# SAMPLE OUESTION OAPER

## **BLUE PRINT**

Time Allowed : 3 hours

#### Maximum Marks: 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	_	_	1(5)	
2.	Solutions	2(2)	—	1(3)	_	
3.	Electrochemistry	1(4)	—	_	_	11(23)
4.	Chemical Kinetics	2(2)	—	1(3)	_	
5.	Surface Chemistry	1(1)	1(2)	_	_	
6.	The <i>p</i> -Block Elements	2(2)	_	1(3)	_	
7.	The <i>d</i> - and <i>f</i> -Block Elements	1(4)	1(2)	_	_	8(19)
8.	Coordination Compounds	1(1)	1(2)	_	1(5)	
9.	Haloalkanes and Haloarenes	1(1)	2(4)	_	1(5)	
10.	Alcohols, Phenols and Ethers	1(1)	1(2)	_	_	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	1(2)	1(3)	_	14(28)
12.	Amines	1(1)	1(2)	1(3)	_	
13.	Biomolecules	1(1)	1(2)	_	_	
	Total	16(22)	9(18)	5(15)	3(15)	33(70)

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### Subject Code : 043

# CHEMISTRY

#### Time allowed : 3 hours

Maximum marks : 70

#### General Instructions : Read the following instructions carefully.

- (a) There are 33 questions in this question paper. All questions are compulsory.
- (b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
- (c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- (d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- (e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.
- (f) There is no overall choice. However, internal choices have been provided.
- (g) Use of calculators and log tables is not permitted.

#### **SECTION - A (OBJECTIVE TYPE)**

#### 1. Read the passage given below and answer the following questions :

The study of the conductivity of electrolyte solutions is important for the development of electrochemical devices, for the characterisation of the dissociation equilibrium of weak electrolytes and for the fundamental understanding of charge transport by ions. The conductivity of electrolyte is measured for electrolyte solution with concentrations in the range of  $10^{-3}$  to  $10^{-1}$  mol L<sup>-1</sup>, as solution in this range of concentrations can be easily prepared. The molar conductivity ( $\Lambda_m$ ) of strong electrolyte solutions can be nicely fit by Kohlrausch equation.

$$\Lambda_m = \Lambda_m^\circ - K\sqrt{C} \qquad \qquad '...(i)$$

Where,  $\Lambda_m^{\circ}$  is the molar conductivity at infinite dilution and *C* is the concentration of the solution. *K* is an empirical proportionality constant to be obtained from the experiment. The molar conductivity of weak electrolytes, on the other hand, is dependent on the degree of dissociation of the electrolyte. At the limit of very dilute solution, the Ostwald dilution law is expected to be followed,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^{\circ}} + \frac{\Lambda_m}{(\Lambda_m^{\circ})^2} \frac{C_A}{K_d} \qquad \dots (ii)$$

Where,  $C_A$  is the analytical concentration of the electrolyte and  $K_d$  is dissociation constant. The molar conductivity at infinite dilution can be decomposed into the contributions of each ion.

$$\Lambda_m^\circ = \nu^+ \lambda^+ + \nu^- \lambda^- \qquad \dots (iii)$$

Where,  $\lambda^+$  and  $\lambda^-$  are the ionic conductivities of positive and negative ions, respectively and  $\nu^+$  and  $\nu^-$  are their stoichiometric coefficients in the salt molecular formula.

#### The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Which statement about the term infinite dilution is correct?
  - (a) Infinite dilution refers to hypothetical situation when the ions are infinitely far apart.

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- (b) The molar conductivity at infinite dilution of NaCl can be measured directly in solution.
- (c) Infinite dilution is applicable only to strong electrolytes.
- (d) Infinite dilution refers to a real situation when the ions are infinitely far apart.
- (ii) Which of the following is a strong electrolyte in aqueous solution?

	(a)	HNO <sub>2</sub>	(b) HCN	(c)	NH <sub>3</sub>	(d)	HCl
			OF	2			
	Which of the following is a weak electrolyte in aqueous solution?						
	(a)	K <sub>2</sub> SO <sub>4</sub>	(b) Na <sub>3</sub> PO <sub>4</sub>	(c)	NaOH	(d)	$H_2SO_3$
(iii)	If the 18.73	e molar conductivitie 8 S cm <sup>2</sup> mol <sup>-1</sup> respect	s at infinite dilution for Na tively at 25°C, then the mo	I, CH lar co	$I_3$ COONa and (CH <sub>3</sub> Conductivity of MgI <sub>2</sub> at	OO) <sub>2</sub> infin	Mg are 12.69, 9.10 and ite dilution is

- (b)  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ (d)  $3.89 \times 10^{-2} \text{ S cm}^2 \text{ mol}^{-1}$ (a)  $25.96 \text{ S cm}^2$ , mol<sup>-1</sup>
- (c)  $189.0 \text{ S cm}^2 \text{ mol}^{-1}$
- (iv) Which of the following is the correct order of molar ionic conductivities of the following ions in aqueous solutions?

(a)	$\mathrm{Li}^+ < \mathrm{Na}^+ < \mathrm{K}^+ < \mathrm{Rb}^+$	(b)	$Li^+ > Na^+ > K^+ > Rb^+$
(c)	$Rb^{+} < Na^{+} < Li^{+} < K^{+}$	(d)	$Li^+ < Rb^+ < Na^+ < K^+$

#### 2. Read the passage given below and answer the following questions :

The lanthanide series is a unique class of 15 elements with relatively similar chemical properties. They have atomic number ranging from 57 to 71, which corresponds to the filling of the 4f orbitals with 14 electrons. This configuration leads to phenomenon known as lanthanide contraction. The lanthanides are sometimes referred to as the 'rare earth elements', leading to misconception that they are rare. In fact many of the rare earth elements are more common than gold, silver and in some cases, lead. The lanthanides are commonly found in nature as a mixture in a number of monazite  $(LnPO_4)$  and bastnaesite  $(LnCO_3F)$  in the +3 oxidation state.

The chemical and physical properties of lanthanides provide the unique features that set them apart from other elements. Lanthanides are most stable in the +3 oxidation state. Yb and Sm though stable in the +3 state, also have accessible +2 oxidation states. The ease of accessibility of both oxidation states is quite important in chemical synthesis and these elements act as Lewis acid in the +3 oxidation state and single electron reductant in the +2 oxidation state.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- (i) Assertion : The elements scandium and yttrium are called "rare earths". Reason : Scandium and yttrium are rare on earth's crust.
- (ii) Assertion : Separation of lanthanide elements is difficult. Reason : They have similar chemical properties.

#### OR

Assertion : There is continuous increase in size among lanthanides. **Reason :** Lanthanides show lanthanide contraction.

(iii) Assertion :  $Yb^{2+}$  is more stable than  $Yb^{3+}$ . **Reason :** Electronic configuration of  $Yb^{2+}$  is  $[Xe]4f^7$ .

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(iv) Assertion : All lanthanides have similar chemical properties. **Reason :** Because the lanthanoids differ only in the number of 4*f* - electrons.

#### Following questions (Q. No. 3-11) are multiple choice questions carrying 1 mark each:

- For a zero order reaction, the plot of conc. of reactants vs time is a straight line with 3.
  - (a) +ve slope and zero intercept
- (b) -ve slope and zero intercept (d) -ve slope and non-zero intercept.
  - (c) +ve slope and non-zero intercept
- 4. The correct order of reactivity of aldehydes and ketones towards hydrogen cyanide is
  - (a)  $CH_3COCH_3 > CH_3CHO > HCHO$
- (b)  $CH_3COCH_3 > HCHO > CH_3CHO$ (d)  $HCHO > CH_3CHO > CH_3COCH_3$
- (c)  $CH_3CHO > CH_3COCH_3 > HCHO$
- OR

In a set of reactions *m*-bromobenzoic acid gave a product *D*. Identify the product *D*.



- 5. Which of the following reactions is most suitable for the preparation of *n*-propylbenzene?
  - (a) Friedel-Crafts alkylation
  - (c) Wurtz-Fittig reaction
- What are the products obtained when ammonia is reacted with excess of chlorine? 6.
  - (a)  $N_2$  and  $NCl_3$
  - (c)  $N_2$  and  $NH_4Cl$
- 7. Identify 'X'.

 $C_6H_5COCl + (CH_3)_2NH \xrightarrow{Pyridine} 'X$ 

- (a) *N*, *N*-Dimethylbenzamide
- (c) N-Methyl-N-phenylamine
- (b) *N*, *N*-Dimethylbenzene

(b) Wurtz reaction (d) Grignard reaction

(b)  $N_2$  and HCl

(d) NCl<sub>3</sub> and HCl

(d) N, N-Diphenylmethanamine

#### OR

Which of the following is the correct increasing order of basicity of amines in gaseous phase?

- (a)  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- (b)  $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$
- (c)  $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$
- (d)  $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH > NH_3$

#### 8. Which of the following defect, if present, lowers the density of the crystal?

(a) Frenkel

(c) Edge dislocation

- (b) Schottky
- (d) Constitution of *F* centres
- Which plot is the adsorption isobar for chemisorption? 9.





If we add dilute aqueous solution of KI dropwise to AgNO<sub>3</sub> aqueous solution like KI is in slight excess the AgI colloid formed will have

OR

- (a) negative charge
- (c) neutral

(b) positive charge

(b) *p*-bromophenol

- (d) nothing can be predicted.
- 10. Henry's law constant for oxygen dissolved in water is  $4.34 \times 10^4$  atm at 25° C. If the partial pressure of oxygen in air is 0.4 atm at 25° C, the oncentration (in moles per litre) of the dissolved oxygen in water in equilibrium with air at 25°C is
  - (a)  $1.3 \times 10^{-3}$  M (b)  $0.13 \times 10^{-3}$  M (c)  $0.28 \times 10^{-4}$  M (d)  $5.11 \times 10^{-4}$  M
- **11.** The given ether



Phenol reacts with bromine in carbon disulphide at low temperature to give

- (a) *m*-bromophenol
- (c) *o*-and *p*-bromophenol (d) 2, 4, 6-tribromophenol.

In the following questions (Q. No. 12-16) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- **12. Assertion :** Relative lowering of vapour pressure is directly proportional to the number of ions present in the solution.

Reason : The relative lowering of vapour pressure of 0.1 M sugar solution is less than that of 0.1 M urea.

13. Assertion : Glucose when treated with  $CH_3OH$  in presence of dry HCl gas gives  $\alpha$ -and  $\beta$ -methyl glucosides. Reason : Glucose reacts with phenylhydrazine to form crystalline osazone.

OR

**Assertion :** A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little hydrochloric acid, it becomes laevorotatory.

**Reason :** Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

- 14. Assertion : Many reactions occuring on solid surface are zero order reactions. **Reason :**  $2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$  rate = k
- **15.** Assertion : OF<sub>2</sub> is named as oxygen difluoride.**Reason :** In OF<sub>2</sub>, oxygen is less electronegative than fluorine.
- Assertion : The [Ni(*en*)<sub>3</sub>]Cl<sub>2</sub> has higher stability than [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>
   Reason : In [Ni(*en*)<sub>3</sub>]Cl<sub>2</sub>, the geometry around Ni is octahedral.

Chemistry



#### **SECTION - B**

#### The following questions, Q. No. 17-25 are short answer type and carry 2 marks each :

- 17. (a) Why do the *d*-block elements exhibit a large number of oxidation states than the lanthanides?
  - (b) How do the transition elements form interstitial compounds?
- **18.** Write the IUPAC names of the products (*A*) and (*B*) in the following reactions :

(a) 
$$CH_3COOH \xrightarrow{NH_3} A$$
 (b)  $\xrightarrow{O} B$ 

#### OR

How will you convert ethanal into the following compounds?

- (i) Butan-1,3-diol (ii) But-2-enal
- **19.** Explain the following terms :
  - (a) Dialysis (b) Electro-osmosis
- **20.**  $[Cr(NH_3)_6]^{3+}$  is paramagnetic while  $[Ni(CN)_4]^{2-}$  is diamagnetic. Explain why?
- **21.** Identify *A*, *B*, *C* and *D* in the following reactions :

$$CH_{3}COOH \xrightarrow{NH_{3}} A \xrightarrow{Br_{2} + KOH} B \xrightarrow{CHCl_{3} + NaOH} C \xrightarrow{LiAlH_{4}} D$$

$$OR$$

- (a) How are amines prepared from amides?
- (b) Acylation of amines with acid chloride is carried out in presence of stronger base. Why?
- **22.** Identify the compound that on hydrogenation produces an optically inactive compound from the following compounds.



Arrange the following in the increasing reactivity for  $S_N1$  reaction. Give reason.  $C_6H_5CH_2Br$ ,  $C_6H_5CH(C_6H_5)Br$ ,  $C_6H_5CH(CH_3)Br$ ,  $C_6H_5C(CH_3)(C_6H_5)Br$ 

- **23.** Account for the following :
  - (i) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.
  - (ii) The boiling points of ethers are lower than isomeric alcohols.
- 24. Amino acids may be acidic, alkaline or neutral, how does this happen? What are essential and non-essential amino acids? Name one of each type.
- **25.** Explain giving reason :
  - (i)  $S_N 1$  reaction of optically active compounds undergo racemisation whereas  $S_N 2$  reaction led to inversion.
  - (ii) No effect on reactivity of haloarene is observed by the presence of electron withdrawing group at *meta* position.

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#### **SECTION - C**

#### Q. No. 26-30 are short answer type II carrying 3 marks each.

- **26.** Hydrogen peroxide,  $H_2O_{2(aq)}$  decomposes to  $H_2O_{(l)}$  and  $O_{2(g)}$  in a reaction that is first order in  $H_2O_2$  and has a rate constant  $k = 1.06 \times 10^{-3} \text{ min}^{-1}$ .
  - (i) How long will it take for 15% of a sample of  $H_2O_2$  to decompose?
  - (ii) How long will it take for 85% of the sample to decompose?

#### OR

- (i) For a reaction,  $A + B \rightarrow$  Product, the rate law is given by, Rate =  $k[A]^1[B]^2$ . What is the order of the reaction?
- (ii) Write the unit of rate constant k for the first order reaction.
- (iii) For the reaction  $A \rightarrow B$ , the rate of reaction becomes twenty seven times when the concentration of A is increased three times. What is the order of reaction?
- 27. Describe the following about halogens (Group 17 elements):
  - (i) Relative oxidising power of halogens.
  - (ii) Relative acidic strength of the hydrogen halides.
  - (iii) Perchloric acid is a stronger acid than chloric acid.
- **28.** (a) Write a test to differentiate between pentan-2-one and pentan-3-one.
  - (b) Compound 'A' was prepared by oxidation of compound 'B' with alkaline KMnO<sub>4</sub>. Compound 'A' on reduction with lithium aluminium hydride gets converted back to compound 'B'. When compound 'A' is heated with compound 'B' in the presence of H<sub>2</sub>SO<sub>4</sub> it produces fruity smell of compound 'C'. To which families the compounds 'A', 'B' and 'C' belong to?

OR

Complete the following reactions :

(i) 
$$(i) \xrightarrow{CHO} \xrightarrow{NaCN/HCl}$$

(ii) CH<sub>3</sub>COCH<sub>2</sub>COOC<sub>2</sub>H<sub>5</sub> 
$$\frac{(i) \text{ NaBH}_4}{(ii) \text{ H}^+}$$
  
(...) CrO<sub>3</sub>

(iii) 
$$\langle -OH \xrightarrow{CrO_3} \rangle$$

- **29.** Explain why
  - (a) Liquid ammonia bottle first cooled in ice before opening it.
  - (b) aquatic species feel more comfortable in winter than in summer.
  - (c) a solution of chloroform and acetone shows negative deviation from Raoult's law.
- **30.** (i) Account for the following :
  - (a) Aqueous solution of methyl amine reacts with iron(III) chloride to precipitate iron(III) hydroxide.
  - (b) The boiling points of amines are lower than those of corresponding alcohols.
  - (ii) How is aminoethane obtained from ethanal?

#### **SECTION - D**

#### Q. No. 31-33 are long answer type carrying 5 marks each.

- **31.** (a) Give the IUPAC name of  $[PtCl(NH_2CH_3)(NH_3)_2]Cl$ .
  - (b) Compare the magnetic behaviour of the complex entities  $[Fe(CN)_6]^{4-}$  and  $[FeF_6]^{3-}$ . [Atomic number of Fe = 26].
  - (c) Tetrahedral complexes are always of high spin. Explain.

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OR

- (a) What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
- (b) FeSO<sub>4</sub> solution mixed with  $(NH_4)_2SO_4$  solution in 1:1 molar ratio gives the test of Fe<sup>2+</sup> ion but CuSO<sub>4</sub> solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu<sup>2+</sup> ion. Explain why?
- **32.** (a) An element crystallises in *fcc* structure. Its density is 7.2 g cm<sup>-3</sup>. 208 g of this element has  $4.283 \times 10^{24}$  atoms. Calculate the edge length of the unit cell.
  - (b) Analysis shows that nickel oxide has the formula  $Ni_{0.98}O_{1.00}$ . What fractions of nickel exist as  $Ni^{2+}$  and  $Ni^{3+}$  ions?

#### OR

- (a) Schottky defects generate an equal number of cation and anion vacancies while doping produces only cation vacancies and not anion vacancies. Why?
- (b) A metallic element crystallizes into a lattice containing a sequence of layers of *ABABAB*..... Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?
- (c) Why urea has a sharp melting point but glass does not?
- **33.** (a) Compound *A* with molecular formula  $C_4H_9Br$  is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound *A* only. When another optically active isomer *B* of this compound was treated with *aq*. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
  - (i) Write down the structural formula of both compounds *A* and *B*.
  - (ii) Out of these two compounds, which one will be converted to the product with inverted configuration.
  - (b) Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

#### OR

- (a) An alkyl halide, *X*, of formula  $C_6H_{13}Cl$  on treatment with potassium tertiary butoxide gives two isomeric alkenes *Y* and *Z* ( $C_6H_{12}$ ). Both alkenes on hydrogenation give 2,3-dimethylbutane. Predict the structures of *X*, *Y* and *Z*.
- (b) Vinyl halides are less reactive than alkyl halides, but allyl halides are more reactive than alkyl halides. Explain.

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#### 1. (i) (a) (ii) (d) OR

(d) : Weak electrolytes do not dissociate in aqueous solution.

(iii) (a): According to Kohlrausch's law

 $\begin{aligned} \Lambda^{\circ}_{(MgI_2)} &= \Lambda^{\circ}_{[(CH_3 COO)_2Mg]} + 2\Lambda^{\circ}_{(NaI)} - 2\Lambda^{\circ}_{(CH_3 COONa)} \\ &= 18.78 + 2(12.69) - 2(9.10) = 25.96 \text{ S cm}^2 \text{ mol}^{-1} \\ \textbf{(iv) (a)} \end{aligned}$ 

**2.** (i) (c) : The elements scandium and yttrium are called "rare earths because they were originally discovered together with lanthanides in rare minerals and isolated as oxides or "earths". Collectively, these metals are also called rare earth elements.

(ii) (a) OR

(d) : In lanthanide series, with increasing atomic number, there is a progressive decrease in the atomic as well as on radii of trivalent ions form  $La^{3+}$  to  $Lu^{3+}$ . (iii) (c) : Yb<sup>2+</sup> is more stable than Yb<sup>3+</sup> because it will acquire stable configuration of completely filled 4f subshell after loosing 2 electrons. Electronic configuration of Yb<sup>2+</sup> is [Xe]4f<sup>14</sup>.

3. (d):  

$$\begin{bmatrix} A \end{bmatrix}$$
Time (t) =  $\begin{bmatrix} A_0 \end{bmatrix}$ 

**4.** (d) : Alkyl group attached to carbonyl carbon increases the electron density on the carbonyl carbon and lowers its reactivity towards nucleophilic addition reactions.

Also, as the number and size of alkyl group increases, the attack of nucleophile on the carbonyl group becomes more and more difficult due to steric hindrance.

Hence, the reactivity order will be : HCHO > CH<sub>3</sub>CHO > CH<sub>3</sub>COCH<sub>3</sub>



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**5.** (c): Friedel–Crafts alkylation of benzene with *n*-propyl bromide will give isopropylbenzene as the major product. Therefore, Wurtz-Fittig reaction is the right choice.

$$\begin{array}{c} & & \\ & &$$

6. (d) :  $NH_3 + 3Cl_2$  (excess)  $\longrightarrow NCl_3 + 3HCl$ 



(b) : Alkyl amines  $(1^\circ, 2^\circ \text{ and } 3^\circ)$  are stronger bases than ammonia. This can be explained in terms of electron releasing inductive effect of alkyl group. As a result, the electron density on the nitrogen atom increases and thus, they can donate the lone pair of electrons more easily than ammonia.

The electron releasing effect is maximum in tertiary amines and minimum in primary amines (in gas phase).  $3^{\circ}$  amine >  $2^{\circ}$  amine >  $1^{\circ}$  amine >  $NH_3$ .

**8.** (b) : In Schottky defect, equal number of cations and anions are missing from the lattice. Thus, mass of the lattice becomes less and density gets lowered.

**9.** (c) : The chemisorption isobar shows an initial increase with temperature and then the expected decrease. The initial increase is because of the fact that the heat supplied acts as activation energy required in chemisorption.

(a) 
$$\operatorname{AgNO}_{3(aq)} + \operatorname{KI}_{(aq)} \xrightarrow{} \operatorname{AgI} + \operatorname{KNO}_{3}_{\operatorname{Colloid}}$$

AgI will absorb I<sup>-</sup> from KI electrolyte to form [AgI]I<sup>-</sup>. Therefore, it is negatively charged.

**10.** (d) : Given Henry's law constant,  $K_{\rm H} = 4.34 \times 10^4$  atm.  $p_{\rm O_2} = 0.4$  atm.  $p = K_{\rm H} \cdot x$  $\therefore p_{\rm O_2} = K_{\rm H} \cdot x_{\rm O_2}$ 

or 
$$x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$$

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Moles of water  $(n_{\rm H_2O}) = \frac{1000}{18} = 55.5 \text{ mol}$ Mole fraction of oxygen  $(x_{O_2}) = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}}$ 

Since  $n_{O_2}$  is very small in comparison to  $n_{H_2O}$ ,

$$\therefore \quad x_{\rm H_2O} = \frac{n_{\rm O_2}}{n_{\rm H_2O}}$$

or  $x_{O_2} \times n_{H_2O} = n_{O_2}$ 

 $9.2 \times 10^{-6} \times 55.5 = n_{\text{O2}}$ 

or  $n_{\text{O}_2} = 5.11 \times 10^{-4}$  mol since  $5.11 \times 10^{-4}$  mol are present in 1000 mL of solution, therefore, molarity  $= 5.11 \times 10^{-4}$  M.



(c) Phenol reacts with bromine in CS<sub>2</sub> (or CHCl<sub>3</sub>) at low temperature to form a mixture of ortho and para bromophenols.



12. (c) : Relative lowering of vapour pressure is directly proportional to number of ions present in solution. Sugar and urea both being non electrolytes with same molar concentration, will have same relative lowering of vapour pressure.

**13.** (b) : Because of the ring structure  $C_1$  in glucose becomes chiral and hence glucose exists in two stereoisomeric forms, *i.e.*,  $\alpha$ - and  $\beta$ -corresponding to each stereoisomeric form, glucose forms two methyl glucosides, *i.e.*,  $\alpha$ - and  $\beta$ -methyl glucosides.

#### OR

(c) : On hydrolysis sucrose gives equimolar mixture of D(+)-glucose and D(-)-fructose. Since the laureation on of fructose (-92°4°) is much more than westernization of glucose +52.5°, therefore the resulting mixture becomes levorotatory.

#### 14. (b)

15. (a) : The compounds of oxygen and fluorine are not called oxides of fluorine but oxygen fluorides as fluorine is more electronegative than oxygen.

16. (b) : The chelate complexes are more stable than similar complexes containing unidentate ligands. Ni<sup>2+</sup> with coordination number six forms octahedral complexes.

17. (a) All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the (n - 1) and *ns*-orbitals is very little. Hence, electrons from both the energy levels can be used for bond formation.

(b) Transition metals form a number of interstitial compounds in which small atoms such as H,C, B and N occupy the empty spaces in their lattices.



(ii) 
$$2CH_3CHO \xrightarrow{(i) dil. NaOH}_{(ii) H^+, \Delta} CH_3CH = CHCHO$$
  
Ethanal

Ethanal

**CLICK HERE** 

19. (a) Dialysis: It is a process to separate a crystalloid from a colloid by diffusion through a semipermeable membrane.

(b) **Electro-osmosis**: It is the movement of the molecules of the dispersion medium under the influence of an electric field whereas colloidal particles are not allowed to move.

**20.** 
$$[Cr(NH_3)_6]^{3+}$$
:  
 $Cr(24) : [Ar] 3d^54s^1, Cr^{3+} : [Ar] 3d^34s^0$   
 $[Cr(NH_3)_6]^{3+}$ 
 $4s \qquad 4p$   
 $d^2sp^3$  hybridisation

It is paramagnetic due to presence of unpaired electrons.  $[Ni(CN)_4]^{2-}$ :

It is diamagnetic due to absence of unpaired electrons.

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21. 
$$CH_{3}COOH \xrightarrow{NH_{3}} CH_{3}CONH_{2} \xrightarrow{Br_{2} + KOH} (A) \xrightarrow{LiAlH_{4}} CH_{3}NC \xleftarrow{CHCl_{3} + NaOH} CH_{3}NH_{2} \xrightarrow{(C)} (B) \xrightarrow{(B)} OR$$

(a) Amides on reduction with  $LiAlH_4$  or by reaction with  $Br_2$  and alkali give amines.

$$R \xrightarrow{\text{O}} R \xrightarrow{\text{(i) LiAlH}_4} R \xrightarrow{\text{(i) LiAlH}_4} R \xrightarrow{\text{C}} R \xrightarrow{\text{O}} R \xrightarrow{O} R \xrightarrow{\text{O}} R \xrightarrow{O} R \xrightarrow{O$$

(b) During acylation reaction HCl is formed. In order to remove HCl and shift the equilibrium to the right hand side a stronger base like pyridine is added.

$$R - \mathrm{NH}_2 + R\mathrm{COCl} \xrightarrow{\mathrm{Pyndme}} R - \mathrm{NHCOR} + \mathrm{HCR}$$

**22.** Compound(I) on hydrogenation produces an optically inactive compound. Products obtained by hydrogenation of compounds (I) and (II) are respectively



For  $S_N 1$ , carbocation formed is resonance stabilised which is in the order :



II is more stable than I since —  $CH_3$  group is electron donating group.

III (2° benzyl) is more stable than II due to delocalisation of +ve charge on two aromatic rings.

IV (3° benzyl) is more stable than III.

Thus, the reactivity order for  $S_N 1$  is



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**23.** (i) Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers. Due to steric hindrance of nucleophilic attack by the alcohol molecule on the protonated alcohol molecule, does not occur. The protonated 2° and 3° alcohols lose water molecules to form stable 2° and 3° carbocations.

(ii) The boiling points of ethers are much lower than those of alcohol of comparable molar masses because like alcohols they cannot form intermolecular hydrogen bonds.



**24.** Amino acids are classified as acidic, basic or neutral depending upon the relative number of amino and carboxyl groups in their molecules.

(a) Equal number of amino and carboxyl groups makes it neutral (b) more number of amino groups than carboxyl groups make it basic and (c) more number of carboxyl groups as compared to amino groups make it acidic.

Amino acids which cannot be synthesised in the body and must be obtained through diet are known as essential amino acids, *e.g.*, valine and leucine. There are ten essential amino acids. Amino acids which can be synthesised in the body are known as non-essential amino acids, *e.g.*, alanine and glutamic acids.

**25.** (i) In  $S_N 1$  reaction carbocation intermediate is formed which is a planar molecule so, an incoming nucleophile can attack from either side and a equilmolar mixture of two components are formed and resulting mixture is optically inactive.

While in  $S_N^2$  reaction an incoming nucleophile can attack from opposite side and inversion takes place.



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In case of *meta*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the  $-NO_2$  group. Therefore, the presence of nitro group at *meta*- position does not stabilise the negative charge and no effect on reactivity is observed by the presence of  $-NO_2$  group at *meta*-positions.

26. (i) Given, 
$$k = 1.06 \times 10^{-3} \text{ min}^{-1}$$
,  $\frac{[A]_0}{[A]} = \frac{100}{85}$   
 $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$   
 $t = \frac{2.303}{1.06 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{85}$   
 $t = \frac{2303}{1.06} [2 \log 10 - \log 85] \text{ min}$   
 $t = \frac{2303}{1.06} [2 \times 1 - 1.9294] = \frac{2303 \times 0.0706}{1.06}$   
 $t = 153.39 \text{ min} \approx 153.4 \text{ min.}$   
(ii) Given  $k = 1.06 \times 10^{-3} \text{ min}^{-1}$ ,  $\frac{[A]_0}{[A]} = \frac{100}{15}$   
 $t = \frac{2.303}{1.06 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{15}$   
 $= \frac{2303}{1.06} [2 \times 1 - 1.1761] = \frac{2303 \times 0.8239}{1.06} \text{ min} = 1790 \text{ min.}$ 

(i) Order of reaction is sum of powers of concentration terms.

 $\therefore \text{ Order of reaction} = 1 + 2 = 3$ (ii) Unit of rate constant for first order reaction is s<sup>-1</sup>. (iii) Let  $r = k[A]^n$  ...(i) Then,  $27r = k[3A]^n$  ...(ii) If eqn. (ii) is divided by eqn. (i), we get  $\frac{27r}{r} = \frac{k[3A]^n}{k[A]^n} \text{ or } 3^3 = 3^n$ 

 $\therefore$  Thus, order = 3

**27.** (i) From top to bottom in group-17 oxidising power of halogens decreases.

 $F_2 > Cl_2 > Br_2 > I_2.$ 

(ii) The acidic strength of the hydrohalic acids increases in the order : HF < HCl < HBr < HI

This order is a result of bond dissociation enthalpies of H - X bond, which decreases from H - F to H - I as the size of halogen atom increases.

(iii) The oxidation state of chlorine in perchloric acid  $(HOClO_3)$  is +7 and in chloric acid  $(HOClO_2)$  is +5. So, perchloric acid is a stronger acid than chloric acid.

**28.** (a) Pentan-2-one and pentan-3-one can be differentiated by iodoform test. Pentan-2-one will give yellow precipitate of iodoform while pentan-3-one will not.

$$CH_{3}CH_{2}CH_{2} - \overset{O}{C} - CH_{3} + NaOH + I_{2} \longrightarrow CHI_{3} \downarrow_{Yellow ppt.} + CH_{3}CH_{2}CH_{2}COONa$$

$$CH_{3}CH_{2} - \overset{O}{C} - CH_{2}CH_{3} \xrightarrow{I_{2}/NaOH} No yellow ppt.of CHI_{3}$$
(b) (A) is a carboxylic acid, (B) is an alcohol and (C) is an ester.
$$RCH_{2}OH \xrightarrow{alk.} RCOOH_{(A)} RCOOH_{(A)} RCOOH_{(A)} \xrightarrow{CHO} RCOOCH_{2}R_{(A)} \xrightarrow{CH} RCH_{2}OH$$
(i) 
$$CHO \xrightarrow{CHO} H^{2}SO_{4} + RCH_{2}OH \xrightarrow{CO} RCOOCH_{2}R_{Fruity smell}$$

$$OR$$
(i) 
$$CHO \xrightarrow{NaCN/HCl} OH \xrightarrow{CHO} COOH$$
(ii) 
$$H_{3}C \xrightarrow{C} CH_{2} - C - OC_{2}H_{5} \xrightarrow{(i) NaBH_{4}} OH_{(ii) H^{+}} \xrightarrow{OH} H_{3}C \xrightarrow{C} CH_{2}COOC_{2}H_{5}$$
(iii) 
$$ACH_{2} - CH_{2} - CH_{2}$$

**29.** (a) At room temperature, the vapour pressure of liquid ammonia is very high. On cooling, vapour pressure decreases. Hence, the liquid ammonia will not splash out.

(b) In winter season at low temperature solubility of oxygen in water is higher than that in summer at high temperature. Hence, aquatic species feel more comfortable in winter than in summer.

(c) A mixture of chloroform and acetone shows negative deviation from Raoult's law because chloroform molecule forms H-bonding with acetone molecule. As a result of this A-B interaction becomes stronger than A-A and B-B interactions. This leads to the decrease in vapour pressure and resulting in negative deviation.



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**30.** (i) (a) Methyl amine reacts with water to form methyl ammonium hydroxide which is more basic than  $NH_4OH$  and ionizes to give  $OH^-$  ions.

$$CH_{3}NH_{2} + H_{2}O \rightarrow CH_{3}NH_{3} + OH^{-}$$
  
FeCl<sub>3</sub> + 3OH<sup>-</sup>  $\rightarrow$  Fe(OH)<sub>3</sub>  $\downarrow$  + 3Cl<sup>-</sup>  
Red brown ppt.

(b) As oxygen is more electronegative than nitrogen therefore, hydrogen bonding among alcohol molecules is stronger than among amine molecules. So, alcohols have higher boiling points than amines.

(ii) 
$$CH_3 - \overset{H}{C} = O + NH_3 \xrightarrow{\Delta} CH_3 - \overset{H}{C} = NH$$
  
Ethanal Acctaldimine  
 $H_2/Ni \rightarrow CH_3CH_2NH_2$   
Aminoethane

**31.** (a) Diamminechlorido(methylamine)

platinum(II) chloride



 $Fe^{2+}$  ion is hybridised under the influence of strong field ligand.

 $[Fe(CN)_6]^{4-}$  ion formation :

Since the complex ion does not contain any unpaired electron, so it is diamagnetic.

(ii)  $[FeF_6]^{3-}$  ion



 $\mathrm{Fe}^{3+}$  ion is hybridised under the influence of weak field ligand.

 $[FeF_6]^{3-}$  ion formation :



Six electron pairs from six F<sup>-</sup>ions.

As the complex ion contains five unpaired electrons, it is highly paramagnetic in nature.

$$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ B.M.}$$

(c) For tetrahedral complexes, crystal field splitting energy  $\Delta_t$  is always less than pairing energy. So, tetrahedral complexes are always high spin.

OR

(a) The crystal field splitting,  $\Delta_o$ , depends upon the field produced by the ligand and charge on the metal **Chemistry** 

ion. Some ligands are able to produce strong fields in which, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d-orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :

$$\begin{split} &I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < \\ &H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO. \\ &Such a series is termed as spectrochemical series. \end{split}$$

Ligands for which  $\Delta_o < P$  are known as weak field ligands and form high spin complexes. In this case  $\Delta_o$ , the fourth electron enters one of the  $e_g$  orbitals giving the configuration  $t_{2g}^3 e_g^1$  Ligands for which  $\Delta_o > P$ are known as strong field ligands and form low spin complexes. In this case it becomes more energetically favourable for the fourth electron to occupy a  $t_{2g}$ orbital with configuration  $t_{2g}^4 e_g^0$ .

(b) When FeSO<sub>4</sub> and  $(NH_4)_2SO_4$  solutions are mixed in 1 : 1 molar ratio, Mohr's salt (a double salt) is formed. FeSO<sub>4(aq)</sub> +  $(NH_4)_2SO_{4(aq)} \rightarrow FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ FeSO<sub>4</sub> ·  $(NH_4)_2SO_4 \cdot 6H_2O \Longrightarrow$ 

$$Fe_{(aa)}^{2+} + 2NH_{4(aa)}^{+} + 2SO_{4(aa)}^{2-} + 6H_2O$$

Because  $Fe^{2+}$  ions are formed on dissolution of Mohr's salt, its aqueous solution gives the test of  $Fe^{2+}$  ions. When  $CuSO_4$  is mixed with ammonia, following reaction occurs :

 $CuSO_{4(aq)} + 4NH_{3(aq)} \rightarrow [Cu(NH_3)_4]SO_4$ 

This complex does not produce  $Cu^{2+}$  ion, so the solution of  $CuSO_4$  and  $NH_3$  does not give the test of  $Cu^{2+}$  ion.

**32.** (a) Given, structure = fcc, d = 7.2 g cm<sup>-3</sup>, m = 208 g  $N = 4.283 \times 10^{24}$  atoms, a = ?

Number of unit cells = 
$$\frac{4.283 \times 10^{24}}{4} = 1.07 \times 10^{24}$$

Volume of unit cell =  $a^3$ 

:. Total volume = Number of unit cells

× Volume of one unit cell

$$= 1.07 \times 10^{24} \times a^3$$

Total mass = Total volume × density 208 g =  $1.07 \times 10^{24} a^3 \times 7.2 \text{ g cm}^{-3}$ 

or 
$$a^3 = \frac{208 \text{ g}}{1.07 \times 10^{24} \times 7.2 \text{ g cm}^{-3}} = 26.99 \times 10^{-24} \text{ cm}^3$$

or  $a = 3 \times 10^{-8}$  cm = 300 pm

(b) 98 Ni-atoms are associated with 100 O-atoms. Out of 98 Ni-atoms, suppose Ni present as  $Ni^{2+} = x$ 

Then Ni present as  $Ni^{3+} = 98 - x$ 

Total charge on x Ni<sup>2+</sup> and (98 – x) Ni<sup>3+</sup> should be equal to charge on 100  $O^{2-}$  ions.

Hence,  $x \times 2 + (98 - x) \times 3 = 100 \times 2$ or 2x + 294 - 3x = 200 or x = 94

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 $\therefore \text{ Fraction of Ni present as Ni}^{2+} = \frac{94}{98} \times 100 = 96\%$ 

Fraction of Ni present as Ni<sup>3+</sup> =  $\frac{4}{98} \times 100 = 4\%$ 

#### OR

(a) Schottky defects exist in pairs to maintain electrical neutrality. So it generates equal number of cation and anion vacancies.

Ionic solids are doped with metal ions of higher valency. Therefore, some cations of lower valency are displaced to maintain electrical neutrality. Hence, only cation vacancies are produced not anion vacancies.

(b) In case of *hcp* unit cell, there are 6 atoms per unit cell. If the radius of metal atom is  $r_1$  then,

Volume occupied by the metal atom =  $6 \times \frac{4}{3} \times \pi r^3$ 

$$= 6 \times 1.33 \times \frac{22}{7} \times r^3 = 25.08 r^3$$

It has been shown geometrically that the base area of

*hcp* unit cell = 
$$6 \times \frac{\sqrt{3}}{4} \times 4 \times r^2$$

and the height =  $4r \times \sqrt{2/3}$ 

 $\therefore$  Volume of unit cell = Area × Height

$$= 6 \times \frac{\sqrt{3}}{4} \times 4r^2 \times 4r \times \sqrt{2/3} = 33.94 r^3$$

Volume of the empty space of one unit cell  $22.04 x^3 - 25.08 x^3$ 

$$= 33.94 r^{3} - 25.08 r^{3} = 8.86 r^{3}$$
  
Hence, percentage void =  $\frac{8.86 r^{3}}{33.94 r^{3}} \times 100$  or 26.10%

(c) Urea is crystalline solid whereas glass is amorphous. Crystalline solids have sharp melting points where is amorphous solids do not possess sharp melting points.

**33.** (a) (i) As the rate of reaction depends upon the concentration of compound A (C<sub>4</sub>H<sub>9</sub>Br) only therefore, the reaction is proceeded by S<sub>N</sub>1 mechanism and the given compound will be tertiary alkyl halide, *i.e.*, 2-bromo-2-methylpropane and the structure of (*A*) is (CH<sub>3</sub>)<sub>3</sub>CBr. Optically active isomer of *A* is 2-bromobutane and its structural formula (*B*) is CH<sub>3</sub>CH<sub>2</sub>CH(Br)CH<sub>3</sub>.

(ii) The rate of reaction of compound *B* depends both upon the concentration of compound *B* and KOH. Hence, the reaction follows  $S_N$ 2 mechanism. In  $S_N$ 2 reaction, nucleophile attacks from the backside, therefore the product of hydrolysis will have opposite configuration.



(b) Grignard reagents are highly reactive and react with even traces of water to give corresponding hydrocarbons.  $RMgX + H_2O \longrightarrow RH + Mg(OH)X$ 

(a) 
$$C_6H_{13}Cl \xrightarrow{(CH_3)_3COK}$$
 Two isomeric alkenes Y and Z  
X  
 $H_2 \xrightarrow{CH_3} CH_3$   
 $H_2 \xrightarrow{CH_3} -CH - CH - CH_3$   
2, 3-Dimethylbutane

The two isomeric alkenes which on hydrogenation yield 2,3-dimethylbutane are

$$\begin{array}{ccc} CH_3 CH_3 & CH_3 CH_3 \\ I & I \\ CH_3 - C = C - CH_3 & \text{and} & CH_2 = C - CH - CH \end{array}$$

One of these is *Y* and the other is *Z*.

These structures explain the given facts as follows :



(b) Vinyl halide itself shows resonance and is thus stabilized.

$$H_2 \stackrel{\checkmark}{C} = CH \stackrel{\checkmark}{-} \stackrel{:}{X} \longleftrightarrow \bar{C}H_2 - CH = \overset{+}{X}$$

On the other hand, allyl carbonium ion formed after removal of  $X^-$  is stabilized by resonance and thus allyl halide is more reactive than alkyl halide.

$$CH_2 = CH - CH_2 \iff CH_2 - CH = CH_2$$



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