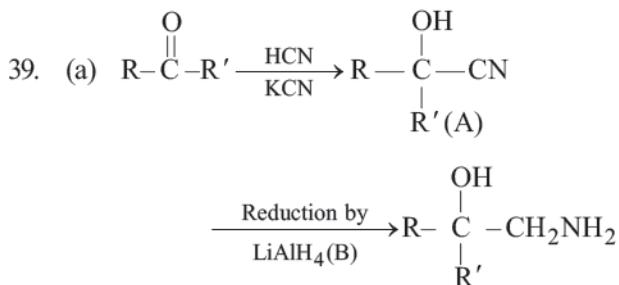
36. (c) The degree of hydrolysis increases as the magnitude of positive charge on carbonyl group increases. Electron withdrawing group increases the positive charge and electron releasing group decreases the positive charge. Among these  $\text{NO}_2$  & -CHO are electron withdrawing group from which  $-\text{NO}_2$  exhibit more  $-I$  effect than -CHO. On the other hand  $-\text{CH}_3$  is an electron releasing group therefore the order of reactivity towards hydrolysis is



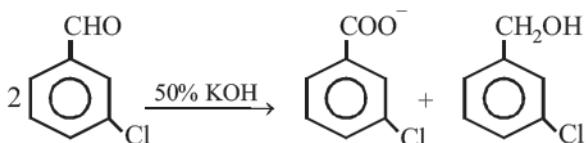
37. (d) Out of given compound only acetaldehyde can form optical active hydroxy acid as it contains one asymmetric carbon atom as marked below:



38. (c) Aldehydes are more reactive than ketones due to +I effect of  $-\text{CH}_3$  group. There are two  $-\text{CH}_3$  group in acetone which reduces +ve charge density on carbon atom of carbonyl group. More hindered carbonyl group too becomes less reactive. So, in the given case  $\text{CH}_3\text{CHO}$  is the right choice.



40. (c) It is a simple Cannizzaro reaction.



41. (d)  $\text{CH}_3 - \overset{\text{H}}{\underset{\text{CN}}{\text{C}}} = \text{O} + \text{HCN} \rightarrow \text{CH}_3 - \overset{\text{H}}{\underset{\text{CN}}{\text{C}}} - \text{OH}$

$$\xrightarrow{\text{H}^+ / \text{H}_2\text{O}} \text{OH} - \overset{\text{H}}{\underset{\text{COOH}}{\text{C}}} - \text{CH}_3 + \text{CH}_3 - \overset{\text{H}}{\underset{\text{COOH}}{\text{C}}} - \text{OH}$$

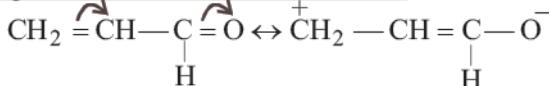
50% L-Lactic acid                    50% D-Lactic acid

42. (a) Acetophenone is a ketone, cyclopentanone doesn't contain  $(4n + 2)\pi$  electron hence is not aromatic. Diastase is an enzyme used in the preparation of Maltose (Malt sugar,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) through hydrolysis of starch.

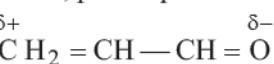
43. (c) Tollen's reagent is used to detect aldehyde group. Tollen's reagent is an ammonical solution of silver nitrate. When aldehyde is added to Tollen's reagent, silver oxide is reduced to metallic silver which deposits as mirror.



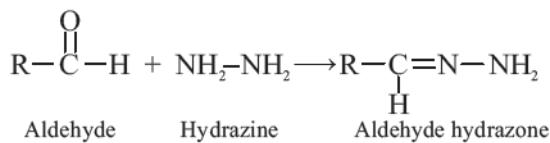
44. (c) In  $\text{CH}_2 = \text{CH} - \text{CHO}$  due to  $-M$  effect of  $-\text{CHO}$  group, polarization of electron takes place as follows:



Hence, partial polarization is represented as

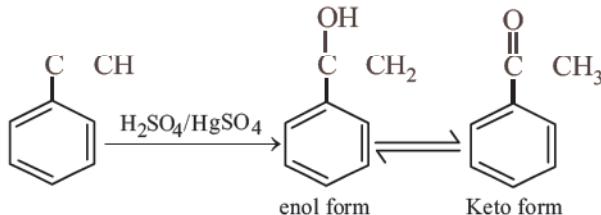


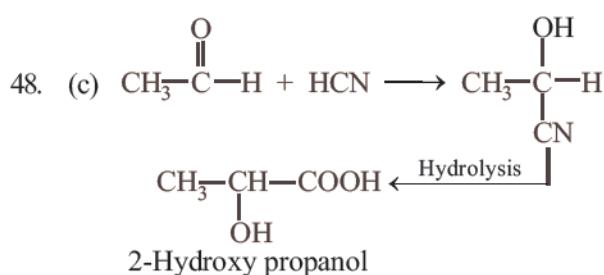
45. (a)



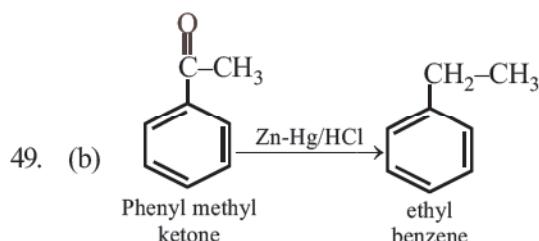
46. (d) Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones and those alcohols which possess  $\text{CH}_3\text{CH}(\text{OH})$ -group. As 3-pentanone does not contain  $\text{CH}_3\text{CO}$ -group therefore it does not give iodoform test.

47. (a)





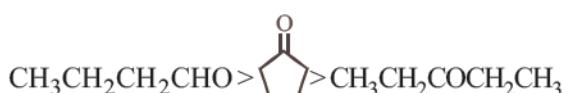
(As it has a chiral C-atom thus, it is optically active)



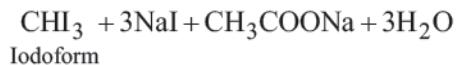
This reaction is known as Clemmensen's reduction.

50. (c) Aldol condensation is given by the compounds which contain  $\alpha$ -hydrogen atom. As the given compound does not contain  $\alpha$  hydrogen atom. Hence, it does not undergo aldol condensation.

51. (c) More is the electron - deficiency of the carbonyl carbon, greater will be the reactivity of the carbonyl compounds towards nucleophilic addition.

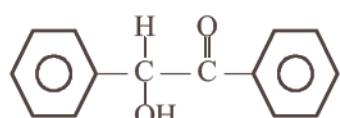
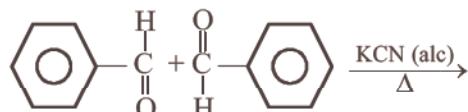


52. (b)  $\text{CH}_3\text{COCH}_3 + 3\text{I}_2 + 4\text{NaOH} \longrightarrow$   
Acetone



Thus, acetone reacts with iodine to form iodoform in the presence of NaOH.

53. (b) When benzaldehyde is refluxed with aqueous alcoholic potassium cyanide, two molecules of benzaldehyde condense together to form benzoin

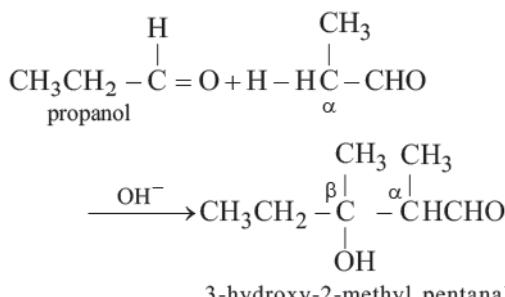


NOTES

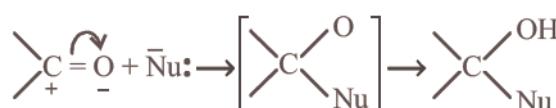
In benzoin condensation potassium cyanide act as a catalyst. Chiral catalyst can make benzoins with stereoselectivity with a significant enantiomeric excess.

54. (d) Dihydrogen sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) does not have a lone pair of electrons on the P atom hence, can not act as a nucleophile and hence, does not react with aldehydes and ketones.

55. (d) Aldehydes which contain an  $\alpha$  -hydrogen on a saturated carbon, undergo aldol condensation.

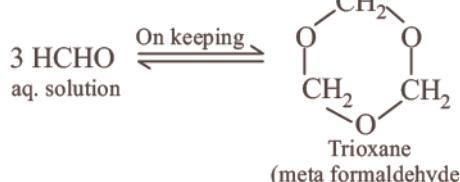


56. (b) Acetaldehyde reacts only with nucleophiles. Since, the mobile  $\pi$ -electrons of carbon–oxygen double bond are strongly pulled towards oxygen, carbonyl carbon is electron-deficient and carbonyl oxygen is electron-rich. Thus, the electron deficient (acidic) carbonyl carbon is most susceptible to attack by electron rich nucleophilic reagents, that is, by base. Hence, the typical reaction of aldehydes and ketones is nucleophilic addition.

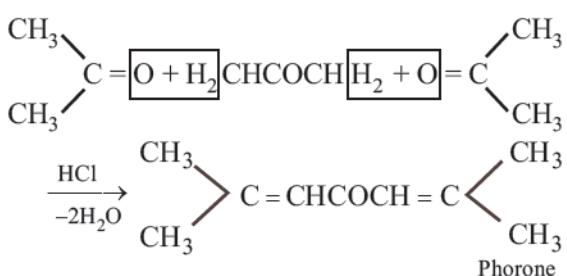


57. (d)  $I_2$  and NaOH react with acetophenone ( $C_6H_5COCH_3$ ) to give yellow ppt. of  $CHI_3$  but benzophenone ( $C_6H_5COC_6H_5$ ) does not and hence, can be used to distinguish between them.

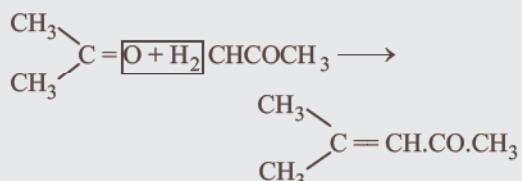
58. (a)



59. (d) Acetone forms mesitylene (1,3,5-trimethyl benzene) on distillation with conc.  $\text{H}_2\text{SO}_4$ .  
60. (a) When 3 molecules are combined in presence of dry  $\text{HCl}$  gas they condense to form phorone.



Two molecules of acetone condense to form mesityl oxide.

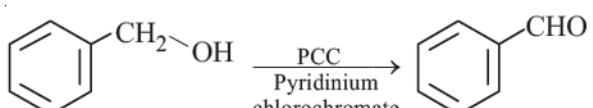


61. (b) Aldehydes containing no  $\alpha$ -hydrogen atom on warming with 50% NaOH or KOH undergo disproportionation i.e. self oxidation - reduction known as Cannizzaro's reaction.



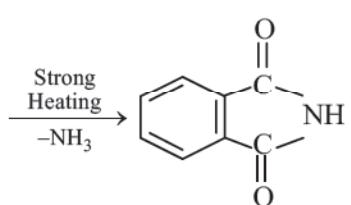
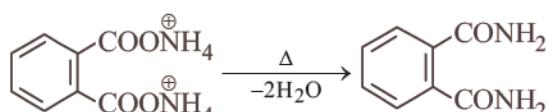
62. (c) Formalin is an aqueous solution (40%) of formaldehyde.

63. (d)



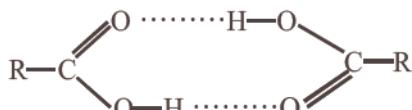
PCC is a mild oxidizing agent which oxidises primary alcohol to aldehyde.

64. (b) 
$$\text{C}_6\text{H}_5\text{COOH} + \text{NH}_3 \longrightarrow$$

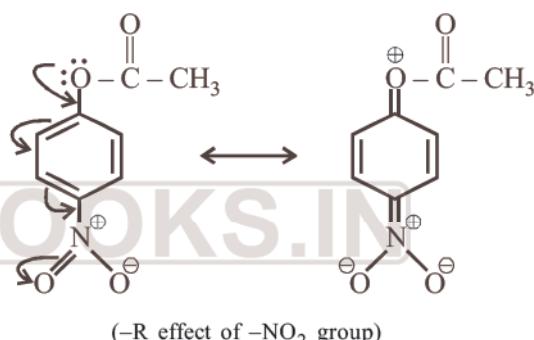


65. (c) Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass.

This is due to more extensive association through intermolecular H-bonding.



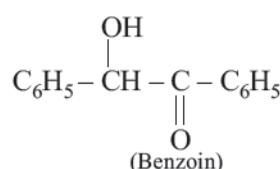
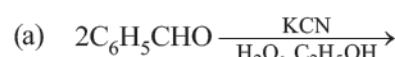
66. (a) Among the substituent attached to the benzene ring,  $-\text{NO}_2$  group is the most electron withdrawing, thus withdraws electron density from carbonyl carbon thus facilitate the attack of  $\text{OH}^-$  ion.

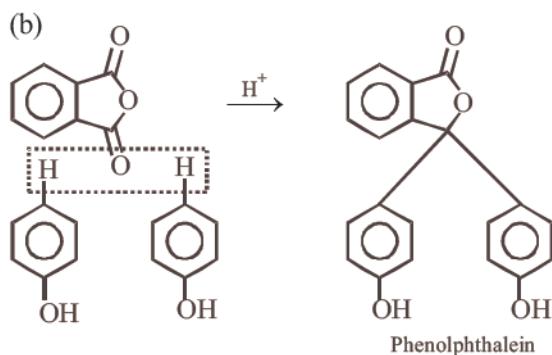


67. (a)  $\text{CF}_3\text{COOH} > \text{CCl}_3\text{COOH} > \text{HCOOH} > \text{CH}_3\text{COOH}$  ( $K_a$  order)

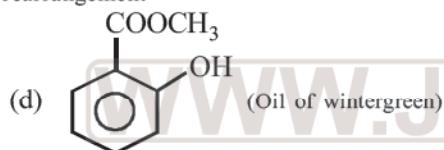
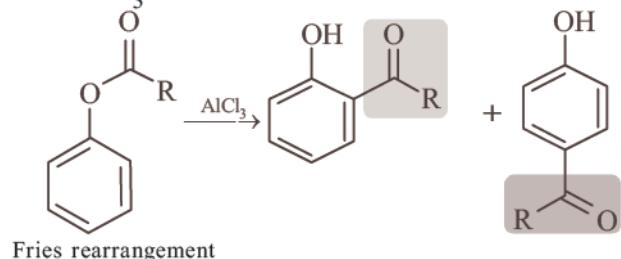
The halogenated fatty acids are much stronger acids than the parent fatty acid and moreover the acidity among the halogenated fatty acid increases almost proportionately with the increase in electronegativity of the halogen present. Further, formic acid having no alkyl group is more acidic than acetic acid.

68. (d)

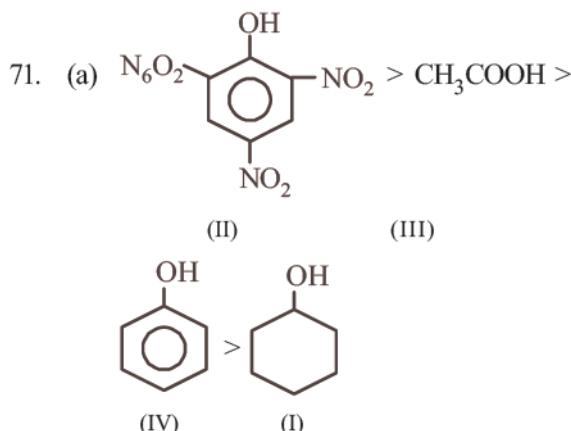
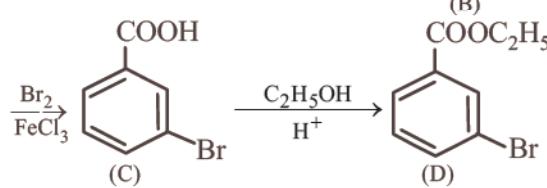
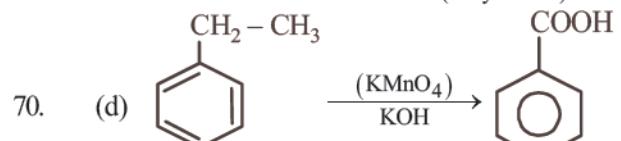
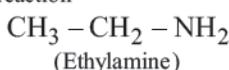
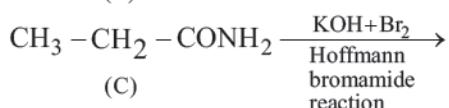
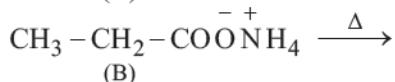
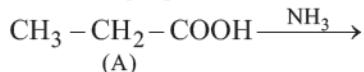




(c) The Fries rearrangement enables the preparation of acylphenols. The reaction is catalysed by Bronsted or Lewis acid such as  $\text{AlCl}_3$ .

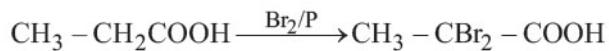


69. (d) Since, C when heated with  $\text{Br}_2$  in presence of KOH produces ethylamine, hence it must be propanamide and hence the organic compound (A) will be propanoic acid. The reactions follows:



**Explanation:** Presence of three  $-\text{NO}_2$  groups in  $o$ -,  $p$ - positions to phenolic groups (in III) makes phenol strongly acidic because its corresponding phenate ion (conjugate base) is highly stabilised due to resonance. Conjugate base of  $\text{CH}_3\text{COOH}$ , II (*i.e.*  $\text{CH}_3\text{COO}^-$ ) is resonance hybrid of two equivalent structures. The conjugate base of phenol, IV is stabilized due to resonance (note that here all resonating structures are not equivalent). The conjugate base of cyclohexanol, I does not exhibit resonance, hence not formed.

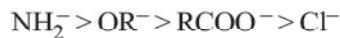
72. (d)  $\text{Cl}^-$  is the weakest base and hence better leaving group.
73. (c) This reaction is an example of Hell - Volhard Zelinsky reaction. In this reaction acids containing  $\alpha$ -H on treatment with  $X_2/\text{P}$  give di-halo substituted acid.



#### Hell-volhard-zelinsky reaction:

Carboxylic acids having an  $\alpha$ -hydrogen are halogenated at the  $\alpha$ -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give  $\alpha$ -halocarboxylic acids. The reaction fails to accomplish the fluorination and iodination of carboxylic acids.

74. (a) The more the basic character of the leaving group, the lesser is the reactivity. The basic character follows the order:



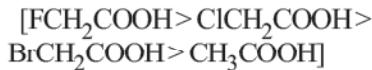
Hence, the relative reactivities of acyl compounds towards nucleophilic substitution follow the order Acyl halides > Acid anhydride > Ester > Amide.

75. (c) Electron withdrawing substituents (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.

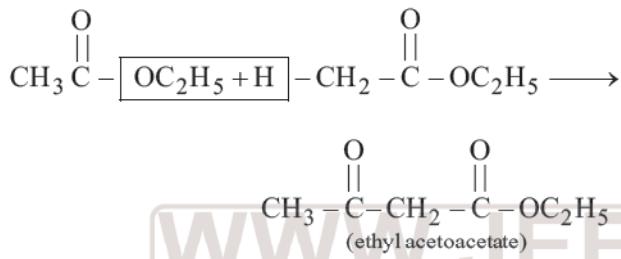
Electronegativity decreases in order



and hence  $-I$  effect also decreases in the same order, therefore the correct option is



76. (a) It is an example of Claisen condensation. The product is acetoacetic ester.



77. (c)  $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{SOCl}_2} \text{CH}_3\text{CH}_2\text{COCl} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow[\text{Br}_2]{\text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2$

78. (d)  $\text{CH}_3\text{COOH} \xrightarrow{\text{SOCl}_2} \text{CH}_3-\text{COCl}$
- Friedel Craft reaction       $\text{C}_6\text{H}_6 / \text{AlCl}_3$
- 

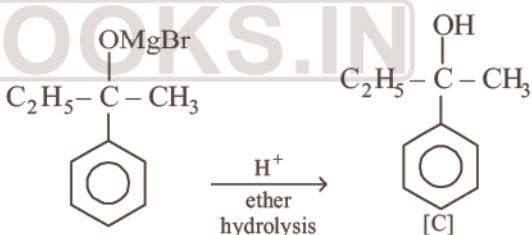
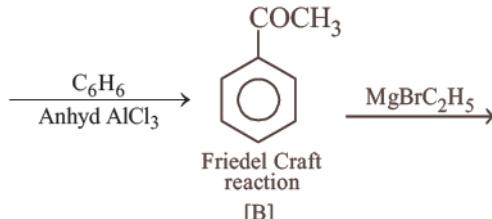
79. (a) Among the given options, only  $\text{PCl}_5$  can convert an alcoholic group as well as a carboxyl group to chloride.



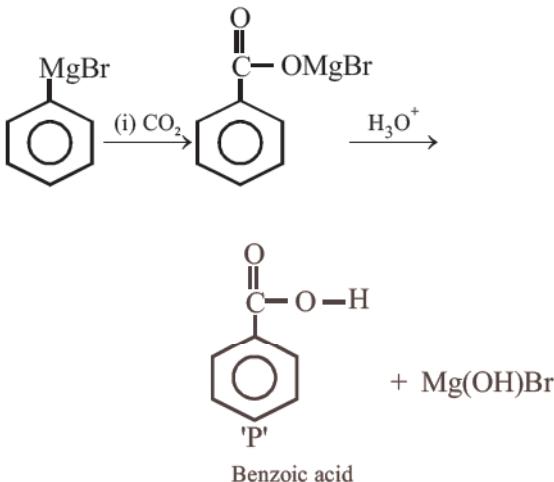
Other than  $\text{PCl}_5$  or  $\text{PCl}_3$ ,  $\text{SOCl}_2$  also can be used.  $\text{SOCl}_2$  is preferred because the other two products in this case are gaseous and escape the reaction mixture. This makes the purification of the products easier.



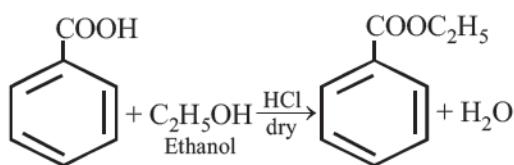
80. (a)  $\text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{COCl}$



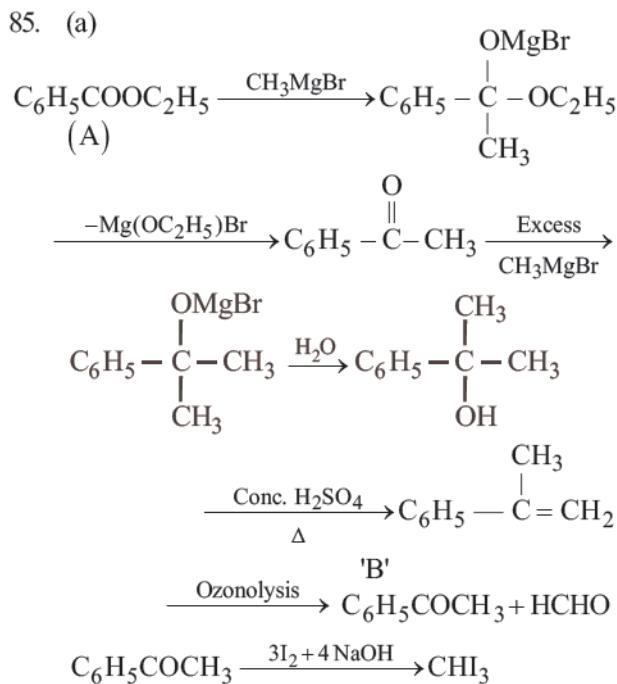
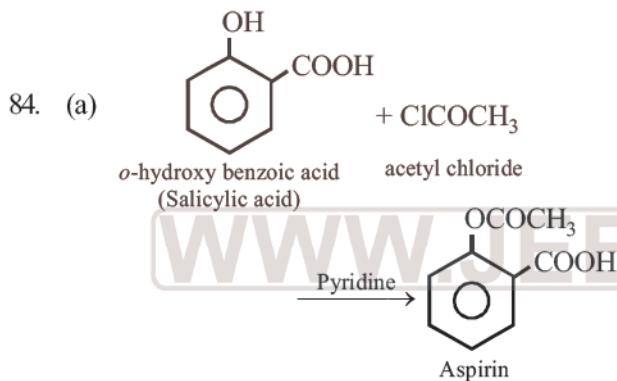
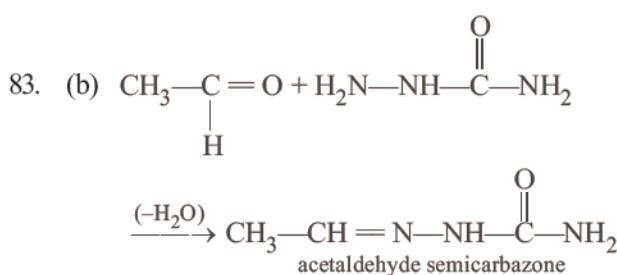
81. (b) Grignard reagent forms addition product with bubbled carbondioxide which on hydrolysis with  $\text{HCl}$  yields benzoic acid.



82. (c)

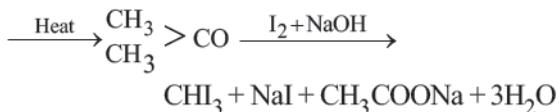


This process is known as esterification.

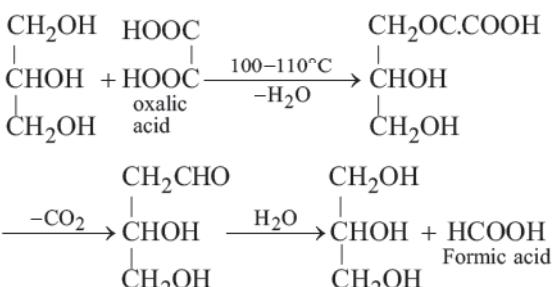


86. (b) The ester having  $\alpha$ -hydrogen atom show Claisen condensation reaction. We know that ethyl benzoate ( $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ ) does not contain  $\alpha$ -hydrogen. Therefore,  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$  does not undergo Claisen self condensation.

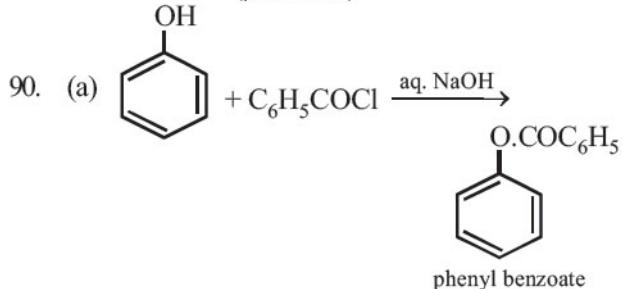
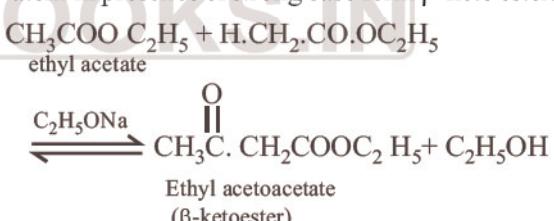
87. (c)  $\text{CH}_3\text{COOH} + \text{CaCO}_3 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca}$



88. (c) When glycerol is heated with oxalic acid following reaction occurs.



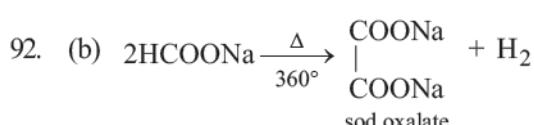
89. (d) In Claisen condensation intermolecular condensation of esters containing  $\alpha$ -hydrogen atom in presence of strong base form  $\beta$ -keto ester.



The function of NaOH is

- (i) To convert phenol to more stronger nucleophile  $\text{PhO}^-$
- (ii) To neutralize the acid formed

91. (d) Methyl acetate and ethyl acetate on hydrolysis give  $\text{CH}_3\text{COOH}$  which is a liquid. Similarly ethyl formate on hydrolysis will give formic acid which is also a liquid. Only ethyl benzoate on hydrolysis will give benzoic acid which is a solid.



93. (a) Among acetic acid, phenol and n-hexanol only  $\text{CH}_3\text{COOH}$  reacts with  $\text{NaHCO}_3$  to evolve  $\text{CO}_2$  gas.
- $$\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$$

94. (b) The only reagent suitable for this conversion is  $\text{NaOI}$  or  $\text{NaOH} + \text{I}_2$  (iodoform test):
- $$(\text{CH}_3)_2\text{C} = \text{CHCOCH}_3 \xrightarrow{\text{NaOI}} (\text{CH}_3)_2\text{C} = \text{CHCOOH} + \text{CHI}_3.$$

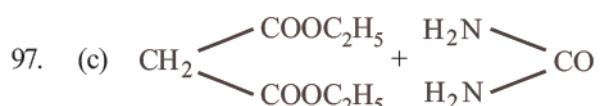


Chromic acid and  $\text{KMnO}_4$  will cleave the molecule at the site of double bond while  $\text{Cu}$  at  $300^\circ\text{C}$  cannot oxidise  $\text{COCH}_3 \longrightarrow \text{COOH}$ .

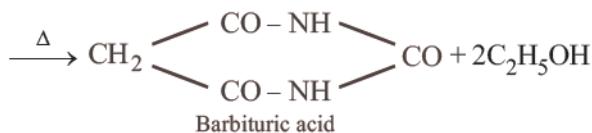
95. (a) Ketones on oxidation give carboxylic acids with lesser number of carbon atoms, i.e.,



96. (d)  $\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{Soda-lime(X)}} \text{C}_6\text{H}_6 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
- $$\text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{Zn dust(Y)}} \text{C}_6\text{H}_6 + \text{ZnO}$$

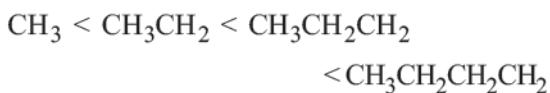


Malonic ester



Barbituric acid

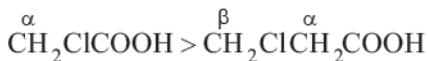
98. (a) An electron releasing substituent (+I effect) intensify the negative charge on the anion resulting in the decrease of stability and thus decreases the acidity of the acid. Hence, acidic character decreases as the + I-effect of the alkyl group increases as



Hence the order of acidic strength becomes:

(i) > (ii) > (iii) > (iv)

99. (c) Chlorine is electron withdrawing group. Further Inductive effect is stronger at  $\alpha$ -position than  $\beta$ -position. i.e.,



# 27

# Amines

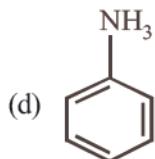
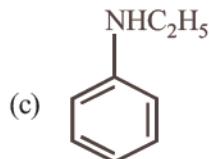
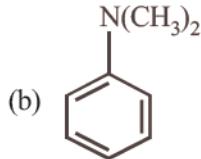
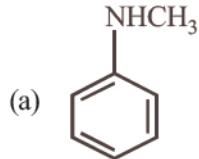
## Trend Analysis with Important Topics & Sub-Topics

		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD								
Aliphatic and aromatic amines	carbylamine reaction	1	E								
	basic strength of amines			1	A			1	A	1	A
	Hoffmann bromamide reaction							1	A		
	electrophilic substitution					1	A				

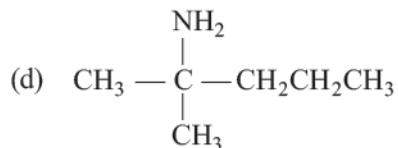
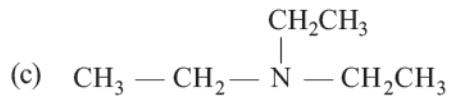
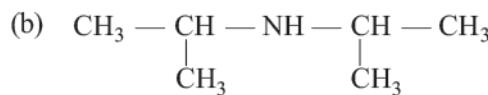
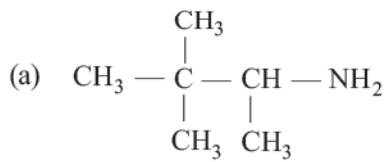
LOD - Level of Difficulty      E - Easy      A - Average      D - Difficult      Qns - No. of Questions

### Topic 1: Aliphatic and Aromatic Amines

1. Which of the following amine will give the carbylamine test? *[2020]*



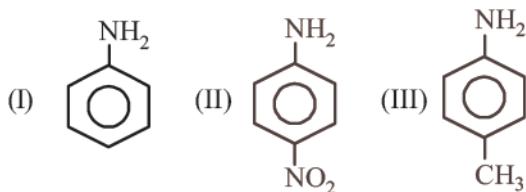
2. The amine that reacts with Hinsberg's reagent to give an alkali insoluble product is *[NEET Odisha 2019]*



3. The correct order of the basic strength of methyl substituted amines in aqueous solution is :



4. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because **[2018]**
- Inspite of substituents nitro group always goes to only *m*-position.
  - In electrophilic substitution reactions, amino group is meta directive.
  - In acidic (strong) medium aniline is present as anilinium ion.
  - In absence of substituents, nitro group always goes to *m*-position.
5. The correct increasing order of basic strength for the following compounds is : **[2017]**



- $\text{III} < \text{I} < \text{II}$
  - $\text{III} < \text{II} < \text{I}$
  - $\text{II} < \text{I} < \text{III}$
  - $\text{II} < \text{III} < \text{I}$
6. Which of the following reactions is appropriate for converting acetamide to methanamine? **[2017]**
- Hoffmann hypobromamide reaction
  - Stephens reaction
  - Gabriels phthalimide synthesis
  - Carbylamine reaction
7. The correct statement regarding the basicity of arylamines is **[2016]**
- Arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalized by interaction with the aromatic ring  $\pi$  electron system.
  - Arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalized by interaction with the aromatic ring  $\pi$  electron system.
  - Arylamines are generally more basic than alkylamines because of aryl group.

- Arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridized.
- The electrolytic reduction of nitrobenzene in strongly acidic medium produces :- **[2015]**

  - Azoxybenzene
  - Azobenzene
  - Aniline
  - p*-Aminophenol

- The number of structural isomers possible from the molecular formula  $\text{C}_3\text{H}_9\text{N}$  is : **[2015 RS]**

  - 4
  - 5
  - 2
  - 3

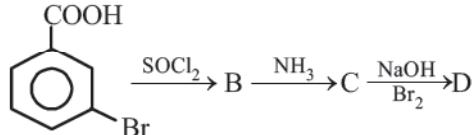
- Method by which aniline cannot be prepared is: **[2015 RS]**

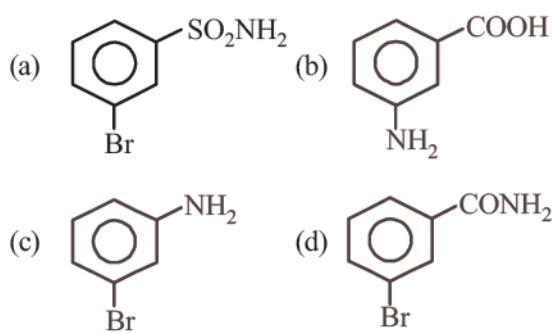
  - hydrolysis of phenylisocyanide with acidic solution
  - degradation of benzamide with bromine in alkaline solution
  - reduction of nitrobenzene with  $\text{H}_2/\text{Pd}$  in ethanol
  - potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous  $\text{NaOH}$  solution.

- Some reactions of amines are given. Which one is not correct ? **[NEET Kar. 2013]**

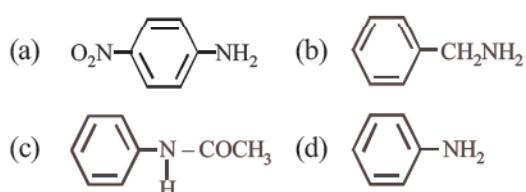
  - $(\text{CH}_3)_2\text{NH} + \text{NaNO}_2 + \text{HCl} \rightarrow (\text{CH}_3)_2\text{N}-\text{N}=\text{O}$
  - $(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_5 + \text{NaNO}_2 + \text{HCl} \rightarrow (\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_5-\text{N}=\text{NCl}$
  - $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{N}_2$
  - $\text{CH}_3\text{NH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{CH}_3\text{NHSO}_2\text{C}_6\text{H}_5$ .

12. In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*. **[2011]**





13. Which of the following compounds is most basic? [2011 M]



14. Which of the following statements about primary amines is 'False'? [2010]

- (a) Alkyl amines are stronger bases than aryl amines
- (b) Alkyl amines react with nitrous acid to produce alcohols
- (c) Aryl amines react with nitrous acid to produce phenols
- (d) Alkyl amines are stronger bases than ammonia

15. Match the compounds given in List - I with their characteristic reactions given in List - II. Select the correct option. [2010]

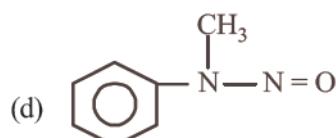
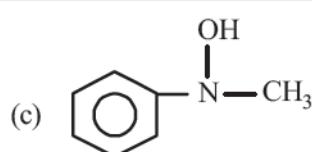
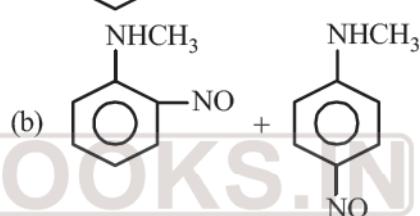
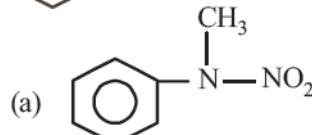
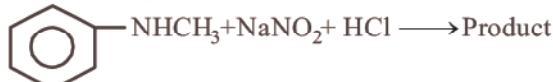
List - I Compounds	List - II Reactions
(1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	(i) alkaline hydrolysis
(2) $\text{CH}_3\text{C}\equiv\text{CH}$	(ii) with KOH (alcohol) and $\text{CHCl}_3$ produces bad smell
(3) $\text{CH}_3\text{CH}_2\text{COOCH}_3$	(iii) gives white ppt. with ammonical $\text{AgNO}_3$

- (4)  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$  (iv) with Lucas reagent cloudiness appears after 5 minutes

**Options :**

- |     |       |       |       |
|-----|-------|-------|-------|
| (1) | (2)   | (3)   | (4)   |
| (a) | (iv)  | (ii)  | (iii) |
| (b) | (ii)  | (i)   | (iv)  |
| (c) | (iii) | (ii)  | (i)   |
| (d) | (ii)  | (iii) | (iv)  |

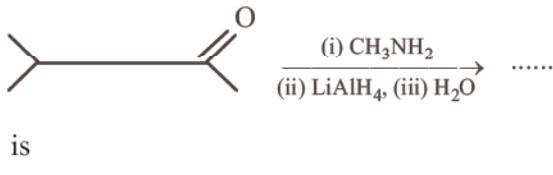
16. Predict the product: [2009]

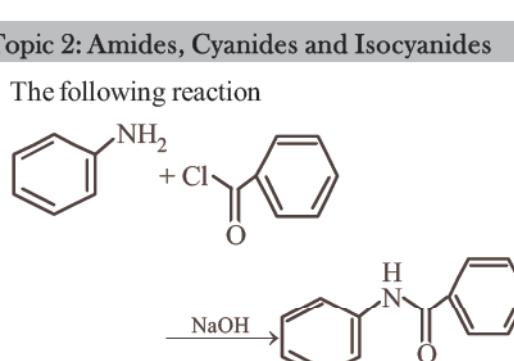


17. Which of the following is more basic than aniline? [2006]

- (a) Triphenylamine
- (b) p-Nitroaniline
- (c) Benzylamine
- (d) Diphenylamine

18. The major organic product formed from the following reaction : [2005]

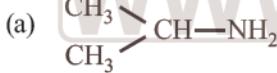


- |  |   |
|--|---|
| <p>(a) </p> <p>(b) </p> <p>(c) </p> <p>(d) </p>  | <p>23. The compound obtained by heating a mixture of a primary amine and chloroform with ethanolic potassium hydroxide (KOH) is <b>[1997]</b></p> <p>(a) an alkyl cyanide (b) a nitro compound<br/>(c) an alkyl isocyanide (d) an amide</p> <p>24. When aniline reacts with oil of bitter almonds (<math>C_6H_5CHO</math>), condensation takes place and benzal derivative is formed. This is known as <b>[1995]</b></p> <p>(a) Million's base (b) Schiff's reagent<br/>(c) Schiff's base (d) Benedict's reagent</p> <p>25. What is the decreasing order of basicity of primary, secondary and tertiary ethylamines and <math>NH_3</math>? <b>[1994]</b></p> <p>(a) <math>NH_3 &gt; C_2H_5NH_2 &gt; (C_2H_5)_2NH &gt; (C_2H_5)_3N</math><br/>(b) <math>(C_2H_5)_3N &gt; (C_2H_5)_2NH &gt; C_2H_5NH_2 &gt; NH_3</math><br/>(c) <math>(C_2H_5)_2NH &gt; C_2H_5NH_2 &gt; (C_2H_5)_3N &gt; NH_3</math><br/>(d) <math>(C_2H_5)_2NH &gt; (C_2H_5)_3N &gt; C_2H_5NH_2 &gt; NH_3</math></p> |
| <p>19. Electrolytic reduction of nitrobenzene in weakly acidic medium gives <b>[2005]</b></p> <p>(a) N-Phenylhydroxylamine<br/>(b) Nitrosobenzene<br/>(c) Aniline<br/>(d) <i>p</i>-Hydroxyaniline</p> <p>20. The constituent of the powerful explosive RDX is formed during the nitration of <b>[2000]</b></p> <p>(a) Toluene (b) Phenol<br/>(c) Glycerol (d) Urotropine</p> <p>21. Which of the following is most basic in nature?<br/>(a) <math>NH_3</math> (b) <math>CH_3NH_2</math> <b>[2000]</b><br/>(c) <math>(CH_3)_2NH</math> (d) <math>C_6H_5NHCH_3</math></p> <p>22. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is</p> <p>(a) 1,3,5-Tribromobenzene <b>[1998]</b><br/>(b) <i>p</i>-Bromofluorobenzene<br/>(c) <i>p</i>-Bromoaniline<br/>(d) 2,4,6-Tribromofluorobenzene</p> | <p>26. Mark the correct statement <b>[1988]</b></p> <p>(a) Methylamine is slightly acidic<br/>(b) Methylamine is less basic than ammonia<br/>(c) Methylamine is a stronger base than ammonia<br/>(d) Methylamine forms salts with alkalies.</p>   |
| <p><b>Topic 2: Amides, Cyanides and Isocyanides</b></p>  |   |
| <p>27. The following reaction</p>  |   |

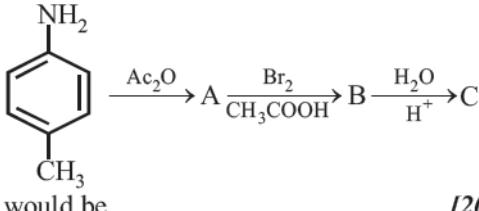
## Topic 2: Amides, Cyanides and Isocyanides

27. The following reaction

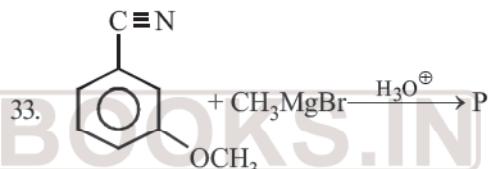
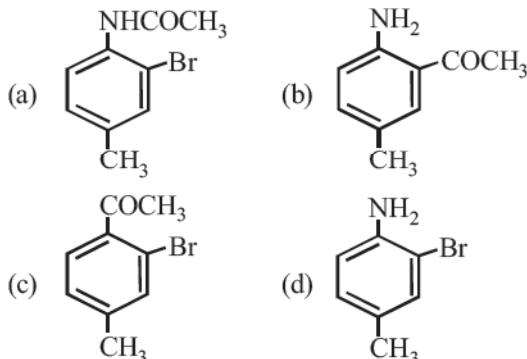
The reaction scheme shows the condensation of aniline with benzoyl chloride followed by deprotection with NaOH. Aniline (benzene ring with NH<sub>2</sub>) reacts with benzoyl chloride (C<sub>6</sub>H<sub>5</sub>COCl) to form N-benzoylaniline (benzene ring with NH-C(=O)-C<sub>6</sub>H<sub>5</sub>). This intermediate is then treated with NaOH, which deprotects the amine group to yield N-benzylbenzene (benzene ring with -NH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>).

- (a) Friedel-Craft's reaction  
 (b) Perkin's reaction  
 (c) Acetylation reaction  
 (d) Schotten-Baumen reaction
28. On hydrolysis of a "compound", two compounds are obtained. One of which on treatment with sodium nitrite and hydrochloric acid gives a product which does not respond to iodoform test. The second one reduces Tollen's reagent and Fehling's solution. The "compound" is [NEET Kar. 2013]  
 (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CON}(\text{CH}_3)_2$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NC}$   
 (c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$   
 (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{ON}=\text{O}$
29. An organic compound ( $\text{C}_3\text{H}_9\text{N}$ ) (A), when treated with nitrous acid, gave an alcohol and  $\text{N}_2$  gas was evolved. (A) on warming with  $\text{CHCl}_3$  and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A).  
 (a)  [2012 MJ]  
 (b)  $\text{CH}_3\text{CH}_2-\text{NH}-\text{CH}_3$   
 (c)  $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{N}}}-\text{CH}_3$   
 (d)  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$
30. Acetamide is treated with the following reagents separately. Which one of these would yield methylamine? [2010]  
 (a)  $\text{NaOH}-\text{Br}_2$   
 (b) Soda lime  
 (c) Hot conc.  $\text{H}_2\text{SO}_4$   
 (d)  $\text{PCl}_5$
31. Which one of the following on reduction with lithium aluminium hydride yields a secondary amine? [2007]  
 (a) Methyl isocyanide  
 (b) Acetamide  
 (c) Methyl cyanide  
 (d) Nitroethane.

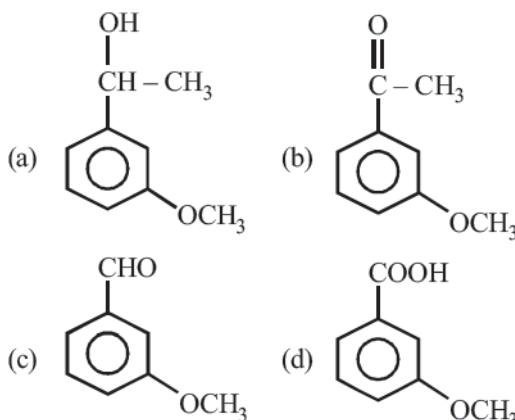
32. The final product C, obtained in this reaction



[2003]



Product 'P' in the above reaction is [2002]



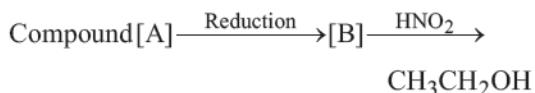
34. Intermediates formed during reaction of  $\text{RCNH}_2$  with  $\text{Br}_2$  and  $\text{KOH}$  are [2001]

- (a)  $\text{RNHBr}$  and  $\text{RCONHBr}$   
 (b)  $\text{RNHCOBr}$  and  $\text{RNCO}$   
 (c)  $\text{RCONHBr}$  and  $\text{RNCO}$   
 (d)  $\text{RCONBr}_2$

35. An isocyanide is prepared by  
 (a) Friedel-Crafts reaction

- (b) Perkin reaction  
 (c) Carbylamine reaction  
 (d) Wurtz reaction

36. Consider the following sequence of reactions :



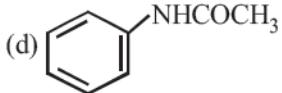
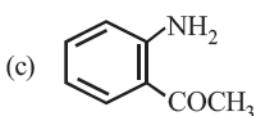
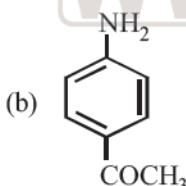
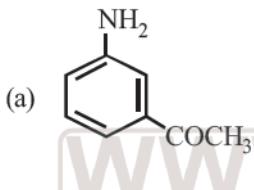
The compound [A] is

[1996]

- (a)  $\text{CH}_3\text{CH}_2\text{CN}$       (b)  $\text{CH}_3\text{NO}_2$   
 (c)  $\text{CH}_3\text{NC}$       (d)  $\text{CH}_3\text{CN}$

37. Aniline is an activated system for electrophilic substitution. The compound formed on heating aniline with acetic anhydride is

[1996]



38. Which is formed, when acetonitrile is hydrolysed partially with cold concentrated HCl? [1995]

- (a) Acetic acid  
 (b) Acetamide  
 (c) Methyl cyanide  
 (d) Acetic anhydrides

[1999]

39. Acetamide and ethylamine can be distinguished by reacting with

[1994]

- (a) Aqueous HCl and heat  
 (b) Aqueous NaOH and heat  
 (c) Acidified  $\text{KMnO}_4$   
 (d) Bromine water.

40. For carbylamine reaction, we need hot alcoholic KOH and

[1992]

- (a) Any primary amine and chloroform  
 (b) Chloroform and silver powder  
 (c) A primary amine and an alkyl halide  
 (d) A monoalkylamine and trichloromethane.

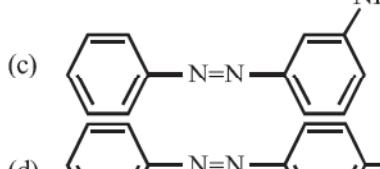
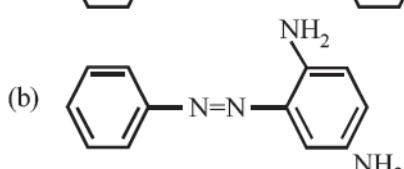
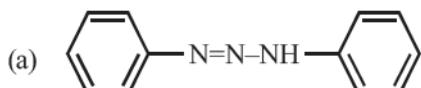
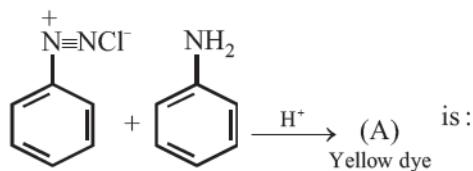
41. Indicate which nitrogen compound amongst the following would undergo Hoffmann reaction (*i.e.*, reaction with  $\text{Br}_2$  and strong KOH) to furnish the primary amine ( $\text{R}-\text{NH}_2$ )

[1989]

- (a)  $\text{RCONHCH}_3$       (b)  $\text{RCOONH}_4$   
 (c)  $\text{RCONH}_2$       (d)  $\text{R}-\text{CO}-\text{NHOH}$ .

### Topic 3: Nitrocompounds, Alkyl Nitrites and Diazonium Salts

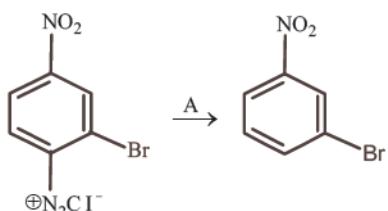
42. In the following reaction, the product (A) [2014]



43. Which of the following will be most stable diazonium salt  $\text{RN}_2^+X^-$ ? [2014]

- (a)  $\text{CH}_3\text{N}_2^+X^-$       (b)  $\text{C}_6\text{H}_5\text{N}_2^+X^-$   
 (c)  $\text{CH}_3\text{CH}_2\text{N}_2^+X^-$       (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{N}_2^+X^-$

44. In the reaction



A is :

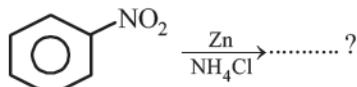
[NEET 2013]

- (a)  $\text{Cu}_2\text{Cl}_2$       (b)  $\text{H}_3\text{PO}_2$  and  $\text{H}_2\text{O}$   
 (c)  $\text{H}^+/\text{H}_2\text{O}$       (d)  $\text{HgSO}_4/\text{H}_2\text{SO}_4$

45. Nitrobenzene on reaction with conc.  $\text{HNO}_3/\text{H}_2\text{SO}_4$  at  $80 - 100^\circ\text{C}$  forms which one of the following products? [NEET 2013]

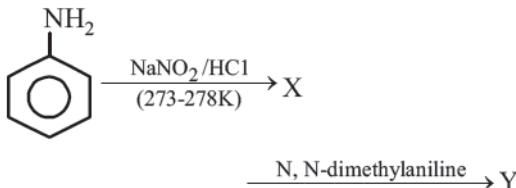
- (a) 1, 3 - Dinitrobenzene  
 (b) 1, 4 - Dinitrobenzene  
 (c) 1, 2, 4 - Trinitrobenzene  
 (d) 1, 2 - Dinitrobenzene

46. What is the product obtained in the following reaction : [2011]



- (a)   
 (b)   
 (c)   
 (d)

47. Aniline in a set of the following reactions yielded a coloured product 'Y' [2002, 2010]



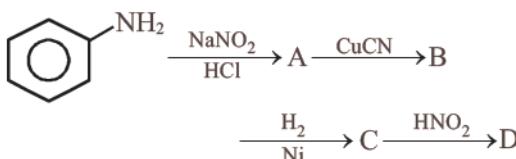
The structure of 'Y' would be ;

- (a)
- (b)
- (c)
- (d)

48. Nitrobenzene can be prepared from benzene by using a mixture of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ; in the mixture, nitric acid acts as a/an: [2009]

- (a) acid      (b) base  
 (c) catalyst      (d) reducing agent

49. Aniline in a set of reactions yielded a product D.



The structure of the product D would be: [2005]

- (a)  $\text{C}_6\text{H}_5\text{NHOH}$       (b)  $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_3$   
 (c)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$       (d)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$

50. Aniline when diazotized in cold and when treated with dimethyl aniline gives a coloured product. Its structure would be [2004]

- (a)

- (b) CCc1ccc(cc1)-N=N-c2ccc(cc2)N
- (c) CN(C)c1ccc(cc1)-N=N-c2ccc(cc2)N
- (d) CN(C)c1ccc(cc1)N-c2ccc(cc2)N
51.  $[A] \xrightarrow{\text{reduction}} [B] \xrightarrow{\text{CHCl}_3 + \text{KOH}} [C] \xrightarrow{\text{reduction}} \text{N-Methylaniline}$ , A is /2000/
- (a) Formaldehyde  
(b) Trichloromethane  
(c) Nitrobenzene  
(d) Toluene
52. Which of the following reagents will convert *p*-methylbenzenediazonium chloride into *p*-cresol?  
(a) Cu powder      (b)  $\text{H}_2\text{O}$  /1999/  
(c)  $\text{H}_3\text{PO}_2$       (d)  $\text{C}_6\text{H}_5\text{OH}$
53. Diazo coupling is useful to prepare some /1994/  
(a) Pesticides      (b) dyes  
(c) proteins      (d) vitamins

## ANSWER KEY

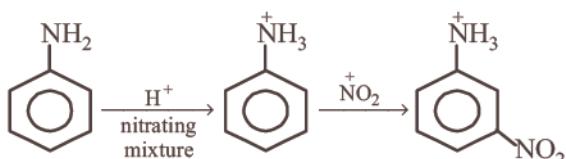
1	(d)	7	(a)	13	(b)	19	(c)	25	(d)	31	(a)	37	(d)	43	(b)	49	(d)
2	(b)	8	(d)	14	(c)	20	(d)	26	(c)	32	(d)	38	(b)	44	(b)	50	(c)
3	(a)	9	(a)	15	(d)	21	(c)	27	(d)	33	(b)	39	(b)	45	(a)	51	(c)
4	(c)	10	(d)	16	(d)	22	(d)	28	(b)	34	(c)	40	(a)	46	(a)	52	(b)
5	(c)	11	(b)	17	(c)	23	(c)	29	(a)	35	(c)	41	(c)	47	(a)	53	(b)
6	(a)	12	(c)	18	(b)	24	(c)	30	(a)	36	(d)	42	(d)	48	(b)		

## Hints &amp; Solutions

- (d) Aliphatic and aromatic primary amines give carbylamine reaction. Since aniline is primary aromatic amine, it gives carbylamine test.
- (b) Hinsberg's reagent is used to distinguish 1°, 2° and 3° amine. Primary amines react with Hinsberg's reagent to give precipitate which is soluble in alkali while secondary amines give a product which is insoluble in alkali. Tertiary amines do not react with Hinsberg's reagent.
- (a) Account for the inductive effect, solvation effect (H-bonding.) and steric hinderance for basic character in aqueous solutions

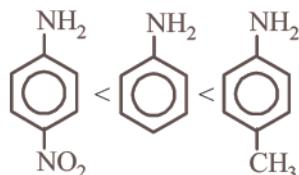


- (c)



In acidic medium aniline is protonated to form anilinium ion which is meta-directing.

- (c)  $-\text{NO}_2$  group has strong  $-R$  effect and  $-\text{CH}_3$  shows  $+R$  effect.  
 $\therefore$  Order of basic strength is



- (a)  $\text{CH}_3-\overset{\text{O}}{\underset{\text{acetamide}}{\text{C}}}-\text{NH}_2 + \text{Br}_2 + 4\text{NaOH} \xrightarrow{\Delta} \text{CH}_3-\text{NH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$   
 methanamine

It is called Hoffmann Bromamide reaction.

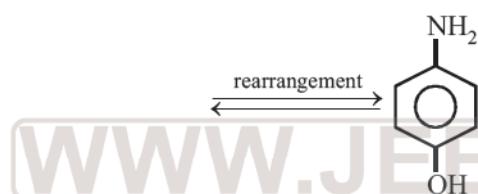
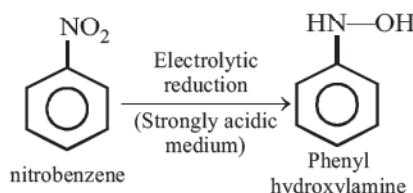


**Hoffmann bromamide reaction:** Reaction of an acid amide with bromine in an aqueous or ethanolic solution of sodium hydroxide to form a primary amine, with one carbon atom less, is known as Hoffmann bromamide reaction.

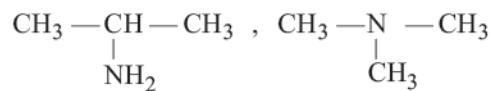
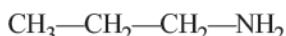
7. (a) Arylamines are generally less basic than alkylamines due to following factors:

- Due to resonance in aromatic amines.
- Lower stability of anilinium ion.

8. (d)

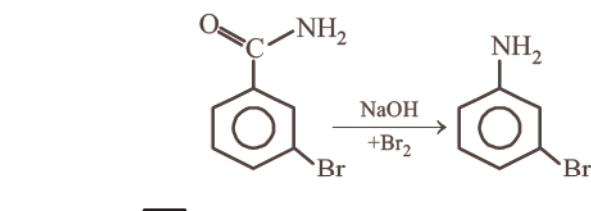
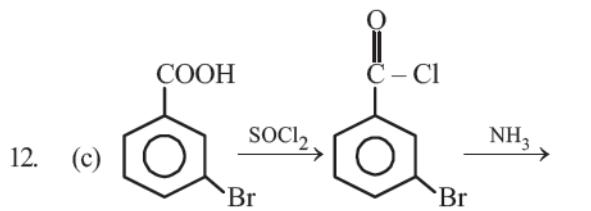
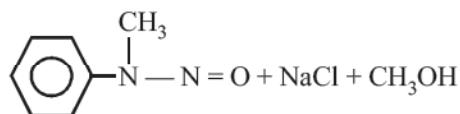
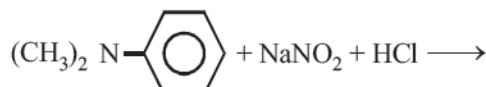


9. (a)  $C_3H_9N$



10. (d) Because arylhalides do not undergo nucleophilic substitution reaction with potassium phthalimide easily.

11. (b) Secondary amine react with nitrous acid to give N-Nitrosoamines.



13. (b)  $C_6H_5 - CH_2 - NH_2$  compound is most basic

due to localized lone pair of electron on nitrogen atom while other compounds have delocalized lone pair of electron.

14. (c) Aryl amines react with nitrous acid to produce diazonium salt and not phenol.

15. (d) (i)  $CH_3 - CH_2 - CH_2 - CH_2 - NH_2$  (primary amine)

(ii) with KOH (alcohol) and  $CHCl_3$  it produces bad smell

(2)  $CH_3C \equiv CH$  (acidic hydrogen)

(iii) gives white ppt with ammonical  $AgNO_3$

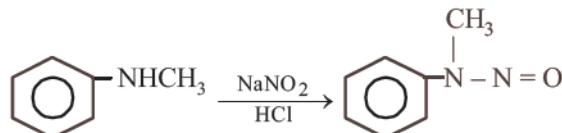
(3)  $CH_3 - CH_2 - COOCH_3$  (ester)

(i) alkaline hydrolysis

(4)  $CH_3 - CHO - CH_3$  (secondary alcohol)

(iv) with Lucas reagent cloudiness appears after 5 minutes

16. (d) Secondary amine with  $(NaNO_2 + HCl)$  gives a nitroso product

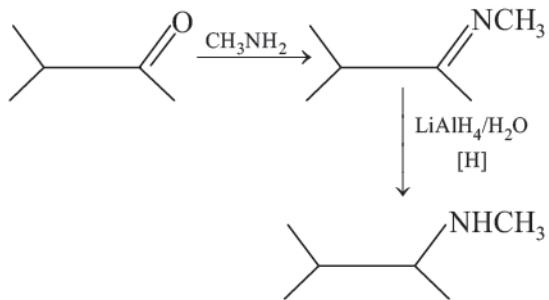


N- Nitroso – N- methylaniline

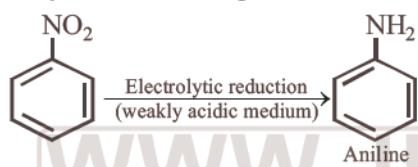
**NOTES** Primary amine with  $NaNO_2/HCl$  produces nitrogen gas. tertiary amine form ammonium salt.

17. (c) Benzylamine is more basic than aniline. The reason is that in aniline, the lone pair of nitrogen is conjugated with benzene ring so it is not available readily for others. On the other hand in Benzylamine, nitrogen is not directly attached with ring so lone pairs are not conjugated with ring.

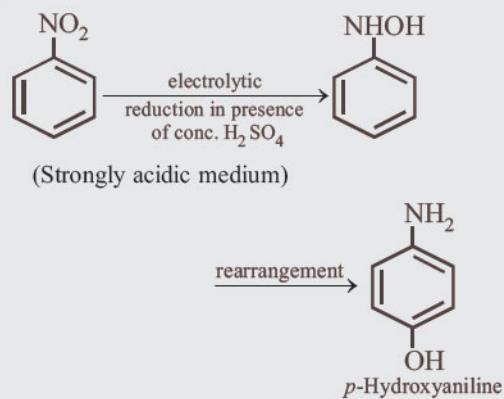
18. (b)



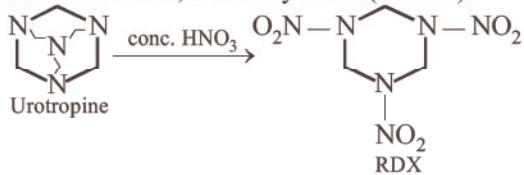
19. (c) Electrolytic reduction of Nitrobenzene in weakly acidic medium give aniline



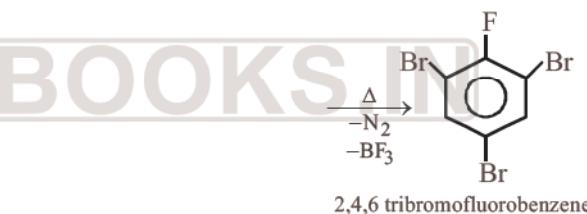
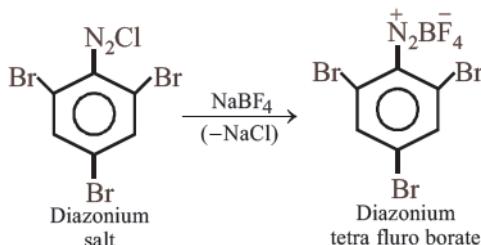
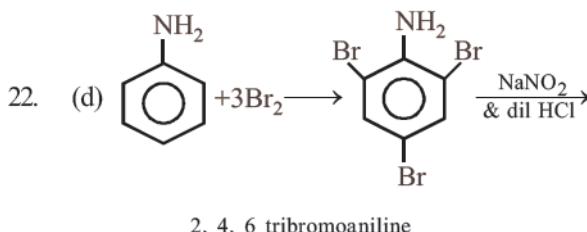
**NOTES**  
Nitroalkane in strongly acidic medium gives p-hydroxyaniline



20. (d) RDX is prepared by treating urotropine with fuming nitric acid. When the inner bridge system is destroyed by oxidation and the peripheral nitrogen atom are nitrated, it forms cyclonite (or RDX).



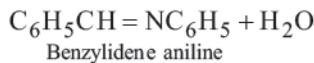
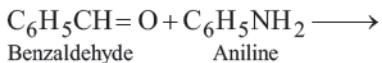
21. (c)  $(\text{CH}_3)_2\text{NH}$  is most basic because two electron releasing groups are present on Nitrogen. Also aromatic amines are less basic than aliphatic amines. The basic character of amines follow the order  $\text{R}_2\text{NH} > \text{RNH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{NH}_3$



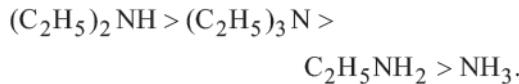
23. (c)  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \longrightarrow \text{CH}_3\text{CH}_2\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O}$

In this reaction, bad smelling compound ethyl isocyanide ( $\text{CH}_3\text{CH}_2\text{NC}$ ) is produced. This equation is known as **carbyl amine reaction**.

24. (c) Benzaldehyde reacts with primary aromatic amine to form schiff's base



25. (d) All aliphatic amines are stronger bases than  $\text{NH}_3$  and among different ethylamines order of basicity is  $2^\circ > 3^\circ > 1^\circ$ . Thus, the correct order is (d) (in polar solvent):

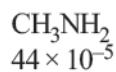
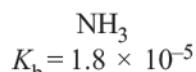


This anomalous behaviour of tertiary ethyl amine is due to steric factors *i.e.*, crowding of alkyl groups cover nitrogen atom from all sides and thus makes the approach and bonding by a lewis acid relatively difficult which results the maximum steric strain in tertiary amines. The electrons are there but the path is blocked resulting the reduction in its basicity.

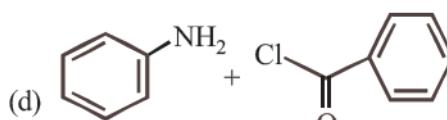
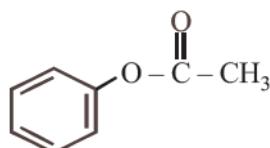
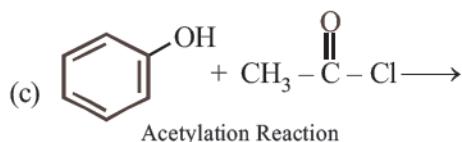
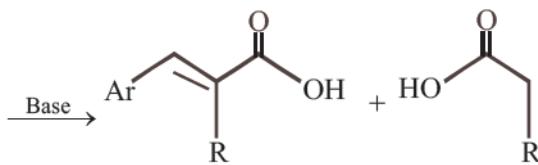
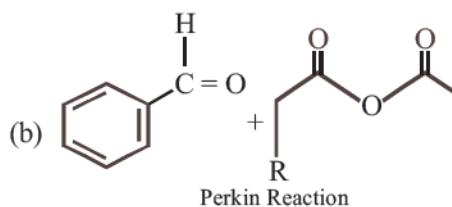
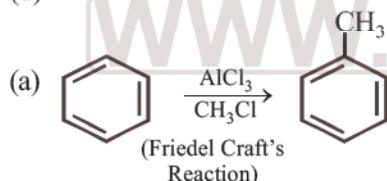


**NOTES** This comparison is true for amines in a protic solvent like water. In gaseous phase, the order of basicity is: tertiary amine > secondary amine > primary amine > NH<sub>3</sub>.

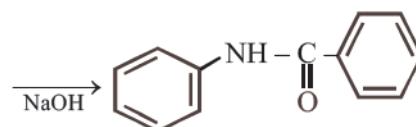
26. (c) Methyl amine is a stronger base than ammonia due to +I effect. The alkyl groups which are electron releasing groups increase the electron density around the nitrogen thereby increasing the availability of the lone pair of electrons to proton or lewis acid and making the amine more basic



27. (d)

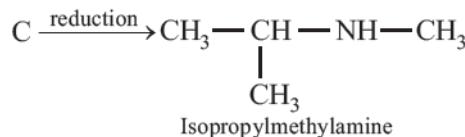
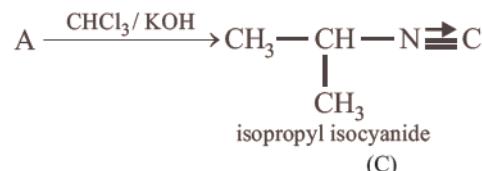
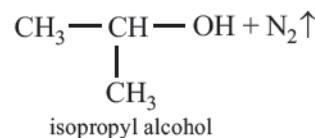
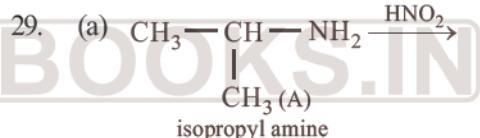
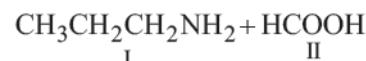


Schotten-Baumen Reaction



28. (b) Hydrolysis of propyl isocyanide (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NC) gives CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> + HCOOH.

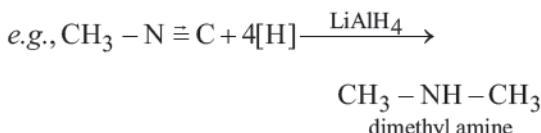
On treatment with NaNO<sub>2</sub> and HCl (I) gives CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH which does not give iodoform test. II (HCOOH) reduces Tollen's reagent and Fehling's solution.



**NOTES** Only primary aliphatic and aromatic amines give carbylamine reaction. Primary amine on reaction with HNO<sub>2</sub> give alcohol

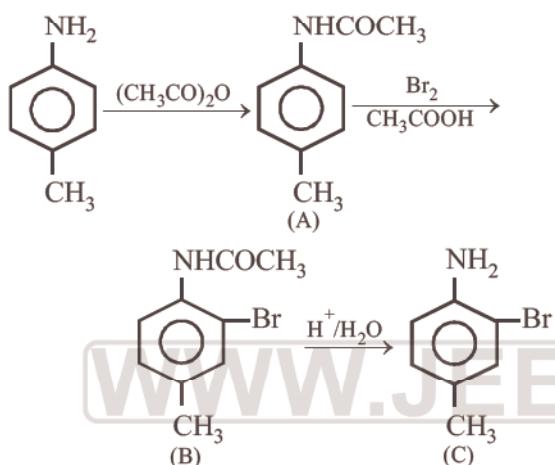
30. (a) CH<sub>3</sub>CONH<sub>2</sub>  $\xrightarrow[\text{Br}_2]{\text{NaOH}}$  CH<sub>3</sub>NH<sub>2</sub>  
(Hofmann bromamide reaction)

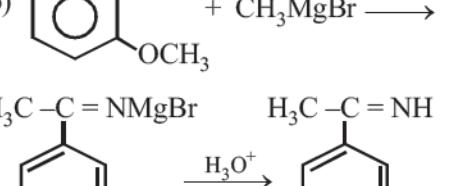
31. (a) Reduction of alkyl isocyanides in presence of  $\text{LiAlH}_4$  yields secondary amines containing methyl as one of the alkyl group.



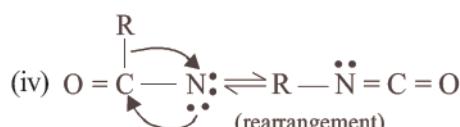
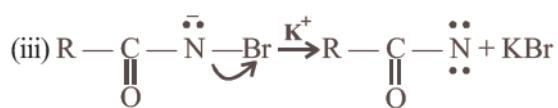
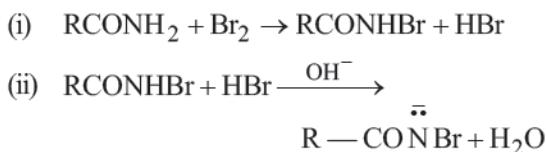
whereas, alkyl cyanides give 1° amine on reduction.

32. (d)

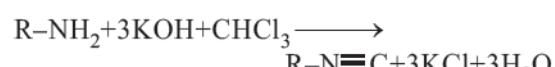


33. (b) 

34. (c) The mechanism of Hoffmann bromamide reaction is



35. (c) Carbylamine reaction :

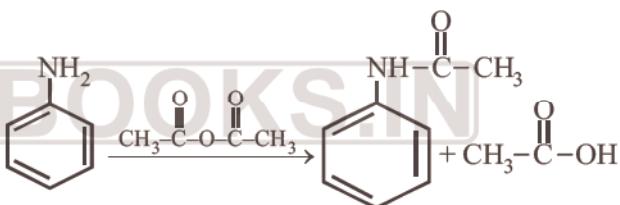


36. (d)  $\text{CH}_3\text{CN} \xrightarrow{\text{Reduction}} \text{CH}_3-\text{CH}_2-\text{NH}_2$

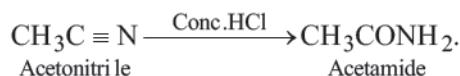
$\text{CH}_2=\text{CH}_2-\text{OH} + \text{N}_2 + \text{HO}_2 \leftarrow$

HONO

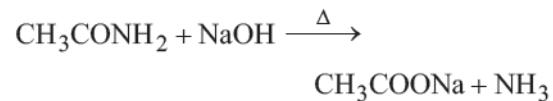
37. (d) Aniline when treated with acetic anhydride forms acetanilide (nucleophilic substitution)



38. (b) Acetonitrile (Methyl cyanide) on treatment with conc. HCl give acetamide.



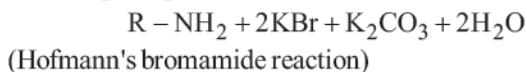
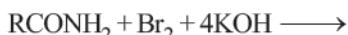
39. (b) Acetamide and ethylamine can be distinguished by heating with NaOH solution. Acetamide evolves  $\text{NH}_3$  but ethylamine does not.



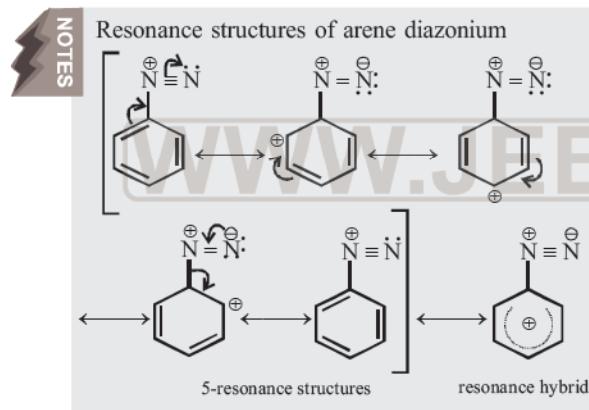
40. (a) Any primary amine means both aliphatic as well as aromatic but monoalkylamines means only  $1^\circ$  aliphatic amines. Therefore, option (a) is correct while (d) is wrong.



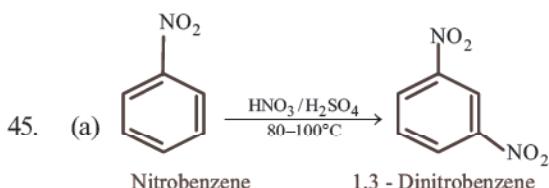
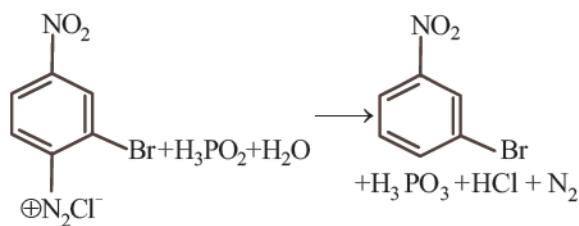
41. (c) Only 1° amides (i.e.  $\text{RCONH}_2$ ) in the present case undergo Hofmann bromamide reaction.



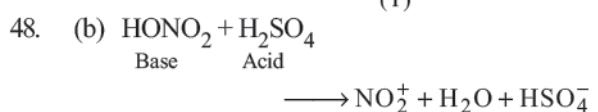
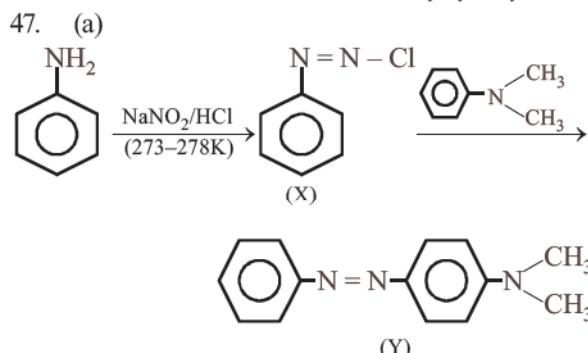
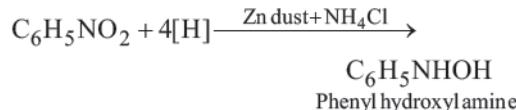
43. (b) Arene diazonium salts are most stable among the given options because of the dispersal of +ve charge on the benzene ring due to resonance.



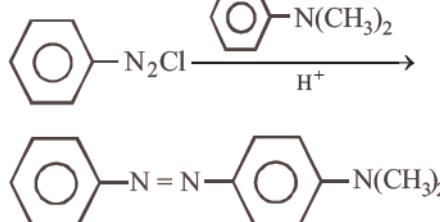
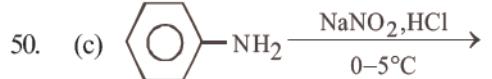
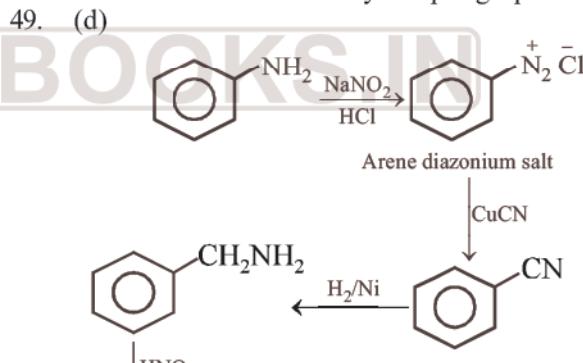
44. (b)



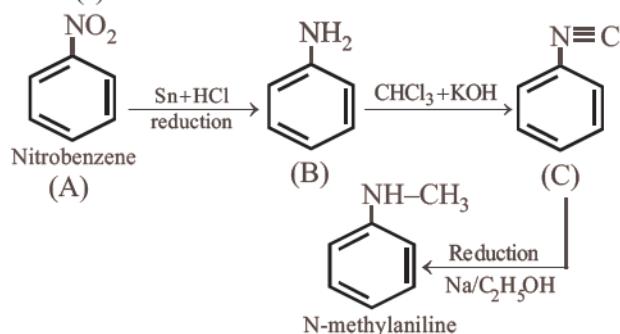
46. (a) When nitro compound is reduced with a neutral reducing agent ( $\text{Zn dust} + \text{NH}_4\text{Cl}$ ) the corresponding hydroxyl amine is formed



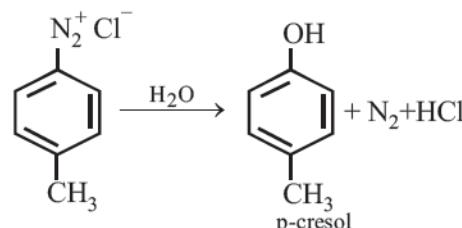
Nitric acid acts as a base by accepting a proton.



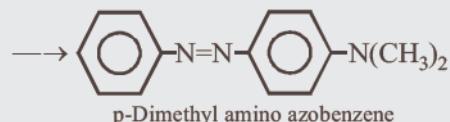
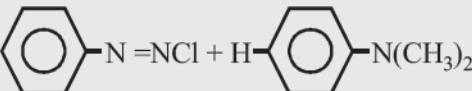
51. (c)



52. (b)



53. (b) Azo dyes can be prepared by diazotizing an aromatic amine and subsequent coupling with a suitable aromatic phenol or amine



p-Dimethyl amino azobenzene is used as a dye for colouring polishes, wax products and soap.

28

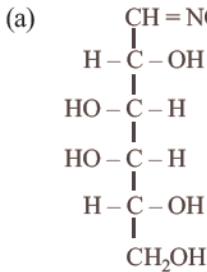
# Biomolecules

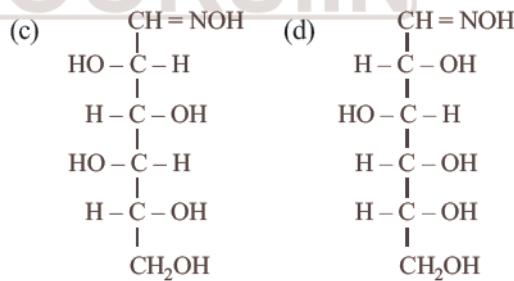
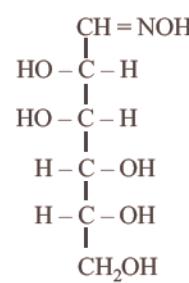
## Trend Analysis with Important Topics & Sub-Topics

## Topic 1: Carbohydrates and Lipids

1. Sucrose on hydrolysis gives: [2020]  
(a)  $\alpha$ -D-Glucose +  $\beta$ -D-Glucose  
(b)  $\alpha$ -D-Glucose +  $\beta$ -D-Fructose  
(c)  $\alpha$ -D-Fructose +  $\beta$ -D-Fructose  
(d)  $\alpha$ -D-Glucose +  $\beta$ -D-Fructose

2. Which one is reducing sugar and which one is non-reducing sugar?



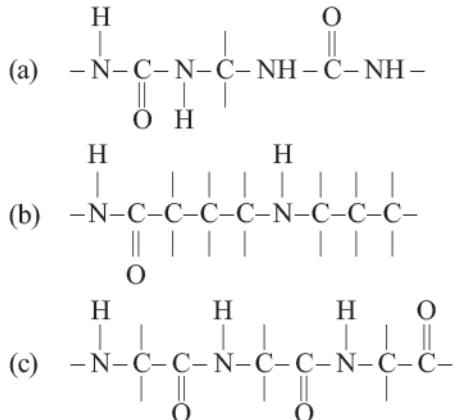
4. Which one of the following sets of monosaccharides forms sucrose? **[2012]**

  - (a)  $\alpha$ -D-Galactopyranose and  $\alpha$ -D-Glucopyranose
  - (b)  $\alpha$ -D-Glucopyranose and  $\beta$ -D-Fructofuranose
  - (c)  $\beta$ -D-Glucopyranose and  $\alpha$ -D-Fructofuranose
  - (d)  $\alpha$ -D-Glucopyranose and  $\beta$ -D-Fructopyranose

5. Which one of the following statements is not true regarding (+) Lactose? **[2011]**

  - (a) On hydrolysis (+) Lactose gives equal amount of D(+) glucose and D(+) galactose.

- (b) (+) Lactose is a  $\beta$ -glycoside formed by the union of a molecule of D(+) glucose and a molecule of D(+) galactose.  
 (c) (+) Lactose is a reducing sugar and does not exhibit mutarotation.  
 (d) (+) Lactose,  $C_{12}H_{22}O_{11}$  contains 8-OH groups.
6. Which one of the following does not exhibit the phenomenon of mutarotation ? *[2010]*  
 (a) (+) – Sucrose      (b) (+) – Lactose  
 (c) (+) – Maltose      (d) (–) – Fructose
7. Fructose reduces Tollen's reagent due to *[2010]*  
 (a) enolisation of fructose followed by conversion to aldehyde by base  
 (b) asymmetric carbons  
 (c) primary alcoholic group  
 (d) secondary alcoholic group
8. The cell membranes are mainly composed of  
 (a) fats                        (b) proteins *[2005]*  
 (c) phospholipids            (d) carbohydrates
9. Number of chiral carbons in  $\beta$  – D – (+) – glucose is *[2004]*  
 (a) five                        (b) six  
 (c) three                       (d) four
10. Glycolysis is *[2003]*  
 (a) conversion of glucose to haem  
 (b) oxidation of glucose to glutamate  
 (c) conversion of pyruvate to citrate  
 (d) oxidation of glucose to pyruvate
11. Phospholipids are esters of glycerol with *[2003]*  
 (a) Three phosphate groups  
 (b) Three carboxylic acid residues  
 (c) Two carboxylic acid residues and one phosphate group  
 (d) One carboxylic acid residue and two phosphate groups
12. Cellulose is a polymer of *[2002]*  
 (a) Glucose                    (b) Fructose  
 (c) Ribose                    (d) Sucrose
13. Which of the following gives positive Fehling solution test ? *[2001]*  
 (a) Protein                    (b) Sucrose  
 (c) Glucose                   (d) Fats
14. Which is correct statement? *[2001]*  
 (a) Starch is a polymer of  $\alpha$ -glucose  
 (b) In cyclic structure of fructose, there are four carbons and one oxygen atom  
 (c) Amylose is a component of cellulose  
 (d) Proteins are composed of only one type of amino acids
15. Mg is present in which of the following : *[2000]*  
 (a) Starch                    (b) Chlorophyll  
 (c) Both                      (d) None
16. Which of the following is the sweetest sugar?  
 (a) Sucrose                   (b) Glucose *[1999]*  
 (c) Fructose                  (d) Maltose
17. In cells, the net production of ATP molecules generated from one glucose molecule is *[1999]*  
 (a) 46                        (b) 32  
 (c) 36                        (d) 40
18. The number of molecules of ATP produced in the lipid metabolism of a molecule of palmitic acid is *[1998]*  
 (a) 130                      (b) 36  
 (c) 56                        (d) 86
19. Glucose molecule reacts with 'X' number of molecules of phenylhydrazine to yield osazone. The value of 'X' is *[1998]*  
 (a) four                      (b) one  
 (c) two                       (d) three
20. Sucrose in water is dextro-rotatory,  $[\alpha]_D = +66.4^\circ$ . When boiled with dilute HCl, the solution becomes leavo-rotatory,  $[\alpha]_D = -20^\circ$ . In this process, the sucrose molecule breaks into *[1996]*  
 (a) L-glucose + D-fructose  
 (b) L-glucose + L-fructose  
 (c) D-glucose + D-fructose  
 (d) D-glucose + L-fructose
21. The  $\alpha$ -D glucose and  $\beta$ -D glucose differ from each other due to difference in carbon atom with respect to its *[1995]*  
 (a) Conformation  
 (b) Configuration  
 (c) Number of OH groups  
 (d) Size of hemiacetal ring
22. On hydrolysis of starch, we finally get *[1991]*  
 (a) Glucose                   (b) Fructose  
 (c) Both (a) and (b)        (d) Sucrose
- Topic 2: Amino Acids and Proteins**
23. Which of the following is a basic amino acid ?  
 (a) Alanine                   (b) Tyrosine *[2020]*  
 (c) Lysine                    (d) Serine
24. Which structure(s) of proteins remain(s) intact during denaturation process? *[NEET Odisha, 2019]*  
 (a) Tertiary structure only  
 (b) Both secondary and tertiary structures  
 (c) Primary structure only  
 (d) Secondary structure only



- (d)  $\begin{array}{ccccccccc} & \text{H} & & \text{O} & & \text{H} & & \text{H} & \\ & | & & || & & | & & | & \\ -\text{N}-\text{C}- & \text{C}- & \text{C}- & \text{N}- & \text{C}- & \text{C}- & \text{N}- & \text{C}- & \text{C}- \\ | & & | & & | & & | & & | \\ \text{H} & & \text{H} & & \text{H} & & \text{O} & & \text{O} \end{array}$

32. The correct statement in respect of protein haemoglobin is that it [2004]  
 (a) functions as a catalyst for biological reactions  
 (b) maintains blood sugar level  
 (c) acts as an oxygen carrier in the blood  
 (d) forms antibodies and offers resistance to diseases

33. The helical structure of protein is stabilized by [2004]  
 (a) dipeptide bonds (b) hydrogen bonds  
 (c) ether bonds (d) peptide bonds

34. Which is not a true statement? [2002]  
 (a)  $\alpha$ -Carbon of  $\alpha$ -amino acid is asymmetric  
 (b) All proteins are found in L-form  
 (c) Human body can synthesize all proteins they need  
 (d) At pH = 7 both amino and carboxylic groups exist in ionised form

35. For  $-\text{C}(=\text{O})-\ddot{\text{N}}\text{H}-$  (peptide bond) [2001]  
 Which statement is incorrect about peptide bond?  
 (a) C — N bond length in proteins is longer than usual bond length of the C — N bond  
 (b) Spectroscopic analysis shows planar structure of the  $-\text{C}(=\text{O})-\text{NH}-$  group  
 (c) C — N bond length in proteins is smaller than usual bond length of the C—N bond  
 (d) None of the above

36. The number of essential amino acids in man is  
 (a) 8 (b) 10 [2000]  
 (c) 18 (d) 20

37. The dominant cation in the blood plasma (extracellular fluid) is [1999]  
 (a) potassium (b) calcium  
 (c) magnesium (d) sodium

38. The reactions of (a) oxygen and (b) carbon monoxide with haeme (the prosthetic group of haemoglobin) give [1997]  
 (a) only oxygen-haeme complex  
 (b) only carbon monoxide-haeme complex  
 (c) both oxygen-haeme and carbon monoxide-haeme complexes but oxygen-haeme complex is more stable

## Topic 3: Nucleic Acid and Enzymes

43. The correct statement regarding RNA and DNA, respectively is **[2016]**

  - The sugar component in RNA is arabinose and the sugar component in DNA is 2'-deoxyribose.
  - The sugar component in RNA is ribose and the sugar component in DNA is 2'-deoxyribose.
  - The sugar component in RNA is arabinose
  - The sugar component in RNA is 2'-deoxyribose and the sugar component in DNA is arabinose

44. In DNA, the linkages between different nitrogenous bases are: **[NEET Kar. 2013]**

  - peptide linkage
  - phosphate linkage
  - H-bonding
  - glycosidic linkage

45. Which one of the following, statements is incorrect about enzyme catalysis? **[2012]**

  - Enzymes are mostly proteinous in nature.
  - Enzyme action is specific.
  - Enzymes are denatured by ultraviolet rays and at high temperature.
  - Enzymes are least reactive at optimum temperature.

(b) Pepsin and Trypsin  
(c) Invertase and Zymase  
(d) Amylase and Maltase

50. A sequence of how many nucleotides in messenger RNA makes a codon for an amino acid? **[2004]**

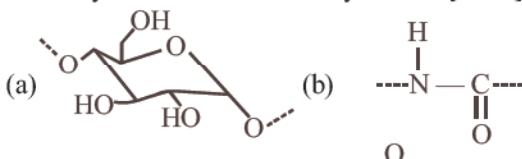
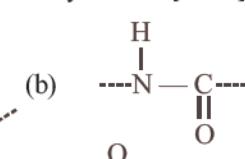
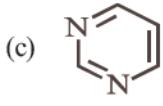
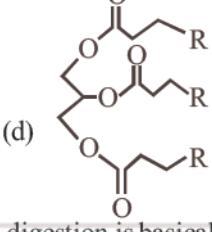
  - Three
  - Four
  - One
  - Two

51. The enzyme which hydrolyses triglycerides to fatty acids and glycerol is called **[2004]**

  - Maltase
  - Lipase
  - Zymase
  - Pepsin

52. Chargaff's rule states that in an organism **[2003]**

  - Amounts of all bases are equal
  - Amount of adenine (A) is equal to that of thymine (T) and the amount of guanine (G) is equal to that of cytosine (C)
  - Amount of adenine (A) is equal to that of guanine (G) and the amount of thymine (T) is equal to that of cytosine (C)
  - Amount of adenine (A) is equal to that of cytosine (C) and the amount of thymine (T) is equal to that of guanine (G)

53. Enzymes are made up of /2002]  
 (a) Edible proteins  
 (b) Proteins with specific structure  
 (c) Nitrogen containing carbohydrates  
 (d) Carbohydrates
54. Which of the following is correct about H-bonding in nucleotide? /2001]  
 (a) A --- A and T --- T (b) G --- T and A --- C  
 (c) A --- G and T --- C (d) A --- T and G --- C
55. Which one of the following chemical units is certainly to be found in an enzyme? /1997]  
 (a)   
 (b)   
 (c)   
 (d) 
56. Chemically considering, digestion is basically /1994]  
 (a) Anabolism (b) Hydrogenation  
 (c) Hydrolysis (d) Dehydrogenation.
57. Enzymes take part in a reaction and /1993]  
 (a) decrease the rate of a chemical reaction  
 (b) increase the rate of a chemical reaction  
 (c) both (a) and (b)  
 (d) none of these
58. The couplings between base units of DNA is through : /1992]  
 (a) Hydrogen bonding  
 (b) Electrostatic bonding  
 (c) Covalent bonding  
 (d) van der Waals forces

## ANSWER KEY

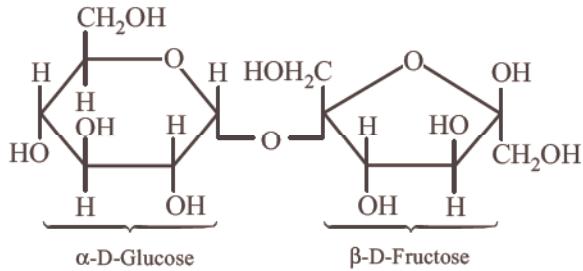
1	(b)	8	(c)	15	(b)	22	(a)	29	(c)	36	(b)	43	(b)	50	(a)	57	(b)	64	(d)
2	(d)	9	(a)	16	(c)	23	(c)	30	(c)	37	(d)	44	(c)	51	(b)	58	(a)	65	(a)
3	(d)	10	(d)	17	(c)	24	(c)	31	(c)	38	(d)	45	(d)	52	(b)	59	(c)	66	(d)
4	(b)	11	(c)	18	(a)	25	(c)	32	(c)	39	(b)	46	(b)	53	(b)	60	(b)	67	(c)
5	(c)	12	(a)	19	(d)	26	(c)	33	(b)	40	(a)	47	(a)	54	(d)	61	(c)	68	(d)
6	(a)	13	(c)	20	(c)	27	(c)	34	(b)	41	(d)	48	(c)	55	(b)	62	(a)		
7	(a)	14	(a)	21	(b)	28	(c)	35	(a)	42	(a)	49	(b)	56	(c)	63	(d)		

## Topic 4: Vitamins and Hormones

59. Which of the following hormones is produced under the condition of stress which stimulates glycogenolysis in the liver of human beings?  
 (a) Thyroxin (b) Insulin /2014]  
 (c) Adrenaline (d) Estradiol
60. Deficiency of vitamin B<sub>1</sub> causes the disease  
 (a) Convulsions (b) Beri-Beri /2012]  
 (c) Cheilosis (d) Sterility
61. Which of the following hormones contains iodine?  
 (a) Testosterone (b) Adrenaline  
 (c) Thyroxine (d) Insulin
62. Which one of the following is an amine hormone?  
 (a) Thyroxine (b) Oxypurin /2008]  
 (c) Insulin (d) Progesterone
63. Which of the following is water-soluble? /2007]  
 (a) Vitamin E (b) Vitamin K  
 (c) Vitamin A (d) Vitamin B
64. Which one of the following is a peptide hormone?  
 /2006]  
 (a) Testosterone (b) Thyroxin  
 (c) Adrenaline (d) Glucagon
65. The human body does not produce /2006]  
 (a) Vitamins (b) Hormones  
 (c) Enzymes (d) DNA
66. The hormone that helps in the conversion of glucose to glycogen is /2004]  
 (a) Cortisone (b) Bile acids  
 (c) Adrenaline (d) Insulin
67. Vitamin B<sub>12</sub> contains /2003]  
 (a) Ca(II) (b) Fe(II)  
 (c) Co(III) (d) Zn(II)
68. Which of the following is a steroid hormone?  
 /1999]  
 (a) Cholesterol (b) Adrenaline  
 (c) Thyroxine (d) Progesterone

## Hints & Solutions

1. (b) Sucrose  $\xrightarrow{\text{Hydrolysis}}$   $\alpha$ -D-Glucose +  $\beta$ -D-Fructose

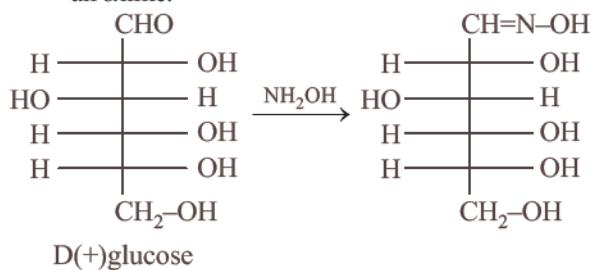


**NOTES** Sucrose on hydrolysis brings about a change in the sign of rotation from dextro to laevo and the product is called as invert sugar.

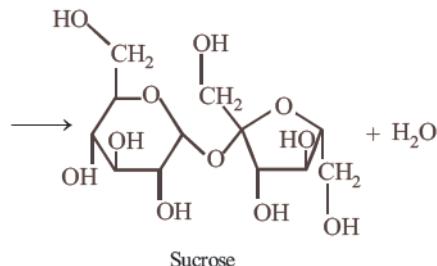
2. (d) Sucrose is non-reducing disaccharide as the two monosaccharide units are linked through their respective carbonyl groups.

**NOTES** Only carbonyl group can be reduced as with other carbons, -OH group is attached.

3. (d) Glucose reacts with hydroxyl amine to form an oxime.



4. (b)  $\alpha$ -D-Glucopyranose +  $\beta$ -D-Fructofuranose



Sucrose is a disaccharide of  $\alpha$ -D-Glucopyranose and  $\beta$ -D-Fructofuranose.

**NOTES** The glycoside linkage is between C1 and C2.

5. (c) All reducing sugar shows mutarotation.

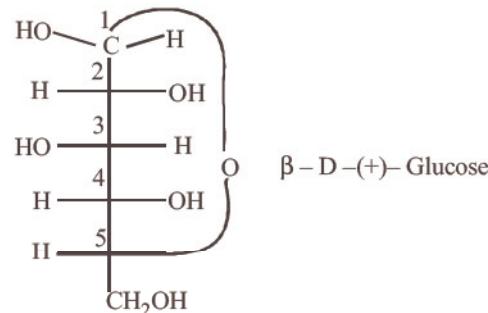
**NOTES** Reducing sugars have hydroxyl group at the anomeric C1 position. In solution, a carbohydrate can open up to its aldehyde form. Hence, it can switch configuration between  $\alpha$ - and  $\beta$ - forms.

6. (a) Sucrose does not have free — CHO or CO group, hence it does not undergo mutarotation.

7. (a) Fructose, a ketose as the substrate, under the alkaline medium of Tollen's reagent, a part of fructose is transformed into glucose and mannose, both aldoses. Then these aldoses give positive silver mirror test.

8. (c) Cell membranes (Plasma membranes) constitutes bilayer of phospholipid with embedded proteins. In humans, lipids accounts for upto 79% of cell membrane.

9. (a)

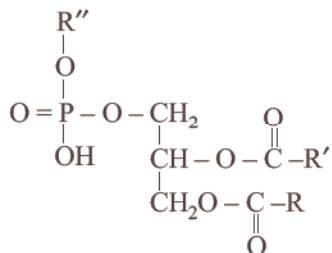


Carbon atoms from C<sub>1</sub> to C<sub>5</sub> are chiral

Biomolecules –

10. (d) It is a common pathway for both the aerobic & anaerobic respiration in which 1 glucose molecule is converted to 2 molecules of pyruvate.

11. (c) Phospholipids are derivatives of glycerol in which two of the hydroxyl groups are esterified with fatty acids while the third is esterified with some derivative of phosphoric acid with some alcohol such as choline, ethanolamine, serine or inositol.



12. (a) We know that cellulose ( $C_6H_{12}O_6$ )<sub>n</sub> is the chief constituent of cell walls of plants. It is the most abundant organic substance found in nature. It is a polymer of glucose with 3500 repeating units in a chain.

13. (c) Glucose contain aldehyde group. Hence, it gives positive fehling solution test.

14. (a) Starch is also know as amyłum which occurs in all green plants. A molecule of starch ( $C_6H_{10}O_5$ )<sub>n</sub> is built of a large number of  $\alpha$ -glucose ring joined through oxygen-atom.

15. (b) Chlorophyll contain Mg.

16. (c) Fructose is the sweetest sugar.

17. (c)  $C_6H_{12}O_6 + 6O_2 + 2ATP \longrightarrow$

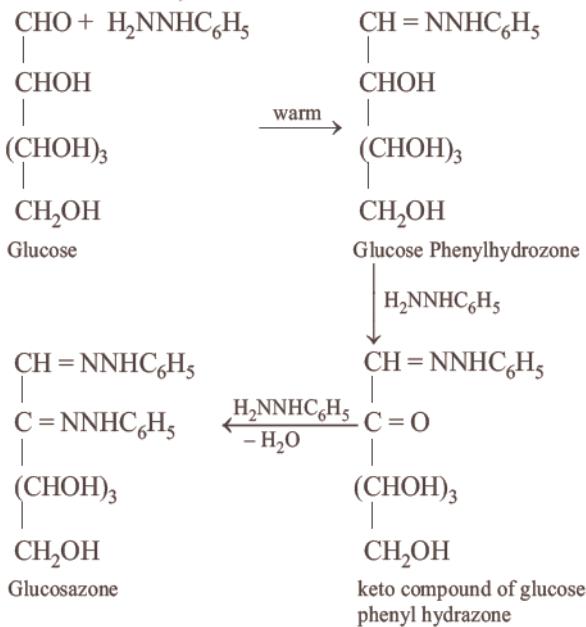
Net total number of ATP molecules evolved = 36 molecules.

18. (a) In the lipid metabolism, when palmitic acid is oxidised, two carbon fragments are removed sequentially to form acetyl coenzyme. It enters the citric acid cycle for production of 130 ATP.

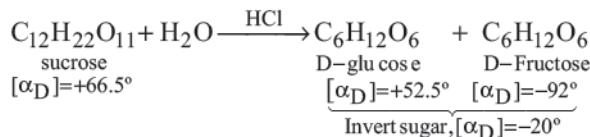
19. (d) Glucose reacts with one molecule of phenyl hydrazine to give phenyl hydrazone. When warmed with excess of phenylhydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine to a ketonic group. With this

ketonic group, the third molecule of phenylhydrazine condenses to glucosazone.

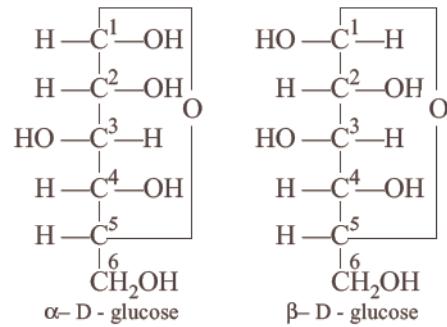
Therefore, the value of  $X$  is 3



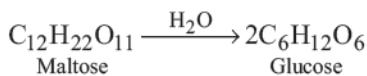
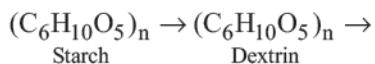
20. (c) The hydrolysis of sucrose by boiling with mineral acid or by enzyme invertase or sucrase produces a mixture of equal molecules of D(+) glucose and D(−) Fructose.



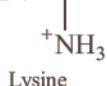
21. (b)  $\alpha$ -D glucose and  $\beta$ -D glucose are the isomers which differ in the orientation (configuration) of H and OH groups around C<sub>1</sub> atom.



22. (a) Manufacture - By hydrolysis of starch with hot dil. mineral acids



23. (c)  $H_2N-(CH_2)_4-CH-NH_3^+$



Since it contains more number of  $-NH_2$  groups as compared to  $-COOH$  groups, hence it is basic amino acid.

24. (c) During denaturation primary structure of proteins remain intact while secondary and tertiary structures are destroyed.

25. (c) Alanine is non-essential amino acid.

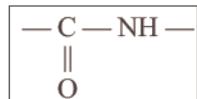
26. (c)  $HOOC-CH_2-NH_2 \rightleftharpoons$



Zwitter ion

27. (c) Due to denaturation of proteins, helix get uncoiled and protein loses its biological activity.

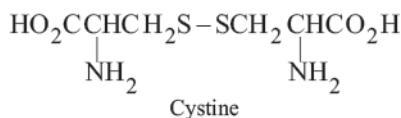
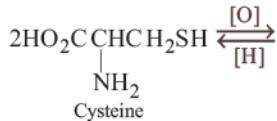
28. (c) Peptide bond



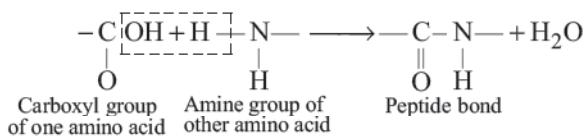
29. (c) When the proteins are subjected to the action of heat, mineral acids or alkali, the water soluble form of globular protein changes to water insoluble fibrous protein. This is called denaturation of proteins. During denaturation, secondary and tertiary structures of protein destroyed but primary structures remains intact.

30. (c)  $2R-S-H \rightleftharpoons R-S-S-R$
- Thiol                                      Disulphide

Example:



31. (c) The bond formed between two amino acids by the elimination of a water molecule is called a peptide linkage or bond. The peptide bond is simply another name for amide bond.



The product formed by linking amino acid molecules through peptide linkages.  $—CO—NH—$ , is called a peptide.

32. (c) Haemoglobin acts as an oxygen carrier in the blood since it reacts with oxygen to form unstable oxyhaemoglobin which easily breaks to give back haemoglobin and oxygen.

33. (b) Hydrogen bonding between different units is responsible for holding helix in a position. NH group in one unit is linked to carbonyl oxygen of the third unit by hydrogen bonding.



The  $\alpha$ -helix structure is formed when the chain of  $\alpha$ -amino acids coils as a right handed screw (called  $\alpha$ -helix) because of the formation of hydrogen bonds between amide groups of the same peptide chain.

34. (b) All proteins are not found in L-form but they may be present in form of D or L

35. (a) Due to resonance C — N bond in protein acquires double bond character and is smaller than usual C — N bond.



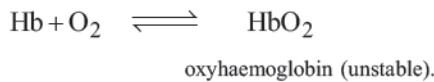
36. (b) There are 20 amino acid in man, out of which 10 amino acids are essential amino acids.



Essential amino acids are supplied to our bodies by food which we take because they cannot be synthesised in the body. These are (i) valine (ii) leucine (iii) Isoleucine (iv) Phenylalanine (v) Threonine (vi) Methionine (vii) Lysine (viii) Tryptophan (ix) Arginine (x) Histidine.

37. (d)  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  are the electrolytes present in blood plasma.  $\text{Na}^+$  and  $\text{Cl}^-$  helps in maintainence of osmotic pressure and fluid balance.

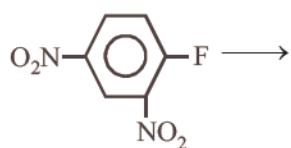
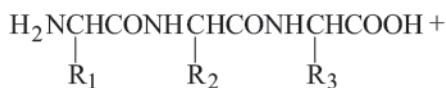
38. (d)  $\text{Hb} + \text{CO} \longrightarrow \text{HbCO}$  (stable compound)  
carboxy haemoglobin



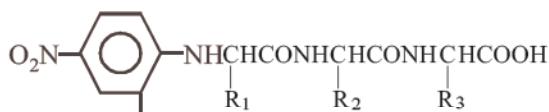
39. (b) Water oxidation is catalyzed by a manganese containing cofactor. Here, cofactor is a species which increases the activity of an enzyme.

40. (a)
- (a)  $\text{Ca}^{2+}$  ions are responsible for triggering contraction of muscles and functions of nerves.
  - (b)  $\text{K}^+$  (and  $\text{Na}^+$  ions) are responsible for maintaining right electrical potential across cell membrane.
  - (c)  $\text{Mg}^{2+}$  act as a cofactor for hydrolysis of ATP.

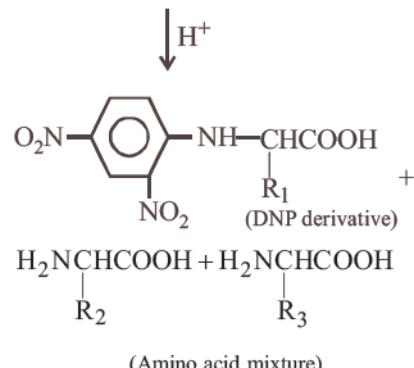
41. (d) 2, 4-Dinitrofluorobenzene, also known as Sanger's reagent, reacts with the  $\text{H}_2\text{N}$ - group of the peptide to from 2, 4-dinitrophenyl (DNP) derivative of the peptide. The DNP derivative of the peptide is hydrolysed to give DNP derivative of the single amino acid



2, 4, Dinitrofluoro benzene



(DNP derivative of polypeptide)



42. (a) When antigens enter in to the body cells and destroy them, then antibodies being proteins are synthesised in the body and combine with antigens and destroy these antigens by forming inactive complexes. Therefore, antibodies protein destroy antigens.
43. (b) Sugar in DNA is 2-deoxyribose whereas sugar in RNA is ribose.
44. (c) The base pairs of the two strands of DNA are linked together through H-bonds.
45. (d) Enzymes are most reactive at optimum temperature. The optimum temperature for enzyme activity is the human body temp.
46. (b) The DNA sequence that codes for a specific protein is called a Gene and thus every protein in a cell has a corosponding gene.
47. (a) In DNA the complimentary bases are Adenine and thymine; Guanine and cytosine.

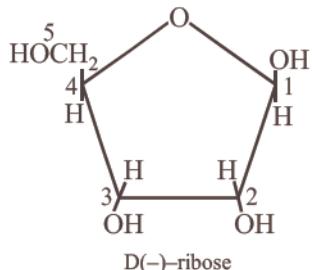
The genetic information for cell is contained in the sequence of bases A, T, G and C in DNA molecule.



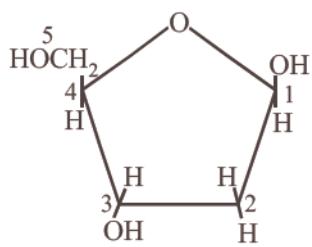
Adenine pair with thymine with two hydrogen bonds and Guanine pairs with cytosine with three hydrogen bonds.

48. (c) Each nucleic acid consists of a pentose sugar a heterocyclic base, and phosphoric acid. The sugar present in DNA is -D (-)-2-deoxyribose and the sugar present in RNA is D (-)-

ribose. The chirality of DNA and RNA molecules are due to the presence of sugar components.

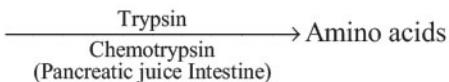
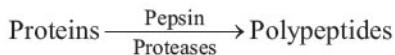


C1, C2, C3 and C4 are chiral carbons.



C1, C3 and C4 are chiral carbons.

49. (b) Pepsin and Trypsin are two enzymes involved in the process (hydrolysis of proteins)



50. (a) The sequence of bases in mRNA are read in a serial order in groups of three at a time. Each triplet of nucleotides (having a specific sequence of bases) is known as codon. Each codon specifies one amino acid.



There are four bases A, G, C, T, therefore,  $4^3 = 64$  triplets or codons are possible.

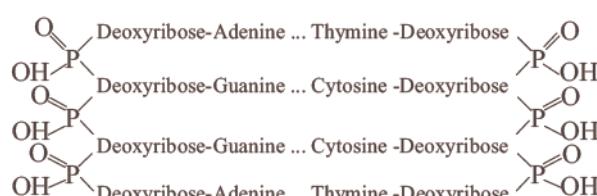
51. (b) Triglycerides are lipids, hence these are hydrolysed by lipases to glycerol and fatty acids.

52. (b)  $\frac{A}{T} = \frac{G}{C} = 1$

Amount of A = T and that of G = C.

53. (b) Enzymes are made up of protein with specific structure.

54. (d)



The hydrogen bonds are formed between the base (shown by dotted lines). Because of size and geometrics of the bases, the only possible pairing in DNA are between G (Guanine) and C (Cytosine) through three H-bonds and between A (Adenosine) and T (Thymine) through two H-bonds.

55. (b) Peptide bonds are present in enzyme.



56. (c) In digestion, large molecules are hydrolysed to give smaller molecules. For example, protein gets hydrolysed to amino acids. Thus, chemically considering, digestion is basically hydrolysis.

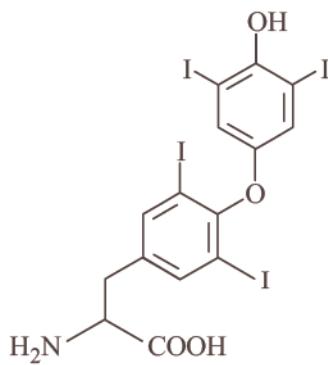
57. (b) Enzymes being biocatalyst can increase the rate of a reaction upto 10 million times. Even very small amount can accelerate a reaction.

58. (a) DNA consists of two polynucleotide chains, each chain forms a right handed helical spiral with ten bases in one turn of the spiral. The two chains coil to double helix and run in opposite direction held together by hydrogen bonding.

59. (c) Adrenaline is a hormone produced by adrenal glands during high stress or exciting situations. This powerful hormone is part of the human body's acute stress response system, also called the fight or flight response.

60. (b) Beri-Beri.

61. (c) Thyroxine is the only hormone among the given choices that contains iodine. Its structure is as follows:



62. (a) Thyroxine is an amino hormone.  
 63. (d) Vitamin B is water soluble whereas all other are fat soluble.



Vitamin H also known as Biotin is part of B complex group of vitamin.

64. (d) Testosterone and Adrenaline are steroid hormone, Thyroxin is a non-steroid hormone and glucagon is a peptide hormone.  
 65. (a) Vitamins are organic substances which does not provide energy but are essential for healthy growth and proper functioning of body. Vitamins are not synthesized inside human body but they are essential part of our diet.  
 66. (d) Insulin helps in converting glucose to glycogen.  
 67. (c) Vit B<sub>12</sub> also called Cyanocobalamin, is anti-pernicious anaemia vitamin.  
 68. (d) Progesterone (Gestogens) is a steroid hormone, which controls the development and maintainance of pregnancy. Thryoxine and Adrenaline are Amine hormones.

# 29

## Polymers



### Trend Analysis with Important Topics & Sub-Topics



Topic Name	Sub-Topic	2020		2019		2018		2017		2016	
		QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Classification of polymers	natural polymers	1	E								
	biodegradable polymers			1	E						
Preparation and properties of polymers	properties of polymers					1	A				
	properties of natural rubber										
LOD - Level of Difficulty		E - Easy		A - Average		D - Difficult		Qns - No. of Questions			

#### Topic 1: Classification of Polymers

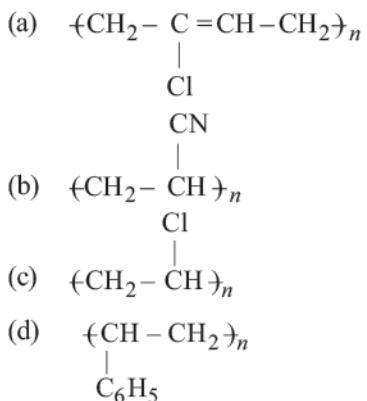
1. Which of the following is a natural polymer?  
 (a) poly(Butadiene-styrene) **[2020]**  
 (b) polybutadiene  
 (c) poly(Butadiene-acrylonitrile)  
 (d) cis-1, 4-polyisoprene
2. The biodegradable polymer is: **[2019]**  
 (a) nylon-6, 6  
 (b) nylon 2-nylon 6  
 (c) nylon-6  
 (d) Buna-S
3. Nylon is an example of: **[NEET 2013]**  
 (a) Polysaccharide (b) Polyamide  
 (c) Polythene (d) Polyester
4. Which one of the following is not a condensation polymer? **[2012]**  
 (a) Melamine (b) Glyptal  
 (c) Dacron (d) Neoprene
5. Of the following which one is classified as polyester polymer? **[2011]**  
 (a) Terylene (b) Bakelite  
 (c) Melamine (d) Nylone-66
6.  $\sim\sim\{NH(CH_2)_6 NHCO(CH_2)_4 CO\}_n\sim\sim$  is a **[2006]**  
 (a) addition polymer  
 (b) thermosetting polymer  
 (c) homopolymer  
 (d) copolymer
7. Which one of the following is a chain growth polymer? **[2004]**  
 (a) Starch (b) Nucleic acid  
 (c) Polystyrene (d) Protein
8. In elastomer, intermolecular forces are **[1995]**  
 (a) strong (b) weak  
 (c) nil (d) none of these

**Topic 2: Preparation and Properties  
of Polymers**

9. Regarding cross-linked or network polymers, which of the following statements is incorrect? **[2018]**
- They contain covalent bonds between various linear polymer chains.
  - They are formed from bi- and tri-functional monomers.
  - They contain strong covalent bonds in their polymer chains.
  - Examples are bakelite and melamine.
10. Natural rubber has **[2016]**
- all cis-configuration
  - all trans-configuration
  - alternate cis-and trans-configuration
  - random cis-and trans-configuration
11. Biodegradable polymer which can be produced from glycine and aminocaproic acid is : **[2015]**
- PHBV
  - Buna - N
  - Nylon 6, 6
  - Nylon 2-nylon 6
12. Caprolactum is used for the manufacture of: **[2015 RS]**
- Nylon - 6
  - Teflon
  - Terylene
  - Nylon - 6,6
13. Which one of the following is an example of a thermosetting polymer? **[2014]**
- $\text{+CH}_2-\underset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2\text{)}_n$
  - $\text{+CH}_2-\underset{\text{Cl}}{\text{CH}}\text{)}_n$
  - $\text{+}\overset{\text{H}}{\underset{\text{O}}{\text{N}}}-(\text{CH}_2)_6-\overset{\text{H}}{\underset{\text{O}}{\text{N}}}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})\text{)}_n$
  -

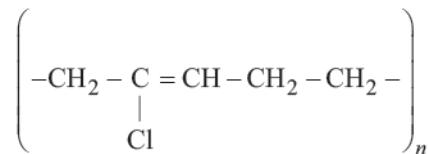
14. Which of the following organic compounds polymerizes to form the polyester Dacron? **[2014]**
- Propylene and para HO—(C<sub>6</sub>H<sub>4</sub>)—OH
  - Benzoic acid and ethanol
  - Terephthalic acid and ethylene glycol
  - Benzoic acid and para HO—(C<sub>6</sub>H<sub>4</sub>)—OH
15. Which is the monomer of Neoprene in the following? **[NEET 2013]**
- $\text{CH}_2=\underset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$
  - $\text{CH}_2=\underset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$
  - $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$
  - $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
16. Which of the following statements is false? **[2012]**
- Artificial silk is derived from cellulose.
  - Nylon-6, 6 is an example of elastomer.
  - The repeat unit in natural rubber is isoprene.
  - Both starch and cellulose are polymers of glucose.
17. Which one of the following sets forms the biodegradable polymer? **[2012 MJ]**
- $\text{CH}_2=\text{CH}-\text{CN}$  and  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
  - $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$  and  $\text{H}_2\text{N}-(\text{CH}_2)_5-\text{COOH}$
  - $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$  and
  - and  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

18. Which of the following structures represents neoprene polymer? *[2010]*



19. Structures of some common polymers are given. Which one is **not** correctly presented? *[2009]*

(a) Neoprene;



(b) Terylene;



(c) Nylon 6, 6;



(d) Teflon; (-CF<sub>2</sub>—CF<sub>2</sub>)<sub>n</sub>

20. Which one of the following statement is *not true*? *[2008]*

(a) In vulcanization the formation of sulphur bridges between different chains make rubber harder and stronger.

(b) Natural rubber has the *trans*-configuration at every double bond

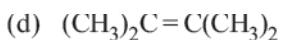
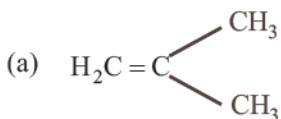
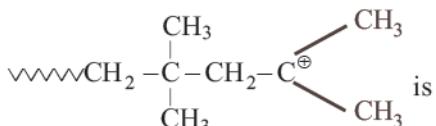
(c) Buna-S is a copolymer of butadiene and styrene

(d) Natural rubber is a 1, 4 - polymer of isoprene

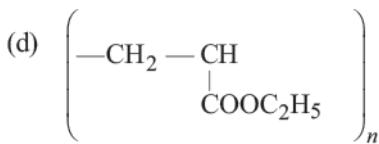
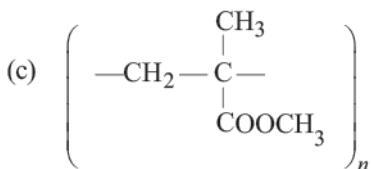
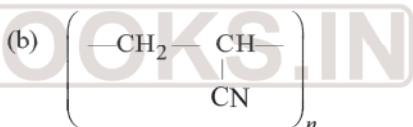
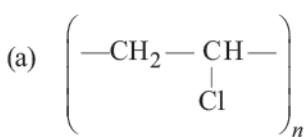
21. Which one of the following polymers is prepared by condensation polymerisation? *[2007]*

(a) Teflon	(b) Natural rubber
(c) Styrene	(d) Nylon-6,6

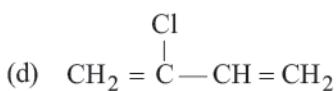
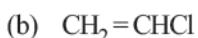
22. The monomer of the polymer; *[2005]*



23. Acrilan is a hard, horny and a high melting material. Which of the following represents its structure ? *[2003]*



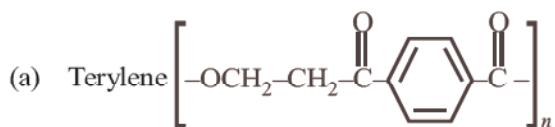
24. Which one of the following monomers gives the polymer neoprene on polymerization ? *[2003]*



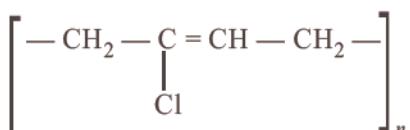
25. Monomer of  $\left[ -\text{C}(\text{CH}_3)_2-\text{CH}_2 - \right]_n$  is [2002]

- (a) 2-methylpropene (b) Styrene  
(c) Propylene (d) Ethene

26. Which of the following is not correctly matched? [2001]



- (b) Neoprene



- (c) Nylon-66



- (d) PMMA  $\left[ -\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{COOCH}_3}{\text{C}}}- \right]_n$

27.  $\text{CF}_2 = \text{CF}_2$  is a unit of [2000]

- (a) Teflon  
(b) Buna-S  
(c) Bakelite  
(d) Polyethene

28. Natural rubber is a polymer of [1999]

- (a) butadiene (b) isoprene  
(c) 2-methylbutadiene (d) Hexa-1, 3-diene

29. Nylon 6, 6 is a polyamide obtained by the reaction of [1996]

- (a)  $\text{COOH}(\text{CH}_2)_4\text{COOH} + \text{NH}_2\text{C}_6\text{H}_4\text{NH}_2 - (p)$   
(b)  $\text{COOH}(\text{CH}_2)_4\text{COOH} + \text{NH}_2(\text{CH}_2)_6\text{NH}_2$   
(c)  $\text{COOH}(\text{CH}_2)_6\text{COOH} + \text{NH}_2(\text{CH}_2)_4\text{NH}_2$   
(d)  $\text{COOH}\text{C}_6\text{H}_4\text{COOH} - (p) + \text{NH}_2(\text{CH}_2)_6\text{NH}_2$

30. Bakelite is prepared by the reaction between [1995]

- (a) urea and formaldehyde  
(b) ethylene glycol  
(c) phenol and formaldehyde  
(d) tetramethylene glycol

31. An example of biopolymer is [1994]

- (a) Teflon (b) Neoprene  
(c) Nylon-6, 6 (d) DNA

### Topic 3: Uses of Polymers

32. The polymer that is used as a substitute for wool in making commercial fibres is [NEET Odisha 2019]

- (a) Buna-N (b) melamine  
(c) nylon-6, 6 (d) polyacrylonitrile

33. Which one of the following is used to make "non-stick" cook-wares ? [1997]

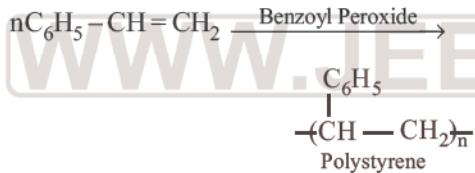
- (a) Polystyrene  
(b) Polyethylene terephthalate  
(c) Polytetrafluoroethylene  
(d) Polyvinyl chloride

### ANSWER KEY

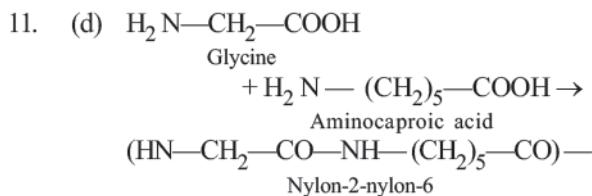
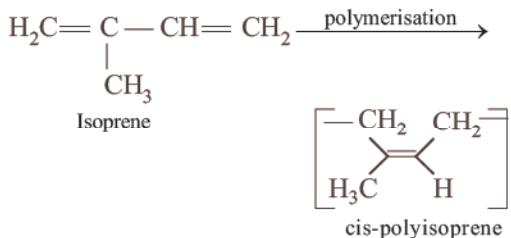
<b>1</b>	(d)	<b>5</b>	(a)	<b>9</b>	(c)	<b>13</b>	(d)	<b>17</b>	(b)	<b>21</b>	(d)	<b>25</b>	(a)	<b>29</b>	(b)	<b>33</b>	(c)
<b>2</b>	(b)	<b>6</b>	(d)	<b>10</b>	(a)	<b>14</b>	(c)	<b>18</b>	(a)	<b>22</b>	(a)	<b>26</b>	(a)	<b>30</b>	(c)		
<b>3</b>	(b)	<b>7</b>	(c)	<b>11</b>	(d)	<b>15</b>	(b)	<b>19</b>	(a)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

## Hints & Solutions

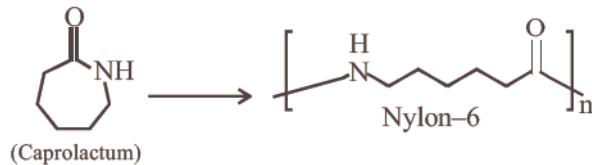
1. (d) *cis*-1,4-Polyisoprene is a natural polymer.
2. (b) nylon 2 – nylon 6
3. (b) Nylon is a synthetic polyamide polymer.
4. (d) Neoprene is an addition polymer of isoprene.
5. (a) Polyesters are condensation polymers of a dibasic acid and a diol. e.g., Terylene.
6. (d) The given compound is a copolymer of hexamethylene diamine and adipic acid. It is actually Nylon-6,6.
7. (c) Chain growth polymers involve a series of reactions, each step of which consumes a reactive particle and produce another similar particle. The reactive particles may be free radicals or ions to which monomers get added by a chain reaction.



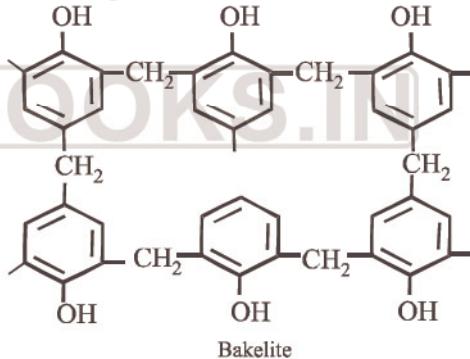
8. (b) Elastomers are the polymers having very weak intermolecular forces of attraction between the polymer chain. The weak forces permit the polymer to be stretched.
9. (c) Cross-linked or network polymers are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains like melamine, bakelite etc.
10. (a) Natural rubber is found to be a polymer of *cis*-isoprene i.e. it is *cis*-polyisoprene



12. (a)

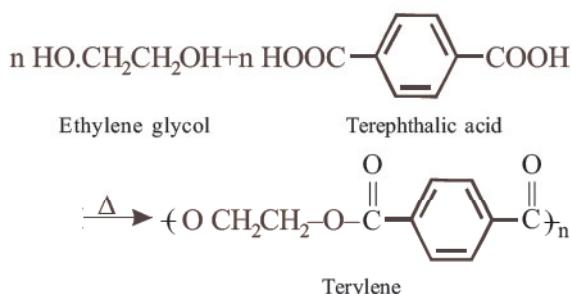


13. (d) Thermosetting polymers undergo chemical changes when heated and set to hard mass when cooled e.g. Bakelite.



Thermoset plastics contain polymers and cross linked together during the curing process to form an irreversible chemical bond. Cross linking process making thermosets plastic ideal for high heat applications.

14. (c)



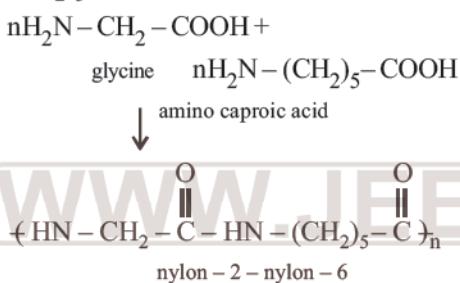
It is resistant to mineral and organic acids. It is used for blending with wool to provide better crease, in safety helmets and aircraft battery boxes.

- Cl

15. (b)  $\text{CH}_2 = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$  (chloroprene) is the monomer of neoprene.

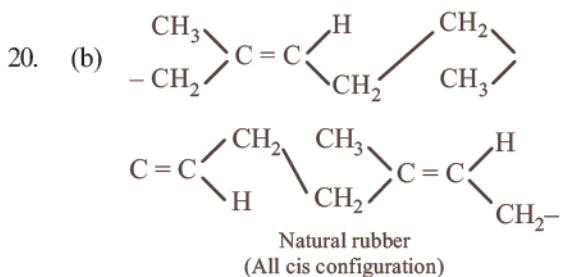
16. (b) Nylon-6,6 is an example of first synthetic fibres produced from simple molecules. It is prepared by condensation polymerisation of adipic acid and hexamethylene diamine.

17. (b) Biodegradable polymer is Nylon-2-Nylon-6 which is copolymer of glycine ( $\text{H}_2\text{N} - \text{CH}_2 - \text{COOH}$ ) and amino caproic acid ( $\text{H}_2\text{N} - (\text{CH}_2)_5 - \text{COOH}$ ).

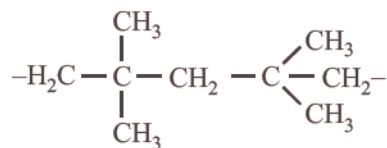
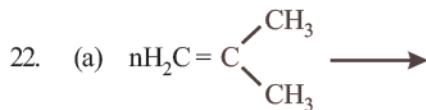
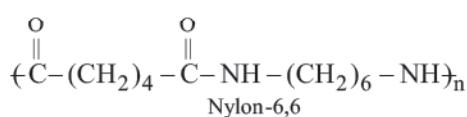
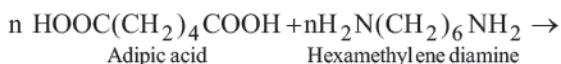


18. (a) Neoprene is a polymer of chloroprene (2-chloro-1,3-butadiene).

19. (a) Neoprene is a polymer of chloroprene.



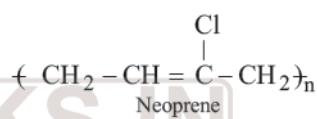
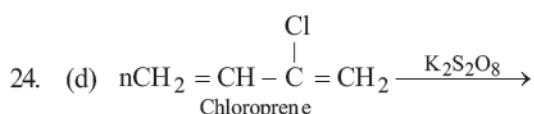
21. (d) Copolymer of adipic acid (6C) and hexamethylene diamine (6C).



23. (b) Acrilan is a polyacrylonitrile ( PAN).



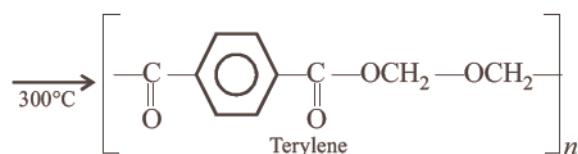
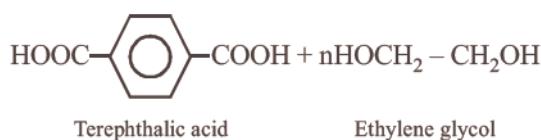
Acrylic fibers are synthetic fibers made from acrylonitrile monomer. Popular brand names are Dralon, Orlon, Drytex, Courtelle, etc.



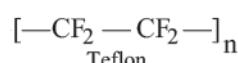
25. (a) Monomer of  $\left[ \begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}-\text{CH}_2- \\ | \\ \text{CH}_3 \end{array} \right]$

polymer is 2-methylpropene.

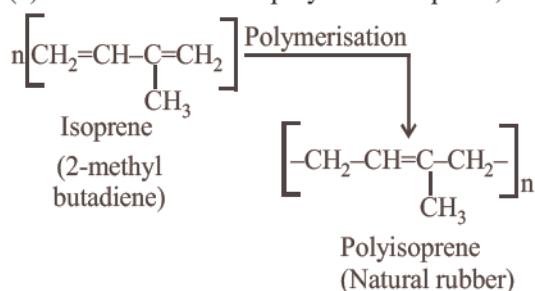
26. (a) Terylene is prepared by condensing terephthalic acid and ethylene glycol.



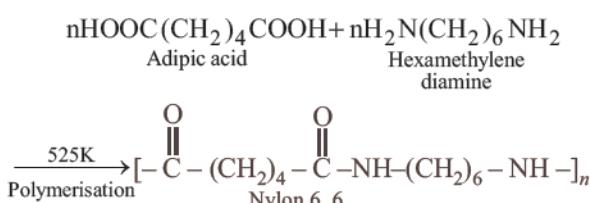
27. (a)  $n \text{ CF}_2 = \text{CF}_2$   $\xrightarrow[\text{Tetrafluoroethene}]{\substack{\text{Benzoyl Peroxide} \\ \text{Ammonium peroxo Sulphate} \\ (\text{NH}_4)_2\text{S}_2\text{O}_8}}$



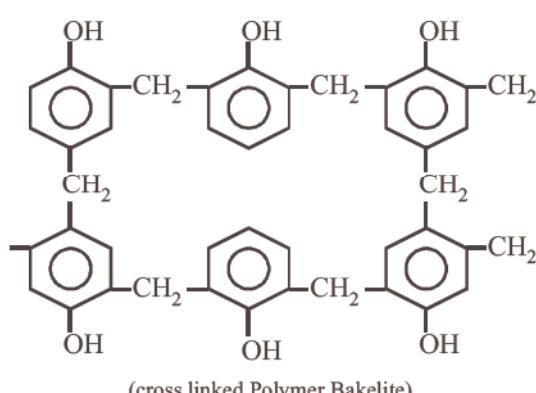
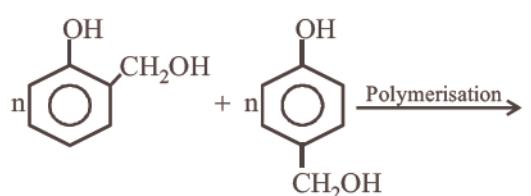
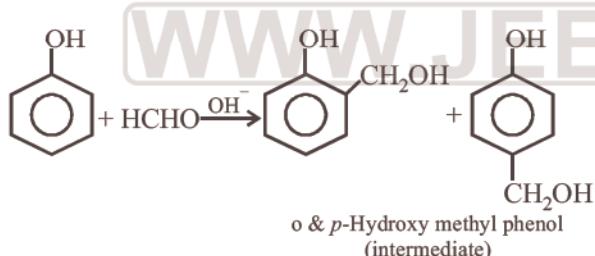
28. (b) Natural rubber is a polymer of isoprene.



29. (b)



30. (c) Phenol and formaldehyde undergo condensation polymerisation under two different conditions to give a cross linked polymer called bakelite.



31. (d) DNA is a biopolymer.

32. (d) Polyacrylonitrile is used as a substitute for wool in making commercial fibre as orlon or acrilan.

33. (c) Polytetrafluoroethylene commonly known as teflon is a tough material. This is resistant to heat and chemicals and have high melting point. Therefore it is used for coating the cookware to make them non-sticky.

# 30

## Chemistry in Everyday Life



Trend Analysis with Important Topics & Sub-Topics



		2020		2019		2018		2017		2016	
Topic Name	Sub-Topic	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD	QNS.	LOD
Drugs and their classification	Therapeutic action of drugs			1	E			1	E	1	E
Cleansing agents	detergents	1	A								
LOD - Level of Difficulty		E - Easy			A - Average			D - Difficult		Qns - No. of Questions	

1. Which of the following is a cationic detergent?  
 (a) Sodium stearate *[2020]*  
 (b) Cetyltrimethyl ammonium bromide  
 (c) Sodium dodecylbenzene sulphonate  
 (d) Sodium lauryl sulphate
2. The artificial sweetener stable at cooking temperature and does not provide calories is  
*[NEET Odisha 2019]*  
 (a) alitame (b) saccharin  
 (c) aspartame (d) sucralose
3. Among the following, the narrow spectrum antibiotic is:  
*[2019]*  
 (a) penicillin G (b) ampicillin  
 (c) amoxycillin (d) chloramphenicol
4. Mixture of chloroxylenol and terpineol acts as:  
*[2017]*  
 (a) antiseptic (b) antipyretic  
 (c) antibiotic (d) analgesic
5. Which of the following is an analgesic? *[2016]*  
 (a) Novalgin (b) Penicillin  
 (c) Streptomycin (d) Chloromycetin
6. Bithionol is generally added to the soaps as an additive to function as a/an : *[2015]*
7. (a) Dryer (b) Buffering agent  
 (c) Antiseptic (d) Softner  
 Artificial sweetener which is stable under cold conditions only is : *[2014]*  
 (a) Saccharine (b) Sucralose  
 (c) Aspartame (d) Alitame
8. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following statements is not true:  
*[NEET 2013]*  
 (a) Chlorine and iodine are used as strong disinfectants.  
 (b) Dilute solutions of Boric acid and Hydrogen Peroxide are strong antiseptics.  
 (c) Disinfectants harm the living tissues.  
 (d) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant.
9. Dettol is the mixture of *[1996, NEET Kar. 2013]*  
 (a) Terpineol and Bithionol  
 (b) Chloroxylenol and Bithionol  
 (c) Chloroxylenol and Terpineol  
 (d) Phenol and Iodine
10. Chloroamphenicol is an : *[2012 MJ]*  
 (a) antifertility drug  
 (b) antihistaminic  
 (c) antiseptic and disinfectant  
 (d) antibiotic-broad spectrum

11. Which one of the following is employed as Antihistamine? [2011]  
 (a) Chloramphenicol  
 (b) Diphenyl hydramine  
 (c) Norothindrone  
 (d) Omeprazole
12. Which one of the following is employed as a tranquilizer drug? [2010]  
 (a) Promethazine (b) Valium  
 (c) Naproxen (d) Mifepristone
13. Which one of the following is employed as a tranquilizer? [2009]  
 (a) Nuproxen (b) Tetracycline  
 (c) Chlorpheniramine (d) Equanil
14. Which one of the following can possibly be used as analgesic without causing addiction and mood modification? [1997]  
 (a) Diazepam  
 (b) Morphine  
 (c) N-acetyl-para-aminophenol  
 (d) Tetrahydrocannabinol

## ANSWER KEY

1	(b)	3	(a)	5	(a)	7	(c)	9	(c)	11	(b)	13	(d)
2	(d)	4	(a)	6	(c)	8	(b)	10	(d)	12	(b)	14	(c)

## Hints & Solutions

1. (b)  $\text{CH}_3 - (\text{CH}_2)^{15} - \underset{\substack{| \\ \text{CH}_3}}{\overset{\oplus}{\text{N}}} - \underset{\substack{| \\ \text{CH}_3}}{\text{CH}_3} \text{Br}^-$   
 Cetyltrimethyl ammonium bromide
2. (d) Sucralose is trichloro derivative of sucrose. It is stable at cooking temperature. It does not provide calories.
3. (a) Penicillin G
4. (a) Dettol is a mixture of chloroxylenol and terpineol which is a very commonly known antiseptic.
5. (a) Novalgin is most widely used as analgesic. Analgesics are pain relieving
6. (c) Bithionol is added to soaps to impart antiseptic properties.
7. (c) Aspartame is stable under cold conditions.



NOTES

8. (b) Dilute solutions of boric acid and hydrogen peroxide are weak antiseptics.  
 Antiseptics are used for humans, pets, etc. but disinfectants are used to kill bacteria etc. on floor, wall surfaces.
9. (c) Dettol is a mixture of chloroxylenol and terpineol.
10. (d) Chloramphenicol is a broad spectrum antibiotic.
11. (b) Diphenyl hydramine also known as benadryl is an antihistamine.
12. (b) Valium is used as a sedative.
13. (d) Equanil is an important medicine used in depression and hypertension.
14. (c) We know that N-acetyl-para-aminophenol (or paracetamol) is an antipyretic which can also be used as an analgesic to relieve pains.

31

# Nuclear Chemistry

- fission products + neutrons +  $3.20 \times 10^{-11}$  J
- The energy released when 1 g of  $^{235}_{92}\text{U}$  finally undergoes fission is [1997]
- $12.75 \times 10^8$  kJ
  - $16.40 \times 10^7$  kJ
  - $8.20 \times 10^7$  kJ
  - $6.50 \times 10^6$  kJ
12. One microgram of radioactive sodium  $^{24}_{11}\text{Na}$  with a half-life of 15 hours was injected into a living system for a bio-assay. How long will it take for the radioactive substance to fall up to 25% of the initial value? [1996]
- 60 hours
  - 22.5 hours
  - 375 hours
  - 30 hours
13. Half-life for radioactive  $^{14}\text{C}$  is 5760 years. In how many years, 200 mg of  $^{14}\text{C}$  will be reduced to 25 mg? [1995]
- 5760 years
  - 11520 years
  - 17280 years
  - 23040 years
14. In a radioactive decay, an emitted electron comes from [1994]
- The nucleus of atom
  - The orbit with principal quantum number 1
  - the inner orbital of the atom
  - the outermost orbit of the atom.
15. India has the world's largest deposits of thorium in the form of [1994]
- rutile
  - magnesite.
  - lignite
  - monazite.
16. If an isotope of hydrogen has two neutrons in its atom, its atomic number and atomic mass number will respectively be [1992]
- 2 and 1
  - 3 and 1
  - 1 and 1
  - 1 and 3.
17. The age of most ancient geological formations is estimated by [1989]
- Potassium–argon method
  - Carbon-14 dating method
  - Radium-silicon method
  - Uranium-lead method.
18. Emission of an alpha particle leads to a [1989]
- Decrease of 2 units in the charge of the atom
  - Increase of 2 units in the mass of the atom
  - Decrease of 2 units in the mass of the atom
  - Increase of 4 units in the mass of the atom.

## ANSWER KEY

1	(c)	3	(c)	5	(a)	7	(a)	9	(a)	11	(c)	13	(c)	15	(d)	17	(d)
2	(c)	4	(c)	6	(d)	8	(a)	10	(c)	12	(d)	14	(a)	16	(d)	18	(a)

# Hints & Solutions

1. (c) For a first order reaction

Total time  $T = \text{no. of half lives} (n) \times \text{half life} (t_{1/2})$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

where  $n = \text{no. of half lives}$

Given  $N_0$  (original amount) = 1.28 mg/l

$N$  (amount of substance left after time  $T$ )  
= 0.04 mgL<sup>-1</sup>

$$\therefore \frac{0.04}{1.28} = \left(\frac{1}{2}\right)^n ; \frac{1}{32} = \left(\frac{1}{2}\right)^n ; \left(\frac{1}{2}\right)^5 = \left(\frac{1}{2}\right)^n$$

$$n = 5$$

$$T = 5 \times 138 = 690$$

2. (c) When IIA group element (Ra) emits one  $\alpha$ -particle its group no. decreases by two unit. i.e., go into zero group (Gr. 16) But as it is radioactive thus due to successive emission last product is Pb i.e., (Gr.14).

3. (c)  $[X] + {}_0^1 n \rightarrow {}_{27}^{60} Co + {}_1^1 H$

Balancing the mass and atomic numbers on both sides  ${}_{28}^{60} X + {}_0^1 n \rightarrow {}_{27}^{60} Co + {}_1^1 H$

Thus  $X$  should be  ${}_{28}^{60} \text{Ni}$

4. (c) Given  $t_{1/2} = 12.3$  years

Initial amount ( $N_0$ ) = 32 mg

Total time = 49.2 years

$$\text{No. of half lives } (n) = \frac{T}{t_{1/2}} = \frac{49.2}{12.3} = 4$$

$$\text{Now } N_t = N_0 \left(\frac{1}{2}\right)^n = 32 \left(\frac{1}{2}\right)^4 = \frac{32}{16} = 2 \text{ mg}$$

Hence 32 mg becomes 2 mg in 49.2 years

5. (a)  ${}_{92}^{92} U + {}_0^1 n \rightarrow {}_{54}^{94} Xe + {}_{38}^{90} Sr + X$

$$92 + 0 = 54 + 38 + a \Rightarrow a = 0$$

$$235 + 1 = 139 + 94 + b \Rightarrow b = 3 \text{ So, } X = {}_3^1 n$$

i.e 3 neutrons.

6. (d) Remaining activity = 0.01M  
after 24 hrs

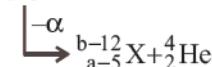
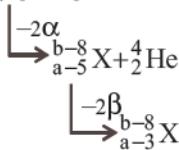
$$\text{Remaining activity} = \text{Initial activity} \times \left(\frac{1}{2}\right)^n$$

$$\text{Used half life time (n)} = \frac{\text{Total time}}{T_{1/2}} = \frac{24}{6} = 4$$

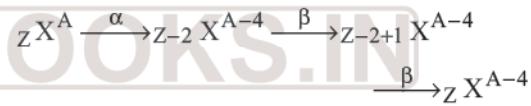
$$\text{So, } 0.01 = \text{Initial activity} \times \left(\frac{1}{2}\right)^4$$

$$\text{Initial activity} = 0.01 \times 16 = 0.16 \text{ M}$$

7. (a)  ${}_{a}^b X \xrightarrow{-2\alpha} {}_{a-5}^{b-8} X + {}_2^4 He$



8. (a) Mass number is affected by emmission of  $\alpha$  particle while  $\beta$ -particle has negligible mass does not effect mass number. e.g.



9. (a)  ${}_{5}^{14} X \xrightarrow{-\beta} {}_{6}^{14} Y \xrightarrow{-\beta} {}_{7}^{14} N$

No. of neutrons = Mass number – No. of proton  
= 14 – 5 = 9

10. (c) By carbon dating method

$$\text{Age of wood} = \frac{2.303}{0.693} \times t_{1/2} \log \left( \frac{N_0}{N} \right)$$

$$\left[ \frac{\text{ratio of } C^{14}/C^{12} \text{ in living wood}}{\text{ratio of } C^{14}/C^{12} \text{ in dead wood}} \right]$$

Hence, it is based upon the ratio of C<sup>14</sup> and C<sup>12</sup>.

11. (c) 1 atom of  ${}_{92}^{235} U$  on fission gives energy

$$= 3.2 \times 10^{-11} \text{ J}$$

$6.023 \times 10^{23}$  atom (1 mole) on fission gives energy  
=  $3.2 \times 10^{-11} \times 6.023 \times 10^{23} \text{ J}$

1 g of  ${}_{92}^{235} U$  on fission gives energy

$$= \frac{6.023}{235} \times 3.2 \times 10^{12} \text{ J} = 8.2 \times 10^7 \text{ kJ}$$

12. (d)  $N = N_0 \left(\frac{1}{2}\right)^n$ ; here,  $N = \frac{N_0}{4}$   
 $\frac{N_0}{4} = N_0 \left(\frac{1}{2}\right)^n \Rightarrow \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^2 \Rightarrow n = 2$   
 Total time ( $T$ ) =  $n \times t_{1/2} = 2 \times 15 = 30$  hrs

13. (c) As we know that

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

where  $N_0$  original amount of radioactive substance

$N$  = Amount of substance remain after  $n$  half lives

$$\therefore \frac{25}{200} = \left(\frac{1}{2}\right)^n \text{ or } \frac{1}{8} = \left(\frac{1}{2}\right)^n$$

$$\text{or } \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n; \therefore n = 3$$

now  $T = n \times t_{1/2}$

where  $T$  = total time

$$T = 3 \times 5760 \text{ years} = 17280 \text{ years}$$

14. (a) When a radioactive elements emits  $\alpha$  or  $\beta$  particle the new element formed may have unstable nucleus. It may further disintegrate by emitting  $\alpha$ - or  $\beta$  particle forming a new element. This process of integration may continue till end product formed, is a stable compound.
15. (d) The ore of thorium is monazite.
16. (d) As number of neutron = Mass number – atomic number  
 Give number of neutron = 2  
 $\therefore$  Mass number will be 3 and atomic number will be one.
17. (d) Age of geological formations (*i.e.* predicting the age of the earth and rocks) is estimated by U–Pb method, also known as helium dating.



C-14 dating method is used to predict the age of fossils or dead animals or a fallen tree.

18. (a) Emission of  $\alpha$ -particle ( ${}^4_2\text{He}$ ) leads to decrease of 2 units of charge. *e.g.*

