# 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(2)	_	_	-	
2.	Solutions	_	1(2)	1(3)	_		
3.	Electrochemistry	_	_	_	1(5)	1(5) <b>9(23)</b>	
4.	Chemical Kinetics	2(5)	_	_	_		
5.	Surface Chemistry	_	1(2)	1(3)	_	-	
6.	The <i>p</i> -Block Elements	1(1)	_	_	1(5)		
7.	The <i>d</i> - and <i>f</i> -Block Elements	2(2)	1(2)	1(3)	_	- 10(19)	
8.	Coordination Compounds	2(2)	2(4)	_	_		
9.	Haloalkanes and Haloarenes	2(2)	1(2)	_	_		
10.	Alcohols, Phenols and Ethers	2(2)	1(2)	_	_		
11.	Aldehydes, Ketones and Carboxylic Acids	1(4)	1(2)	1(3)	_	14(28)	
12.	Amines	1(1)	_	_	1(5)		
13.	Biomolecules	2(2)	_	1(3)			
	Total	16(22)	9(18)	5(15)	3(15)	33(70)	

## Subject Code : 043

# **CHEMISTRY**

#### Time allowed : 3 hours

#### Maximum marks: 70

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

- *There are 33 questions in this question paper. All questions are compulsory. (a)*
- (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.
- There is no overall choice. However, internal choices have been provided. (f)
- Use of calculators and log tables is not permitted. (q)

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

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

The half life of a reaction is the time required for the concentration of a given reactant to reach a value that is arithmetic mean of its initial and final, or equilibrium, values. The half-life of a reaction has an exact quantitative meaning only in the following cases:

- For a first order reaction,  $t_{1/2} = \frac{0.693}{k}$ (i)
- (ii) For a reaction involving more than one reactant, with their concentrations in their stoichiometric ratios. In this case half-life of each reactant is same.

If the concentrations of reactants are not in their stoichiometric ratios, the half-life for the different reactants are not the same.

For second order reaction,  $t_{1/2} = k^{-1} [A]_0^{-1}$ 

#### The following questions (Q.No. i-iv) are multiple choice questions. Choose the most appropriate answer :

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 (i) the half-life is

(a) 
$$\frac{\log 2}{k}$$
 (b)  $\frac{\log 2}{k\sqrt{0.5}}$  (c)  $\frac{\ln 2}{k}$  (d)  $\frac{0.693}{0.5k}$ 

(ii) 87.5% of the substance disintegrated in 45 minutes (first order reaction) what is its half life? (a) 15 min (b) 30 min (c) 45 min (d) 60 min

OR

Half-life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is (a

) 
$$0.5 \times 10^{-2} \text{ s}^{-1}$$
 (b)  $0.5 \times 10^{-3} \text{ s}^{-1}$  (c)  $5.0 \times 10^{-2} \text{ s}^{-1}$  (d)  $5.0 \times 10^{-5} \text{ s}^{-1}$ 

(iii) For a first order reaction, the ratio between the time taken to complete 3/4th of the reaction and time taken to complete half of the reaction is

(a)  $t_{3/4} = 2t_{1/2}$  (b)  $t_{3/4} = t_{1/2}$  (c)  $t_{3/4} = 3t_{1/2}$  (d)  $t_{3/4} = 5t_{1/2}$ 

- (iv) The half-life of a reaction is halved as the initial concentration of the reactant is doubled. The order of reaction is
  - (a) 0.5 (b) 1 (c) 2 (d) 0

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

Carbonyl condensation reactions take place between two carbonyl-containing compounds, one of these must posses an  $\alpha$ -hydrogen atom. The first step of the reaction involves the removal of an  $\alpha$ -hydrogen atom by a base. In the second step, the enolate anion that results this removal attacks the carbonyl-carbon of the second reacting molecule.

In the final step of a reaction, a proton is transferred to the tetrahedral intermediate formed in second step, although in some cases the product that result may subsequently be dehydrated.

The importance of carbonyl condensation reaction to synthetic organic chemistry arises from the large number of combinations of carbonyl compounds that can be used in such reaction.

#### 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 : *p*-*N*, *N*-Dimethylaminobenzaldehyde undergoes benzoin condensation. **Reason :** The aldehydic (–CHO) group is *meta* directing.
- (ii) Assertion : Esters which contain  $\alpha$ -hydrogens undergo Claisen condensation. Reason : LiAlH<sub>4</sub> reduction of esters gives acids.
- (iii) Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction. Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

#### OR

**Assertion :** Acetaldehyde is more reactive than acetone in nucleophilic addition reactions. **Reason :** Two alkyl groups in acetone reduce the electrophilicity of the carbon.

(iv) Assertion : Benzaldehyde is less reactive than ethanal towards nucleophilic attack. **Reason :** The +R effect of phenyl group decreases the electron density on the carbon atom of >C=O group in benzaldehyde.

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

- 3.  $R OH + HX \longrightarrow RX + H_2O$ 
  - In the above reaction, the reactivity of alcohols is

(a) tertiary > secondary > primary

- (b) tertiary < secondary < primary
- (c) tertiary > primary > secondary
- (d) secondary > primary > tertiary.
- **4.** A crystalline solid  $XY_3$  has *ccp* arrangement for its element *Y*. *X* occupies
  - (a) 66% of tetrahedral voids (b) 33% of tetrahedral voids
  - (c) 66% of octahedral voids (d) 33% of octahedral voids.

OR

If the ratio of coordination number P to that of Q be y : z, then the formula of the solid is

(a) 
$$P_y Q_z$$
 (b)  $P_z Q_y$  (c)  $P_{1/y} Q_{1/z}$  (d) none of these.

- 5. The correct sequence of decrease in the bond angle of the following hydrides is
  - (a)  $NH_3 > PH_3 > AsH_3 > SbH_3$  (b)  $NH_3 > AsH_3 > PH_3 > SbH_3$
  - (c)  $SbH_3 > AsH_3 > PH_3 > NH_3$  (d)  $PH_3 > NH_3 > AsH_3 > SbH_3$

6. In the following sequence of reactions,

$$CH_{3}CH_{2}CH_{2}Br \xrightarrow{KOH (alc.)} (A) \xrightarrow{HBr} (B) \xrightarrow{KOH (aq.)} (C)$$

The product (C) is

- (a) propene (b) propyne (c) propan-1-ol (d) propan-2-ol.
- 7. The ionic radii of group-12 metals Zn, Cd and Hg are smaller than those of group-2 metals because Zn, Cd and Hg have
  - (a) 10 *d*-electrons which shield the nuclear charge poorly
  - (b) 10 *d*-electrons which shield the nuclear charge strongly
  - (c) 10 *d*-electrons which have a large radius ratio
  - (d) 10 *d*-electrons which have a large exchange energy.

#### OR

In a transition series, with the increase in atomic number, the paramagnetism

- (a) increases gradually
- (b) decreases gradually
- (c) first increases to a maximum and then decreases
- (d) first decreases to a minimum and then increases.
- 8.  $\alpha$ -D-Glucose and  $\beta$ -D-glucose differ from each other due to difference in one carbon with respect to the
  - (a) size of hemiacetal ring

(b) number of –OH groups

(c) configuration

(d) conformation.

#### OR

Which of the following reagents cannot distinguish between glucose and fructose?

- (a) Tollens' reagent (b) Fehling's solution (c) Benedict's solution (d) All of these
- 9. The hypothetical complex chloridodiaquatriamminecobalt(III) chloride can be represented as
  - (a)  $[CoCl(NH_3)_3(H_2O)_2]Cl_2$  (b)  $[Co(NH_3)_3(H_2O)Cl_3]$
  - (c)  $[Co(NH_3)_3(H_2O)_2Cl]$  (d)  $[Co(NH_3)_3(H_2O)_3]Cl_3$

10. Which of the following undergoes nucleophilic substitution exclusively by  $S_N^1$  mechanism?

(a) Benzyl chloride (b) Ethyl chloride (c) Chlorobenzene

OR

Which compound on nitration will give highest amount of *m*-substituted product?



(d) *iso*-Propyl chloride

- **11.** 0.001 mol of [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>3</sub>)(SO<sub>4</sub>)] was passed through a cation exchanger and the acid coming out of it required 20 mL of 0.1 M NaOH for neutralisation. Hence, the complex is
  - (a)  $[Co(NH_3)_5(SO_4)]NO_3$  (b)  $[Co(NH_3)_5(NO_3)]SO_4$
  - (c)  $[Co(NH_3)_5]NO_3 \cdot SO_4$  (d) none of these.

# 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 :** Phenol is more acidic than ethanol. **Reason :** Phenoxide ion is resonance stabilised.
- 13. Assertion : An examination of the E° values for the redox couple M<sup>3+</sup>/M<sup>2+</sup> shows that Mn<sup>3+</sup> and Co<sup>3+</sup> ions are the strongest oxidising agents in aqueous solutions.
  Reason : The ions Ti<sup>2+</sup>, V<sup>2+</sup> and Cr<sup>2+</sup> are strong reducing agents and will lubricate hydrogen from a dilute acid.
- 14. Assertion : The molecularity of the reaction,  $H_2 + Br_2 \rightarrow 2HBr$ , is two. Reason : The order of this reaction is 3/2.
- 15. Assertion :  $(CH_3)_2$  NH is more basic than  $(CH_3)_3$ N in aqueous solution. Reason : Hyperconjugation in  $(CH_3)_3$ N is more than that in  $(CH_3)_2$ NH.

#### OR

Assertion : Alkyl isocyanides in acidified water give alkyl formamides. Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

**16. Assertion :** Solubility of proteins is minimum at the isoelectric point. **Reason :** At isoelectric point, protein molecule behaves as a zwitter ion.

#### **SECTION - B**

#### The following questions (No. 17-25) are short answer type and carry 2 marks each.

- 17. A solution of  $[Ni(H_2O)_6]^{2+}$  is green but a solution of  $[Ni(CN)_4]^{2-}$  is colourless. Explain.
- **18.** Find the boiling point of a solution containing 0.520 g of glucose  $(C_6H_{12}O_6)$  dissolved in 80.2 g of water. (Given :  $K_b$  for water = 0.52 K/m)

#### OR

Henry's law constant for the molality of methane in benzene at 298 K is  $4.27 \times 10^5$  mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

#### **19.** Give equations of the following reactions :

- (a) Oxidation of propan-1-ol with alkaline KMnO<sub>4</sub> solution.
- (b) Bromine in CS<sub>2</sub> with phenol.

#### OR

3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as the major product. Suggest a suitable mechanism.

Chemistry

- **20.** Explain the following :
  - (a) Low spin octahedral complexes of nickel are not known.
  - (b)  $\Delta_t = \frac{4}{9} \Delta_o$
- **21.** An element crystallises in structure having *fcc* unit cell of an edge 200 pm. Calculate the density if 200 g of this element contains  $24 \times 10^{23}$  atoms.

Following are the transition metal ions of 3*d* series : Ti<sup>4+</sup>, V<sup>2+</sup>, Mn<sup>3+</sup>, Cr<sup>3+</sup> (Atomic numbers : Ti = 22, V = 23, Mn = 25, Cr = 24) Answer the following :

- (a) Which ion is most stable in aqueous solution and why?
- (b) Which ion is strong oxidising agent and why?
- 23. Write two differences between physisorption and chemisorption.

#### OR

Write one difference between each of the following :

- (i) Multimolecular colloid and macromolecular colloid
- (ii) Sol and gel
- 24. Draw the structure of major monohalo product in each of the following reactions :

(i) 
$$\bigcirc$$
 OH  $\xrightarrow{\text{SOCl}_2}$   
(ii)  $\bigcirc$  CH<sub>2</sub>-CH=CH<sub>2</sub>+HBr  $\xrightarrow{\text{Peroxide}}$ 

- 25. Write chemical equations for the following reactions :
  - (i) Propanone is treated with dilute Ba(OH)<sub>2</sub>.
  - (ii) Acetophenone is treated with Zn(Hg)/Conc. HCl

#### **SECTION - C**

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

- 26. Explain what is observed when
  - (a) a beam of light is passed through a colloidal sol.
  - (b) an electrolyte, NaCl is added to hydrated ferric oxide sol.
  - (c) electric current is passed through a colloidal sol.

#### OR

Explain the following terms with suitable examples:

- (a) Alcosol
- (b) Aerosol
- (c) Hydrosol
- 27. (i) Write down the structures and names of the products formed when *D*-glucose is treated with
  - (a) hydroxylamine
  - (b) acetic anhydride.
  - (ii) What is a glycosidic linkage?

Define the following terms as related to proteins :

(i) Peptide linkage (ii) Primary structure (iii) Denaturation

- **28.** Why the depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order as  $CH_3COOH < Cl_3CCOOH < F_3CCOOH$ ? Explain briefly.
- **29.** (a) Write the chemical reaction involved in Wolff-Kishner reduction.
  - (b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction.  $C_6H_5COCH_3$ ,  $CH_3CHO$ ,  $CH_3COCH_3$
  - (c) *A* and *B* are two functional isomers of compound  $C_3H_6O$ . On heating with NaOH and  $I_2$ , isomer *B* forms yellow precipitate of iodoform whereas isomer *A* does not form any precipitate. Write the formulae of *A* and *B*.
- **30.** How would you account for the following :
  - (i) Metal-metal bonding is more extensive in the 4d and 5d series of transition elements than the 3d series.
  - (ii) Mn(III) undergoes disproportionation reaction easily.
  - (iii) Co(II) is easily oxidised in the presence of strong ligands.

#### **SECTION - D**

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

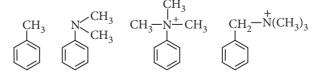
- **31.** (a) Account for the following :
  - (i)  $H_2S$  has lower boiling point than  $H_2O$ .
  - (ii) Reducing character decreases from  $SO_2$  to  $TeO_2$ .
  - (b) What happens when
    - (i) conc.  $H_2SO_4$  is added to Cu?
    - (ii)  $SO_3$  is passed through water?
    - (iii) HCl is added to  $MnO_2$ ?

#### OR

- (a) (i) Fluorine has lower electron affinity than chlorine and yet it is a stronger oxidising agent than chlorine. Explain.
  - (ii) Of HI and HCl which has a weaker covalent bond and what effect has it on their acid strengths?
  - (iii) NaOCl solution become unstable on warming. What happens to it?
- (b) Draw the structure of  $XeF_4$  and  $SF_4$  molecules.
- **32.** (a) Rearrange the following in an increasing order of their basic strengths :

C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>N(CH<sub>3</sub>)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH and CH<sub>3</sub>NH<sub>2</sub>

(b) Give increasing order towards electrophilic substitution of the following compounds :



(c) What is the effect of substituents on basicity of amines?

#### Chemistry

- (i) Give reasons :
  - (a) Electrophilic substitution in aromatic amines takes place more readily than benzene.
  - (b)  $CH_3CONH_2$  is weaker base than  $CH_3CH_2NH_2$ .
- (ii) Write the structures of main products when aniline reacts with the following reagents :
  - (a)  $Br_2$  water (b) HCl (c)  $(CH_3CO)_2O$ /pyridine
- **33.** (a) Write the Nernst equation, for following electrode reaction:  $M_{(aq)}^{n+} + ne^{-} \longrightarrow M_{(s)}$ 
  - (b) Calculate the emf of the following cells at 298 K :
    - (i)  $Mg_{(s)} | Mg^{2+} (0.001 \text{ M}) || Cu^{2+} (0.0001 \text{ M}) | Cu_{(s)}$
    - (ii)  $\operatorname{Fe}_{(s)} | \operatorname{Fe}^{2+}(0.001 \text{ M}) || \operatorname{H}^{+}(1 \text{ M}) | \operatorname{H}_{2(g)}(1 \text{ bar}) | \operatorname{Pt}_{(s)}$

[Given :  $E^{o}_{Mg^{2+}/Mg} = -2.37 \text{ V}, E^{o}_{Cu^{2+}/Cu} = 0.34 \text{ V}, E^{o}_{Fe^{2+}/Fe} = -0.44 \text{ V}$ ]

#### OR

(a) When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

[Specific conductance of 0.1 M KCl =  $1.29 \times 10^{-2}$  ohm<sup>-1</sup> cm<sup>-1</sup>]

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500  $\Omega$ . What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10<sup>-3</sup> S cm<sup>-1</sup>?



(i) (c) : For a 1<sup>st</sup> order kinetics, 1.  $k = \frac{2.303}{100} \log \frac{a}{a}$ 

$$k = \frac{t}{t} \log \frac{a - x}{a - x}$$

$$At t_{1/2}, k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$$

$$\Rightarrow t_{1/2} = \frac{2.303}{k} \log 2 = \frac{\ln 2}{k}$$

(ii) (a): 
$$a = 100$$
;  $a - x = 100 - 87.5 = 12.5$   
 $k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{45} \log \frac{100}{12.5} = 0.046$   
 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.046} = 15 \text{ min}$ 

#### OR

**(b)** : Given,  $t_{1/2} = 1386$  s For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad (k = \text{rate constant})$$
  

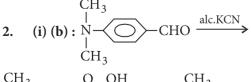
$$\Rightarrow 1386 = \frac{0.693}{k} \Rightarrow k = 5 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

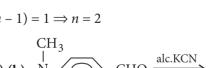
(iii) (a) : 
$$t_{1/2} = \frac{0.693}{k}$$
  
 $t_{3/4} = \frac{2.303}{k} \log \left( \frac{a}{a - \frac{3a}{4}} \right) = \frac{2.303}{k} \log 4$   
 $= \frac{2.303}{k} \times 2 \times 0.310 = \frac{0.693 \times 2}{k}$ 

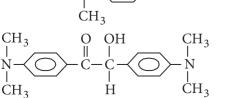
$$\frac{t_{3/4}}{t_{1/2}} = \frac{0.693 \times 2}{k} \times \frac{k}{0.693} \Longrightarrow t_{3/4} = 2t_{1/2}$$
(iv) (c) : For *n*<sup>th</sup> order reaction,

$$\begin{split} t_{1/2} &\propto \frac{1}{a^{n-1}}; \quad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{[a_2]^{n-1}}{[a_1]^{n-1}} = \left[\frac{[a_2]}{[a_1]}\right]^{n-1} \\ &\frac{t_{1/2}}{1/2t_{1/2}} = \left(\frac{2a}{a}\right)^{n-1} \implies 2 = (2)^{n-1} \end{split}$$

$$\Rightarrow$$
  $(n-1) = 1 \Rightarrow n = 2$ 







(ii) (c) : It is known that esters with  $\alpha$ -hydrogens form carbanion when treated with base. It brings about nucleophilic substitution at the carbonyl group of the other molecule of the ester to yield  $\beta$ -keto ester. LiAlH<sub>4</sub> reduces esters to alcohols.

(iii) (c) : Aromatic aldehydes and formaldehyde do not contain  $\alpha$ -hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

OR

(a)

(iv) (c)

3. (a)

(d) : As ratio of *X* and *Y* is 1 : 3, *X* will occupy 4.

 $\frac{1}{3}$ rd of octahedral voids. ∴ % of octahedral voids occupied by  $X = \frac{1}{3} \times 100$ = 33.3%

OR

(b) : If the ratio of two atoms in a unit cell is z : ythen their coordination number are in ratio of y : z. Hence, formula of the solid is  $P_z Q_y$ .

(a) : This is due to decrease in electronegativity 5. difference from N to Sb.

6. (d):  

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow{KOH (alc.)} CH_3 - CH = CH_2$$
  
 $CH_3 - CH - CH_3 \xleftarrow{HBr}$   
 $Br \xrightarrow{KOH (aq.)} CH_3 - CH - CH_3$   
 $Br \xrightarrow{(B)} KOH (aq.) \xrightarrow{(C)} CH_3 - CH - CH_3$   
 $OH$   
 $OH$   
 $CC$   
 $OH$   
 $CC$   
 $OH$   
 $O$ 

7. (a) : Zn, Cd and Hg have smaller ionic radii than group-2 elements because former involve 10 d-electrons which have poor shielding effect so that electrons are more strongly attracted towards nucleus.

#### OR

(c) : In transition series, paramagnetism first increases due to increase in the number of unpaired electrons. Beyond chromium, number of unpaired electrons decreases. So, paramagnetism decreases.

(c) :  $\alpha$ -*D*-glucose and  $\beta$ -*D*-glucose differ from 8. each other in terms of configuration at C-1 atom.

Chemistry

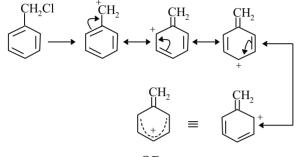
OR

(d) : All these reagents are reduced by both glucose and fructose and thus cannot be used to distinguish between glucose and fructose.

**9.** (a) : Chloridodiaquatriamminecobalt(III) chloride :

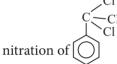
[CoCl(NH<sub>3</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub>

10. (a) : In benzyl chloride, the carbocation formed during  $S_N 1$  mechanism is resonance stabilised.



OR

(d) :  $-CH_3$  group has electron donating inductive effect which decreases with replacement of each hydrogen atom by chlorine atom. Hence, highest amount of *m*-substituted product will be obtained on



11. (b) : Millimoles of acid =  $20 \times 0.1 = 2$  millimoles = 0.002 moles

If 0.001 mol is neutralising 0.002 moles of base. Thus, acid coming out should be dibasic.

 $[Co(NH_3)_5(NO_3)]SO_4 \rightarrow [Co(NH_3)_5(NO_3)]^{2+} + SO_4^{2-}$ 12. (a)

13. (b)

14. (b) : Molecularity of reaction is the number of molecules acting in the rate determing step while order of reaction is the sum total of all powers to which concentration are raised in the rate law expression.

15. (b): Due to steric hinderance of alkyl group,  $(CH_3)_3N$  is less basic than  $(CH_3)_2NH$  in aqueous solution.

#### OR

(a) : In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

 $R'N \equiv \overline{C} + H_2O \longrightarrow RN \equiv CHOH \longrightarrow RNHCHO$ Alkylformamide **16.** (a) : At isoelectric point, protein molecules behave as zwitter ions and hence, do not move toward any electrode or act as neutral molecules. This reduces their solubility to minimum and thus, helps in their separation and purification.

17.  $[Ni(H_2O)_6]^{2+}$  has unpaired electrons due to weak  $H_2O$  ligands which absorb light from visible region and radiate complementary colour *i.e.*, green whereas  $[Ni(CN)_4]^{2-}$  does not have any unpaired electron due to strong  $CN^-$  ligand, therefore, does not absorb light from visible region hence, it is colourless.

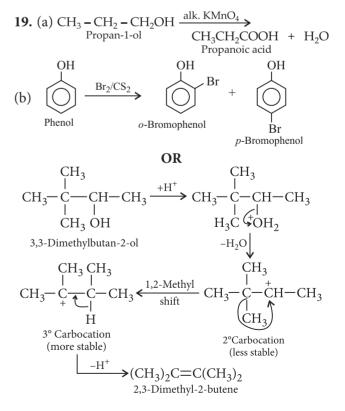
**18.** Given, 
$$w_2 = 0.520$$
 g,  $W_1 = 80.2$  g,  $K_b = 0.52$  K m<sup>-1</sup>  
 $M_2$  of  $C_6 H_{12} O_6 = 6 \times 12 + 12 \times 1 + 6 \times 16 = 180$  g mol<sup>-1</sup>  
 $\Delta T_b = \frac{K_b \times w_2 \times 1000}{M_2 \times W_1} = \frac{0.52 \times 0.520 \times 1000}{180 \times 80.2} = 0.019$  K  
Boiling point of solution,  $T_b = T_b^\circ + \Delta T_b$ 

= 373 K + 0.019 K = 373.019 K

Here,  $K_{\rm H} = 4.27 \times 10^5$  mm Hg, p = 760 mm Hg Applying Henry's law,  $p = K_{\rm H}x$ 

$$\therefore \quad x = \frac{p}{K_{\rm H}} = \frac{760}{4.27 \times 10^5} = 1.78 \times 10^{-3}$$

*i.e.*, solubility in terms of mole fraction of methane in benzene =  $1.78 \times 10^{-3}$ 



**20.** (a) Nickel forms octahedral complexes mainly in +2 oxidation state which has  $3d^8$  configuration. In presence of strong field ligand also it has two unpaired electrons in  $e_q$  orbital.

Hence, it does not form low spin octahedral complexes.(b) Number of ligands in tetrahedral geometry is 4 whereas in octahedral geometry it is 6.

In tetrahedral geometry no orbital lies directly in the path of ligand whereas in octahedral geometry axial orbitals interact directly with the ligand.

That is why,  $\Delta_t = \frac{4}{9} \Delta_o$ . **21.** Edge length = 200 pm Volume of the unit cell =  $(200 \times 10^{-10} \text{ cm})^3$  $= 8 \times 10^{-24} \text{ cm}^3$ 

In a *fcc* unit cell there are four atoms per unit cell.

$$\therefore \text{ Mass of unit cell} = \frac{200 \times 4}{24 \times 10^{23}} = 33.3 \times 10^{-23} \text{g}$$
  
Density =  $\frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \frac{33.3 \times 10^{-23} \text{g}}{8 \times 10^{-24} \text{ cm}^3}$   
= 41.6 g cm<sup>-3</sup>

**22.** (a)  $Ti^{4+}$  has highest oxidation state among the given ions.  $Ti^{4+}$  has stable inert gas configuration and hence, most stable in aqueous solution. On the other hand,  $V^{2+}$ ,  $Mn^{3+}$ ,  $Cr^{3+}$  have unstable electronic configuration and hence, are less stable.

(b) Due to presence of highest oxidation state of  $Ti^{4+}$ , it acts as the strongest oxidising agent among the given ions.

23.	<b>S.</b>	Criteria	Physisorp-	Chemisorption
	No.		tion	
	(i)	Specificity	It is not	It is highly
			specific in	specific in
			nature.	nature.
	(ii)	Tempera-	It decreases	It increases with
		ture	with	increase in
		dependence	increase in	temperature.
			temperature.	Thus, high
			Thus, low	temperature is
			temperature	favourable for
			is favourable	chemisorption.
			for	
			physisorption.	
	(iii)	Reversibil-	Reversible in	Irreversible in
		ity	nature.	nature.
	(iv)	Enthalpy	Low enthalpy	High enthalpy of
		change	of adsorption.	adsorption.
	<b>( )</b>	- (		

(Any two)

(i) The difference between multimolecular and macromolecular colloids is :

Multimolecular	Macromolecular	
Colloids	Colloids	
When a large number of	When substances	
small molecules or atoms	which possess very	
(diameter < 1 nm) of a	high molecular	
substance combine together	masses are dispersed	
in a dispersion medium to	in suitable dispersion	
form aggregates, having	medium, the colloidal	
size in the colloidal range,	solutions thus,	
the colloidal solutions	formed are called	
thus, formed are known as	macromolecular	
multimolecular colloids,	colloids, <i>e.g.</i> , cellulose,	
<i>e.g.</i> , gold sol,	starch, etc.	
sulphur sol, etc.		

(ii) The difference between sol and gel is :

Sol	Gel
Dispersed phase is solid	Dispersed phase is liquid
whereas dispersion	whereas dispersion
medium is liquid.	medium is solid.

24. (i) 
$$H$$
 + SOCl<sub>2</sub>  $\rightarrow$   $H$  + SOCl<sub>2</sub>  $\rightarrow$   $H$  + SO<sub>2</sub> + HCl  
Chlorocyclohexane  
(ii)  $H$  - CH<sub>2</sub>-CH=CH<sub>2</sub> + HBr  $P$  + Peroxide

$$\leftarrow$$
 CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Br

25.

(i) 
$$2_{CH_3}^{CH_3} > C = O \xrightarrow{Ba(OH)_2} CH_3 \xrightarrow{OH}_{I} - CH_2COCH_3$$
  
 $CH_3$   
 $4$ -Hydroxy-4-methyl-  
pentane-2-one

(ii) 
$$4[H] \xrightarrow{\text{COCH}_3} + 4[H] \xrightarrow{\text{Zn(Hg)/Conc.HCl}} + H_2O$$

Ethylbenzene

**26.** (a) Path of light becomes visible and colloidal particles scatter the light (Tyndall effect).

(b) The positively charged colloidal particles of  $Fe(OH)_3$  get coagulated by the oppositely charged Cl<sup>-</sup> ions provided by NaCl.

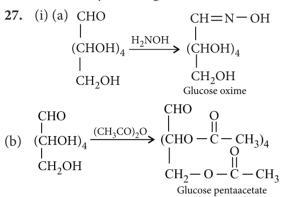
(c) The charged particles of sol get coagulated at oppositely charged electrode (electrophoresis).

#### OR

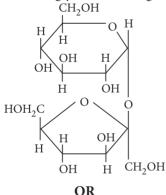
(a) Alcosol : The sol in which alcohol is used as a dispersion medium is called alcosol *e.g.*, sol of cellulose nitrate in ethyl alcohol.

(b) Aerosol : The sol in which dispersion medium is gas and dispersed phase is either solid or liquid, the colloidal system is called aerosol *e.g.*, fog, insecticide sprays, etc.

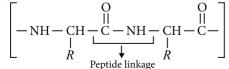
(c) Hydrosol : The sol in which dispersion medium is water is called hydrosol *e.g.*, starch sol.



(ii) The two monosaccharides are joined together by an oxide linkage formed by the loss of water molecule. Such linkage is called glycosidic linkage.



(i) Proteins are the polymers of  $\alpha$ -amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond, *e.g.*,



(ii) **Primary structure :** The specific sequence in which the various amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.

**Secondary structure :** The conformation of the polypeptide chain is known as secondary structure.

The two types of secondary structure are  $\alpha$ -helix and  $\beta$ -pleated sheet structure.

In  $\alpha$ -helix structure, the polypeptide chain forms all the possible hydrogen bonds by twisting into a right handed screw (helix) with the – NH groups of each amino acid residue hydrogen bonded to the c=0

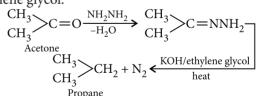
group of an adjacent turn of the helix. In  $\beta$ -pleated sheet structure, all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds.

(iii) **Denaturation :** The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.

During denaturation, secondary and tertiary structure of protein is destroyed but primary structure remains intact.

**28.** The depression in freezing point is in the order : Acetic acid  $(CH_3-COOH) <$  trichloroacetic acid  $(Cl_3C-COOH) <$  trifluoroacetic acid  $(F_3C-COOH)$ Fluorine, being most electronegative, has the highest electron withdrawing inductive effect. Consequently, trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionizes to the largest extent while acetic acid ionizes to the minimum extent to give ions in their solutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is the maximum for the fluoroacetic acid and minimum for acetic acid.

**29.** (a) **Wolff-Kishner reduction :** The carbonyl group of aldehydes and ketones is reduced to  $>CH_2$  group on treatment with hydrazine followed by heating with potassium hydroxide in a high boiling solvent such as ethylene glycol.



(b) Increasing order of reactivity towards nucleophilic addition reaction :

C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub> < CH<sub>3</sub>COCH<sub>3</sub> < CH<sub>3</sub>CHO

(c) Formula of compounds A and  $B = C_3H_6O$ , B forms yellow precipitate of iodoform. Hence, B must contain  $-COCH_3$  group. Therefore, compound 'B' O

must be  $CH_3$ -C-CH<sub>3</sub>.

A does not give iodoform test and it is functional isomer of *B* thus, it may be  $CH_3CH_2CHO$ .

**30.** (i) The metals of 4d and 5d-series have more frequent metal bonding in their compounds than the 3d-metals because 4d and 5d-orbitals are more exposed in space than the 3d-orbitals. So the valence electrons are less tightly held and form metal-metal bonding more frequently.

(ii)  $Mn^{3+}$  is less stable and changes to  $Mn^{2+}$  which is more stable due to half-filled *d*-orbital configuration. That is why,  $Mn^{3+}$  undergoes disproportionation reaction.

(iii) The tendency to form complexes is high for Co(III) as compared to Co(II).  $Co^{2+}$  ions are very stable and are difficult to oxidise.  $Co^{3+}$  ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,

 $[\operatorname{Co}(\operatorname{NH}_3)_6]^{2+} \xrightarrow{\operatorname{Air}} [\operatorname{Co}(\operatorname{NH}_3)_6]^{3+}$ 

This happens because the crystal field stabilisation energy of Co(III) with a  $d^6(t_{2g}^6)$  configuration is higher than for Co(II) with a  $d^7(t_{2g}^6 e_g^1)$  arrangement.

**31.** (a) (i)  $H_2O$   $H_2S$ Boiling point 373 K > 213 K

The abnormally high boiling point of  $H_2O$  is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

(ii) The +6 oxidation state of S is more stable than +4 therefore,  $SO_2$  acts as a reducing agent. Further, since the stability of +6 oxidation state decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, TeO<sub>2</sub> acts as an oxidising agent.

(b) (i) When conc.  $H_2SO_4$  reacts with Cu, CuO is formed which gets further converted into CuSO<sub>4</sub>. Cu +  $2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$ 

(ii) When  $SO_3$  is passed through water, a solution of sulphuric acid is formed.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

(iii) When HCl is added to  $MnO_2$ ,  $Cl_2$  gas is formed.  $MnO_2 + 4HCl \longrightarrow Cl_2 + MnCl_2 + 2H_2O$ 

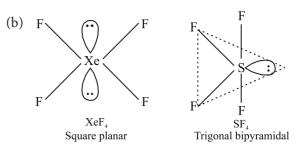
OR

(a) (i) Fluorine has higher standard reduction potential than chlorine, so it is more easily reduced and hence it is stronger oxidising agent than chlorine.

(ii) HI has a weaker covalent bond than HCl, so it is more stronger acid than HCl because of its higher tendency to release  $H^+$  than HCl.

(iii) On warming, NaOCl decomposes as follows :

 $\begin{array}{c} 3 \operatorname{NaOCl} & \xrightarrow{\Delta} & \operatorname{NaClO}_3 + 2 \operatorname{NaCl} \\ \operatorname{Sod. hypochlorite} & \operatorname{Sod. chlorate} \end{array}$ 



**32.** (a) Due to delocalisation of lone pair of electrons of the N-atom over the benzene ring, all aromatic amines are less basic than alkylamines.

Presence of electron donating groups  $(i.e., -CH_3)$  on the N-atom increases the basicity of substituted aniline.

In  $(C_6H_5)_2NH$ , the lone pair of electrons on the N-atom is delocalised over two benzene rings instead of one in  $C_6H_5NH_2$ , therefore,  $(C_6H_5)_2NH$  is much less basic than  $C_6H_5NH_2$ .

Combining all the three trends together the basicity of the four amines increases in the order :

 $(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2.$ (b) Higher the electron density in the benzene ring, more reactive is the aromatic compound towards electrophilic substitution reaction. Now due to the presence of a lone pair of electrons on the N-atom which it can directly donate to the benzene ring,  $-N(CH_3)_2$  is a much stronger electron donating group than  $-CH_3$  group. The remaining two groups contain a positive charge on the N-atom and hence, act as electron withdrawing groups. But in  $(CH_3)_3N^+$ -group, the +vely charged N is directly attached to the benzene ring, therefore, its electron withdrawing ability is much stronger than  $-CH_2N^+(CH_3)_3$ . Thus, the electron density in the benzene ring increases in the order :

$$\overset{+}{\underset{}}^{\text{H}}(\text{CH}_3)_3 \quad \underset{}{\underset{}}^{\text{CH}_2} \overset{+}{\underset{}}^{\text{H}}(\text{CH}_3)_3 \quad \underset{}{\underset{}}^{\text{CH}_3} \quad \underset{}{\underset{}}^{\text{CH}_3} \quad \underset{}{\underset{}}^{\text{N}}(\text{CH}_3)_2$$

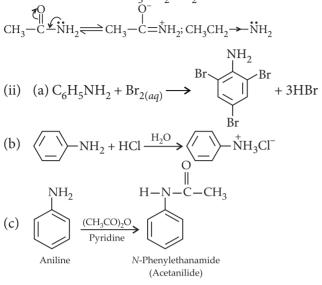
Therefore, their reactivity towards electrophilic substitution reactions also increases in the same order. (c) Electron releasing groups such as –  $OCH_3$ , –  $CH_3$ , increases basic strength and electron withdrawing groups such as –  $NO_2$ , –  $SO_3H$ , – COOH, – *X*, decrease the basic strength of amines.

#### OR

(i) (a) Benzene ring in aromatic amines is highly activated due to the displacement of lone pair of nitrogen towards the ring. It results, increase in the electron density on the ring. This facilitates the electrophilic attack on the ring.



(b) In CH<sub>3</sub>CONH<sub>2</sub>, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence,  $CH_3CONH_2$  is a weaker base than  $CH_3CH_2NH_2$ .



33. (a) For the equation,  $M^{n+}_{(aa)} + ne^- \rightarrow M_{(s)}$ 

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{\left[M_{(aq)}^{n+}\right]}$$
$$= E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{1}{\left[M_{(aq)}^{n+}\right]}$$

(b) (i)  $\operatorname{Mg}_{(s)} | \operatorname{Mg}^{2+}(0.001 \text{ M}) || \operatorname{Cu}^{2+}(0.0001 \text{ M}) | \operatorname{Cu}_{(s)}$ At anode :  $\operatorname{Mg}_{(s)} \longrightarrow \operatorname{Mg}^{2+}_{(aq)} + 2e^{-}$ At cathode :  $\operatorname{Cu}^{2+}_{(aq)} + 2e^{-} \longrightarrow \operatorname{Cu}_{(s)}$ Net cell reaction :  $\operatorname{Mg}_{(s)} + \operatorname{Cu}^{2+}_{(aq)} \longrightarrow \operatorname{Mg}^{2+}_{(aq)} + \operatorname{Cu}_{(s)}$  $\therefore \quad n = 2$ Using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 \ RT}{nF} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

For the given cell,  $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = E_{Cu^{2+}/Cu}^{\circ} - E_{Mg^{2+}/Mg}^{\circ}$  = 0.34 - (-2.37) = 2.71 VGiven :  $[Mg^{2+}] = 0.001 \text{ M}$ ,  $[Cu^{2+}] = 0.0001 \text{ M}$ Putting these values in Nernst equation at 298 K,  $E_{cell} = 2.71 - \frac{0.059}{2} \log \frac{0.001}{0.0001}$ 

 $E_{\text{cell}} = 2.71 - 0.0295 \log 10 = 2.71 - 0.0295 = 2.68 \text{ V}$ (ii)  $\operatorname{Fe}_{(s)} |\operatorname{Fe}^{2+}(0.001 \text{ M})|| H^{+}(1 \text{ M}) |H_{2(g)}(1 \text{ bar}) | Pt_{(s)}$ At anode :  $\operatorname{Fe}_{(s)} \longrightarrow \operatorname{Fe}_{(aa)}^{2+} + 2e^{-}$ At cathode :  $2H_{(aa)}^+ + 2e^- \longrightarrow H_{2(a)}$ Net cell reaction :  $\operatorname{Fe}_{(s)} + 2\operatorname{H}^+_{(aq)} \longrightarrow \operatorname{Fe}^{2+}_{(aq)} + \operatorname{H}_{2(q)}$  $\therefore n=2$ Using Nernst equation at 298 K,  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}] \times p_{\text{H}_2}}{[\text{II}^+]^2}$ For the given cell,  $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{H}^{+}/\text{H}_{2}}^{\circ} - E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}$ = 0 - (- 0.44) = + 0.44 V Given :  $[Fe^{2^+}] = 0.001 \text{ M}; [H^+] = 1 \text{ M}; p_{H_2} = 1 \text{ bar}$ Putting values in Nernst equation,  $E_{\text{cell}} = 0.44 - 0.0295 \log \frac{0.001 \times 1}{1^2}$  $= 0.44 - 0.0295 \log 10^{-3} = 0.44 - [(0.0295) \times (-3)]$ = 0.44 + 0.0885 = 0.53 V(a)  $\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  $\kappa = \frac{1}{p} \times \text{Cell constant}$  $\Rightarrow$  Cell constant =  $\kappa \times R$ =  $1.29 \ \Omega^{-1} \ m^{-1} \times 85 \ \Omega = 109.65 \ m^{-1}$ For second solution,  $\kappa = \frac{1}{R} \times \text{Cell constant} = \frac{1}{96 \Omega} \times 109.65 \text{ m}^{-1}$  $= 1.142 \ \Omega^{-1} m^{-1}$  $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142 \ \Omega^{-1} \text{m}^{-1} \times 1000 \ \text{cm}^3}{0.052 \ \text{mol}}$  $\Lambda_m = \frac{1.142 \ \Omega^{-1} \text{cm}^{-1} \times 10^{-2} \times 1000 \ \text{cm}^3}{0.052 \ \text{mol}}$  $= 219.61 \text{ S cm}^2 \text{ mol}^{-1}$ (b) Here, conductivity ( $\kappa$ ) = 0.146 × 10<sup>-3</sup> S cm<sup>-1</sup>, resistance (R) = 1500  $\Omega$ Cell constant =  $\frac{\text{Conductivity}}{\text{Conductivity}}$ Conductance = Conductivity × Resistance  $\left| \because \text{Conductance} = \frac{1}{\text{Resistance}} \right|$  $= \kappa \times R$  $= 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$ 

 $\odot$   $\odot$   $\odot$