

# **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(4)	1(2)	_	_		
3.	Electrochemistry	1(1)	1(2)	_	1(5)	11(23)	
4.	Chemical Kinetics	1(1)	1(2)	_	_		
5.	Surface Chemistry	1(1)	1(2)	_	_		
6.	The <i>p</i> -Block Elements	1(1)	1(2)	_	1(5)		
7.	The <i>d</i> - and <i>f</i> -Block Elements	1(1)	_	2(6)	_	8(19)	
8.	Coordination Compounds	1(1)	_	1(3)	_		
9.	Haloalkanes and Haloarenes	2(2)	1(2)	1(3)	_		
10.	Alcohols, Phenols and Ethers	1(1)	1(2)	_	_		
11.	Aldehydes, Ketones and Carboxylic Acids	2(5)	1(2)	_	_	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)	

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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 :

Aromatic and aliphatic aldehydes are selectively reduced to primary alcohols under mild conditions with potassium formate in the presence of Pd/C catalyst. The high selectivity obtained is attributed to the presence of the basic potassium bicarbonate generated in situ from the formate salt via the hydrogen transfer process. Molecular hydrogen shows similar activity in the presence of potassium carbonate salts. Ketones do not react under these conditions, therefore this method is used to separate aldehydes selectively from a mixture of aldehydes and ketones.

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

- (i) The hydrogenation process mentioned in the study above cannot be used to convert
  - (a) benzaldehyde to benzyl alcohol
- (b) acetaldehyde to ethanol
- (c) propanone to propanol
- (d) propanal to propanol.
- (ii) This method can be used to separate a mixture of
  - (I) CH<sub>3</sub>CHO and CH<sub>3</sub>CH<sub>2</sub>CHO
  - (II) CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>CHO



- (a) Only I and II
- (c) Only III

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- (b) Only II
- (d) Only II and III

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- (iii) An organic compound A (C<sub>3</sub>H<sub>6</sub>O) on treatment with potassium formate in the presence of Pd/C catalyst forms compound B (C<sub>3</sub>H<sub>8</sub>O). B reacts with HBr to form the compound C. C with Mg forms Grignard reagent D which reacts with A to form a product which on hydrolysis gives hexan-3-ol. Hence A and B are respectively
  - (a) propanone, 2-propanol
  - (c) propanone, propanol

- (b) propanal, propanol
- (d) propanal, propanone.
- 1 1 1

An organic compound *X* forms 2,4-DNP derivative and reduces Tollen's reagent. *X* undergoes Cannizzaro reaction to give *Y* and *Z*. *X* also gives *Y* on treatment with potassium formate in the presence of Pd/C catalyst. Hence *X* is

- (a) acetone (b) benzaldehyde (c) propanone (d) ethanol.
- (iv) Compound *Y* is prepared by the treatment of potassium formate in the presence of Pd/C catalyst with compound *X*. Compound *Y* on oxidation with alkaline  $KMnO_4$  is converted to compound *Z*. When compound *Z* is heated with compound *Y* in the presence of  $H_2SO_4$ , it produces a compound having fruity smell. To which families the compounds *X*, *Y* and *Z* belong to?
  - (a) aldehyde, carboxylic acid and alcohol respectively
  - (b) ketone, alcohol and carboxylic acid respectively
  - (c) ketone, carboxylic acid and alcohol respectively
  - (d) aldehyde, alcohol and carboxylic acid respectively.

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

Raoult first proposed linear relationship between mole fraction and vapour pressure in 1887 and Raoult's law has become a paradigm in chemistry. For dilute solutions, this relation holds good but deviations grow as the solution becomes more concentrated. Dilute solutions which obey Raoult's law over the entire range of concentration are called ideal solutions. In 1908, Calendar explained some of the deviations from Raoult's model in aqueous solutions, solute molecules are hydrated such that some of the water is bound to the solute, so it does not contribute to the vapour pressure. Such kind of deviations from Raoult's model can be positive deviation and negative deviation.

In positive deviation, the total vapour pressure of solution is greater than corresponding vapour pressure expected in case of ideal solution. In such solutions,  $\Delta_{\text{mixing}} H$  and  $\Delta_{\text{mixing}} V$  are positive.

In negative deviation, total vapour pressure of solution is smaller than the corresponding vapour pressure expected in case of ideal solution. In these solutions,  $\Delta_{\text{mixing}} H$  and  $\Delta_{\text{mixing}} V$  are negative.

## 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 : An ideal solution obeys Raoult's law.
   Reason : In an ideal solution, vapour pressure of the solute and solvent and their corresponding activities in solution are proportional to their mole fraction.
- (ii) Assertion : Highly concentrated solutions occur in a wide range of natural processes exhibit non-ideal behaviour.

Reason : Non-ideal solutions do not obey Raoult's law.

(iii) Assertion : Dilute solutions are taken as ideal solutions.Reason : The solutions which follow the Raoult's law at any temperature and concentration are known as ideal solutions.

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(iv) Assertion : Solutions having positive deviation from Raoult's law shows  $\Delta_{\text{mixing}} H = +\text{ve.}$ Reason : Energy is required to break solute-solute or solvent-solvent attractive forces.

OR

**Assertion :** Solutions having negative deviation from Raoult's law shows  $\Delta_{\text{mixing}} V = +\text{ve}$ . **Reason :** Solute-solvent interactions are stronger than solute-solute and solvent-solvent interactions.

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

**3.** The reaction of chloroform with alcoholic KOH and *p*-toluidine forms



(d) Gold sol on mixing with starch sol causes stabilisation of starch sol.

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- 7. The *d*-block elements form coloured ions because these elements
  - (a) cannot absorb the radiation in the visible region
  - (b) involve *d*-*d* transitions which fall in the visible region
  - (c) allow *d-s* transition
  - (d) absorb other colours except those required for *d*-*d* transition.

Lanthanoid contraction is due to

- (a) poor shielding effect by 4f -electrons
- (c) diffused shape of *f*-orbitals

8. In the reaction,  $A + 3B \longrightarrow 2C$ , the rate of formation of *C* is

- (a) the same as rate of consumption of *A*
- (c) twice the rate of consumption of *A*
- (b) the same as the rate of consumption of *B*

(b) efficient shielding effect of *f*-electrons

of A (d) 3/2 times the rate of consumption of B.

(d) both (a) and (c).

9. The end product (Q) in the following sequence of reactions is



10. Glucose molecule reacts with 'X' number of phenylhydrazine to yield osazone. The value of 'X' is
(a) four
(b) one
(c) two
(d) three.

OR

Glucose when treated with  $CH_3OH$  in presence of dry HCl gas gives  $\alpha$ - and  $\beta$ -methyl glucosides because it contains

(a) a -CHO group (b) a  $-CH_2OH$  group (c) a ring structure (d) five -OH groups.

11. The reaction conditions leading to the best yields of  $C_2H_5Cl$  are

(a) 
$$C_2H_6$$
 (Excess) +  $Cl_2 \xrightarrow{\text{UV light}}$  (b)  $C_2H_6 + Cl_2 \xrightarrow{\text{dark room temp.}}$ 

(c) 
$$C_2H_6 + Cl_2$$
 (Excess)  $\xrightarrow{UV \text{ light}}$  (d)  $C_2H_6 + Cl_2 \xrightarrow{UV \text{ light}}$ 

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 : Reaction of  $SO_2$  and  $H_2S$  in the presence of  $Fe_2O_3$  catalyst gives elemental sulphur. Reason : In this reaction  $H_2S$  is acting as a reducing agent.
- **13.** Assertion : Glycine exists as zwitter ion but *o* and *p*-aminobenzoic acid do not. **Reason :** Due to the presence of  $-NH_2$  and -COOH groups within the same molecule, they neutralise each other and hence  $\alpha$ -amino acids exist as dipolar ions or zwitter ions.
- 14. Assertion :  $K_2O$  has fluorite structure. Reason :  $O^{2-}$  are present at the corners and at the centre of all six faces.  $K^+$  ions occupy all the tetrahedral voids.

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15. Assertion : In complex [Cr(NH<sub>3</sub>)<sub>4</sub>BrCl]Cl, the 'spin only' magnetic moment is close to 2.83 B.M.
 Reason: Mononuclear complexes of chromium(III) in strong field ligand have three unpaired electrons.

**16. Assertion :** Phenol is more reactive than benzene.

Reason: In case of phenol, the intermediate carbocation is more resonance stabilised.

OR

**Assertion :** *tert*-Butylmethylether is not prepared by the reaction of *tert*-butylbromide with sodium methoxide.

Reason : Sodium methoxide is a weak nucleophile.

# **SECTION - B**

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

17. Calculate the cell emf at 25°C for the following cell :  $Mg_{(s)} | Mg^{2+} (0.01 \text{ M}) || Sn^{2+} (0.10 \text{ M}) | Sn_{(s)} |$ [Given :  $E^{\circ}_{(Mg^{2+}/Mg)} = -2.34 \text{ V}, E^{\circ}_{(Sn^{2+}/Sn)} = -0.136 \text{ V}, 1 \text{ F} = 96500 \text{ C mol}^{-1}$ ].

S. No.	Rate of reaction (mol L <sup>-1</sup> hr <sup>-1</sup> )	Concentration of $N_2O_5$ (mol L <sup>-1</sup> )		
1.	0.10	0.34		
2.	0.20	0.68		
3.	0.40	1.36		

18. Calculate the order of the reaction for the decomposition of  $N_2O_5$  at 30°C from the following rate data.

19. The freezing point of pure nitrobenzene is 278.8 K. When 2.5 g of unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found to be 276.8 K. If the freezing point depression constant for nitrobenzene is 8 K kg mol<sup>-1</sup>, what is the molar mass of unknown substance?

#### OR

A solution of glucose  $(C_6H_{12}O_6)$  in water is labelled as 10% by weight. What would be the molality of the solution?

OR

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(Molar mass of glucose =  $180 \text{ g mol}^{-1}$ )

- **20.** (a) Draw the molecular structure of the noble gas species which is isostructural with  $ICl_{4}^{-}$ .
  - (b) Why is dioxygen a gas but sulphur a solid?
- 21. Identify the reaction and write the IUPAC name of the product formed :

(a) 
$$(a) + NaOH \xrightarrow{CaO}{\Delta}$$

(b)  $CH_3COOH \xrightarrow{Cl_2/P}$ 

- How will you convert the following :
- (i) Propanone to propan-2-ol
- (ii) Ethanal to 2-hydroxypropanoic acid?
- 22. Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

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- 23. An element has a face centred cubic (*fcc*) structure with a cell edge of 0.2 nm. Calculate its density in g cm<sup>-3</sup> if 400 g of this element contains  $4.8 \times 10^{24}$  atoms. [ $N_A = 6 \times 10^{23}$  mol<sup>-1</sup>]
- 24. A colloidal solution of ferric oxide is prepared by two different methods as shown below :



- (a) What is the charge on colloidal particles in two test tubes (*A*) and (*B*)?
- (b) Give reasons for the origin of charge.
- 25. Write the mechanism of dehydration of alcohol.

(i) Write the IUPAC name of the following compound.

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}-\mathrm{CH}-\mathrm{CH}-\mathrm{CH}_{2}\mathrm{OH}\\ | & | \\ \mathrm{OH} & \mathrm{OH} & \mathrm{Br} \end{array}$$

(ii) Write the distinction test for ethyl alcohol and 2-propanol.

## **SECTION - C**

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

- **26.** Write the IUPAC nomenclature of the following complex along with its hybridisation and structure.  $K_2[Cr(NO)(NH_3)(CN)_4]$ ,  $\mu = 1.73$  BM
- **27.** (a) A solution of KOH hydrolyses CH<sub>3</sub>CHClCH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl. Which one of these is more easily hydrolysed?
  - (b) Write the major product(s) in the following :

(i) 
$$2CH_3 - CH - CH_3 \xrightarrow{Na} Dry \text{ ether}$$

(ii) CH<sub>3</sub>−CH<sub>2</sub>−Br →
(c) RCl is hydrolysed slowly to ROH but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture. Explain.

OR

A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in butane. Write the structures of the possible isomers. Give the IUPAC name of the isomer which can exhibit enantiomerism.

- **28.** Give reasons for the following observations :
  - (i) Cu<sup>+</sup> ion is not stable in aqueous solution.
  - (ii) Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.

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(iii) Iron has higher enthalpy of atomisation than that of copper.

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- 29. (a) Why is Cr<sup>2+</sup> reducing and Mn<sup>3+</sup> is oxidising in nature when both have d<sup>4</sup> configuration?
  (b) Explain how [Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> becomes purple coloured.
- **30.** (a) On which carbon atoms glycosidic linkage is present in sucrose?
  - (b) Name the bases that are common in both DNA and RNA.
  - (c) Despite having an aldehyde group glucose does not give 2,4-DNP test. Why?

What is essential difference between  $\alpha$ -glucose and  $\beta$ -glucose? What is meant by pyranose structure of glucose?

# **SECTION - D**

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

- **31.** (a) (i) Express the relation between the conductivity ( $\kappa$ ) and the molar conductivity ( $\Lambda_m$ ) of a solution.
  - (ii) Electrolytic conductivity of 0.30 M solution of KCl at 295 K is  $3.72 \times 10^{-2}$  S cm<sup>-1</sup>. Calculate the molar conductivity.
  - (b) (i) Solutions of two electrolytes 'A' and 'B' are diluted. It is found that  $\Lambda_m$  value of 'B' increases 2 times while that of 'A' increases 20 times. Which of the two is a strong electrolyte?
    - (ii) A galvanic cell has  $E^{\circ}_{cell} = 1.1$  V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?
    - (iii) How will the pH of brine solution be affected on electrolysis?

#### OR

- (a) Calculate the cell emf and  $\Delta G^{\circ}$  for the cell reaction at 25°C for the cell :  $Zn_{(s)} | Zn^{2+} (0.0004 \text{ M}) || Cd^{2+} (0.2 \text{ M}) | Cd_{(s)}$   $E^{\circ}$  values at 25°C :  $Zn^{2+} / Zn = -0.763 \text{ V}$ ;  $Cd^{2+} / Cd = -0.403 \text{ V}$ ;  $F = 96500 \text{ C mol}^{-1}$ ;  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .
- (b) If  $E^{\circ}$  for copper electrode is 0.34 V, how will you calculate its emf value when the solution in contact with it is 0.1 M in copper ions? How does emf for copper electrode change when concentration of Cu<sup>2+</sup> ions in the solution is decreased?
- **32.** (a) Explain the following :
  - (i) Sulphur exhibits tendency for catenation but oxygen does not.
  - (ii) SF<sub>6</sub> is not easily hydrolysed though thermodynamically it should be. Why?
  - (iii) Why HF acid is stored in wax coated glass bottles?
  - (b) What happens
    - (i) When SO<sub>2</sub> is passed through acidified solution of  $K_2Cr_2O_7$ ?
    - (ii) Chlorine gas is passed into a solution of NaI in water?

#### OR

**CLICK HERE** 

- (a) Explain why NH<sub>3</sub> is basic while BiH<sub>3</sub> is only feebly basic?
- (b) Arrange the following in the order of property indicated against each set giving reason :
  - (i)  $H_2O$ ,  $H_2S$ ,  $H_2Se$ ,  $H_2Te$  increasing acidic character
  - (ii) HF, HCl, HBr, HI increasing acid strength.

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- (c) Complete the following reactions :
  - (i)  $NH_3 + NaOCl \longrightarrow$
  - (ii)  $Cu + HNO_{3(dilute)} \longrightarrow$
- **33.** (a) An aromatic compound '*A*' on treatment with aqueous ammonia and heating forms compound '*B*' which on heating with  $Br_2$  and KOH forms a compound '*C*' of molecular formula  $C_6H_7N$ . Write the structures and IUPAC names of compounds *A*, *B* and *C*.
  - (b) Write distinguish tests for the following pairs of compounds :
    - (i) Aniline and ethylamine
    - (ii) Ethylamine and dimethylamine

- (a) Account for the following :
  - (i) Aniline does not undergo Friedel-Crafts reaction.
  - (ii) It is difficult to prepare pure amines by ammonolysis of alkyl halides.
- (b) Account for the following :
  - (i) Like ammonia, amines are good nucleophiles.
  - (ii) Aryl amines are weaker bases than alkyl amines.
- (c) Arrange the following in the decreasing order of their basic strength in aqueous solutions : CH<sub>3</sub>NH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NH, (CH<sub>3</sub>)<sub>3</sub>N and NH<sub>3</sub>

Chemistry





1. (i) (c) : Ketones are not reduced under these conditions.

(ii) (d) : This method can be used to separate aldehydes selectively from a mixture of aldehydes and ketones since ketones do not react under these conditions.

(iii) (b) : *A* is an aldehyde since ketones do not reduced to alcohols on treatment with potassium formate in the presence of Pd/C.



OR

(b) Since the compound forms 2,4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde. Since *X* undergoes Cannizzaro reaction, hence it has no  $\alpha$ -hydrogen.



#### 2. (i) (a)

(ii) (b) : In non-ideal solution, solute-solute as well as solvent-solvent interactions are not similar to solute-solvent interaction.

(iii) (b): A solution that obeys Raoult's law is known as ideal solution. Raoult's law only work for ideal solutions.

(iv) (a)

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OR

(d) : Solutions having negative deviation from Raoult's law shows  $\Delta_{\text{mixing}} V = -\text{ve}$  because of the increase forces of interaction in the solution, the solution will be held more tightly. Therefore, there will be decrease in volume on mixing.





4. (a) : Cell reaction is

$$\operatorname{Fe}_{(s)} + 2\operatorname{OH}^{-} \longrightarrow \operatorname{FeO}_{(s)} + \operatorname{H}_{2}\operatorname{O} + 2e^{-}$$

 $Ni_2O_{3(s)} + H_2O + 2e^- \longrightarrow 2NiO_{(s)} + 2OH^-$ 

 $\operatorname{Fe}_{(s)} + \operatorname{Ni}_2\operatorname{O}_{3(s)} \longrightarrow \operatorname{FeO}_{(s)} + 2\operatorname{NiO}_{(s)}$ Hence, emf is independent of  $\operatorname{OH}^-$  ions.

5. (d)

6. (a) : When an electric field is applied to purify an impure colloidal solution, the process is known as electrodialysis. The ions present in the colloidal solution migrate out to the oppositely charged electrode.

OR

(b)

(d)

**CLICK HERE** 

7. (b) : This is due to d-d transition. When visible (white) light falls on transition metal compounds, they absorb certain radiation of visible light for transition of electrons from lower d level to higher d level and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.

OR

8. (c) : Rate = 
$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

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9. (c) : 
$$\bigcirc \xrightarrow{Cl_2/FeCl_3} \bigcirc \xrightarrow{Cl} \xrightarrow{Na/ether} \bigcirc \xrightarrow{(Q)} (Q)$$

**10.** (**d**) : One glucose molecule reacts with 3 molecules of phenylhydrazine to give osazone.

#### OR

(c) : 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.

11. (a)

12. (b) :  

$$2^{-}$$
 4+  
 $2H_2S + SO_2 \xrightarrow{\text{oxidising}}{\text{agent}} 2H_2O + 3S$   
 $2H_2O +$ 

13. (b)

**14.** (d) :  $K_2O$  has antifluorite structure.

**15.** (d) :  $Cr^{3+}$  having  $3d^3$  configuration always have 3 unpaired electrons with strong field as well as weak field ligands with three unpaired electrons thus, the magnetic moment is 3.83 B.M.

16. (a)

#### OR

(c) : Sodium methoxide is a strong nucleophile.

17.  $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^{-}$  (Anodic half reaction)  $Sn^{2+}_{(aq)} + 2e^{-} \longrightarrow Sn_{(s)}$  (Cathodic half reaction)

 $\frac{\mathrm{Mg}_{(s)} + \mathrm{Sn}^{2+}{}_{(aq)} \longrightarrow \mathrm{Mg}^{2+}{}_{(aq)} + \mathrm{Sn}_{(s)}}{E^{\circ}_{\mathrm{cell}} = E^{\circ}_{\mathrm{Sn}^{2+}/\mathrm{Sn}} - E^{\circ}_{\mathrm{Mg}^{2+}/\mathrm{Mg}}}$ 

$$= -0.136 + 2.34 = 2.204$$
 V

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.01 \text{ M}}{0.10 \text{ M}}$$
$$= 2.24 - (0.0295 \times -1) = 2.2335 \text{ V}$$

18. From the given data,

 $r_{1} = 0.10 \text{ mol } L^{-1} \text{ hr}^{-1} = k \times (0.34 \text{ mol } L^{-1})^{n}$   $r_{2} = 0.20 \text{ mol } L^{-1} \text{ hr}^{-1} = k \times (0.68 \text{ mol } L^{-1})^{n}$   $r_{3} = 0.40 \text{ mol } L^{-1} \text{ hr}^{-1} = k \times (1.36 \text{ mol } L^{-1})^{n}$   $\frac{r_{1}}{r_{2}} = \frac{0.10 \text{ mol } L^{-1} \text{ hr}^{-1}}{0.20 \text{ mol } L^{-1} \text{ hr}^{-1}} = \frac{k(0.34 \text{ mol } L^{-1})^{n}}{k(0.68 \text{ mol } L^{-1})^{n}}$   $\frac{1}{r_{2}} = \left(\frac{1}{r_{2}}\right)^{n} \implies n = 1$ 

or 
$$\frac{1}{2} = \left(\frac{1}{2}\right) \implies n = 1$$

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19. Given, 
$$w_1 = 2.5 \text{ g}$$
  
 $\Delta T_f = 278.8 - 276.8 = 2 \text{ K}$   
 $w_2 = 100 \text{ g}, K_f = 8 \text{ K kg mol}^{-1}$   
 $\Rightarrow \Delta T_f = K_f \times \frac{w_1}{M_1} \times \frac{1000}{w_2}$   
 $\Rightarrow 2 = 8 \times \frac{2.5}{M_1} \times \frac{1000}{100}$   
 $\Rightarrow M_1 = 4 \times 2.5 \times 10 \Rightarrow M_1 = 10 \times 10$ 

OR

Mass of solution = 100 g

 $M_1 = 100 \text{ g mol}^{-1}$ 

Mass of solute = 10 g

Mass of solvent = 100 - 10 = 90 g

$$=\frac{90}{1000}$$
 kg = 0.09 kg

Number of moles of solute,  $n = \frac{10}{180} = 0.055$  mol

$$m = \frac{0.055 \text{ mol}}{0.09 \text{ kg}} = 0.61 \text{ m}$$

**20.** (a) Structure of  $ICl_4^-$ : I in  $ICl_4^-$  has four bond pairs and two lone pairs. Therefore, according to VSEPR theory, it should be square planar as shown.



Here,  $ICl_4^-$  has  $(7 + 4 \times 7 + 1) = 36$ 

valence electrons. A noble gas species having 36 valence electrons is  $XeF_4$  (8 + 4 × 7 = 36). Therefore, like  $ICI_4^-$ ,  $XeF_4$  is also square planar.

(b)  $O_2$  molecules are held together by weak van der Waals' forces because of the small size and high electronegativity of oxygen.

Sulphur shows catenation and the molecule is made up of eight atoms,  $(S_8)$  with strong intermolecular attractive forces. Hence ,sulphur exists as solid at room temperature.



**CLICK HERE** 

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(i) 
$$\begin{array}{c} CH_{3} \\ CH_{3} \\ Propanone \end{array} C = O + H_{2} \xrightarrow{\text{Ni or Pt}} \begin{array}{c} CH_{3} \\ CH_{3} \\ Propan-2 \text{-ol} \end{array} CHOH \\ (ii) CH_{3}CHO \xrightarrow{\text{HCN}} CH_{3} \\ CH_{3} \\ CH \\ CH_{3} \\ CH \\ OH \end{array} CH_{3} - CH - CN \\ (iii) CH_{3}CHO \xrightarrow{\text{HCN}} OH \\ (iii) CHO \xrightarrow{\text{HCN}} OH \\ (iii) CHO \xrightarrow{\text{HCN}}$$



**22.** There are two reasons :

(a) In case of chlorobenzene, carbon to which chlorine is attached is  $sp^2$ -hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is  $sp^3$ - hybridised. So the net dipole moment is lower in chlorobenzene.

(b) In chlorobenzene C — Cl bond has some double bond character so its bond length is smaller. Hence, dipole moment is lower than cyclohexyl chloride which has a longer C — Cl single bond.

**23.** Given, edge length  $a = 0.2 \text{ nm} = 2 \times 10^{-8} \text{ cm}$ Mass of substance = 400 g

Number of atoms = 
$$48 \times 10^{23}$$
 atoms

$$\therefore \text{ Number of unit cells} = \frac{48 \times 10^{23} \text{ atoms}}{4} = 12 \times 10^{23}$$

:. Volume of one unit cell = 
$$a^3 = (2 \times 10^{-8} \text{ cm})^3$$
  
=  $8 \times 10^{-24} \text{ cm}^3$ 

... Total volume = Number of unit cells

 $\times$  Volume of one unit cell

$$= 12 \times 10^{23} \times 8 \times 10^{-24} = 9.6 \text{ cm}^3$$
  

$$\therefore \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{400 \text{ g}}{9.6 \text{ cm}^3} = 41.7 \text{ g cm}^{-3}$$

**24.** (i) (a) Colloidal particles of test tube (*A*) are positively charged whereas colloidal particles of test tube (*B*) are negatively charged.

(b) In test tube (*A*),  $Fe^{3+}$  ions are adsorbed on the ppt.  $Fe_2O_3 \cdot xH_2O$  [or  $Fe_2O_3 \cdot xH_2O/Fe^{3+}$  is formed]. In test tube (*B*),  $OH^-$  ions are adsorbed on the ppt.  $Fe_2O_3 \cdot xH_2O$  [or  $Fe_2O_3 \cdot xH_2O/OH^-$  is formed].

#### 25. Mechanism of dehydration of alcohol : Step 1 : Formation of protonated alcohol



Step 2 : Formation of carbocation

$$H_{3}C \xrightarrow{I} C \xrightarrow{I} O \xrightarrow{I} H_{3}C \xrightarrow{I} H_$$

Step 3 : Formation of ethene

$$H_2O + H_2C - CH_3 \longrightarrow H_2C = CH_2 + H_3O$$
  
OR

(i) 2-Bromopentane-1,3,4-triol.

(ii) Treat the compound with Lucas reagent

(conc. HCl + anhy. ZnCl<sub>2</sub>) : 2-propanol gives turbidity in 5 min. whereas ethanol gives no turbidity at room temperature.

$$\begin{array}{c} CH_{3}CH_{2}OH + HCl \xrightarrow{Conc. HCl +} \\ \hline Anhy. ZnCl_{2} \end{array} \rightarrow \text{No reaction} \\ CH_{3}CHCH_{3} + HCl \xrightarrow{Conc. HCl +} \\ \downarrow \\ OH & CH_{3}-CH-CH_{3} + H_{2}O \\ \downarrow \\ Cl \\ Turbidity appears in 5 minute \end{array}$$

**26.**  $\mu = \sqrt{n(n+2)} = 1.73$  which gives n = 1This means that chromium ion has one unpaired electron, *i.e.*, it is present as Cr<sup>+</sup> or Cr (I). This implies that NO is present as nitrosonium ion. Hence, the name will be potassium amminetetracyanonitrosonium chromate (I).

$$\mathbf{Cr}^+: \underbrace{\uparrow \uparrow \uparrow \uparrow \uparrow}^{3d} \underbrace{4s}$$

In the complex, as there is only one unpaired electron and coordination number is 6, it will become



*i.e.*, it will undergo  $d^2sp^3$  hybridisation to give octahedral geometry.



27. (a)  $CH_3CH_2CHCH_3$  hydrolyses easily with KOH

because it is secondary alkyl halide.

(b) (i) 
$$CH_3$$
-CH-CH-CH\_3  
 $\downarrow$   
 $CH_3$   $CH_3$ 

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(c) Iodide is a powerful nucleophile and therefore, it reacts rapidly with *R*Cl to form *R*I

$$KI \longrightarrow K^{+} + I^{-}$$
$$I^{-} + R - Cl \longrightarrow R - I + Cl^{-}$$

Also, I<sup>-</sup> ion is a better leaving group than Cl<sup>-</sup> ion and therefore, *R*I is more readily hydrolysed to form *R*OH.



6. 
$$CH_3 - CH_2 - CH_3$$
  
2, 3-dichlorobutane

Due to presence of four different groups around  $C^*$  in (3), (4) and (6), these are chiral compounds and hence exhibit enantiomerism.

**28.** (i) In aqueous solutions,  $Cu^+$  undergoes disproportionation to form a more stable  $Cu^{2+}$  ion.  $2Cu^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$ 

 $Cu^{2+}$  in aqueous solutions is more stable than  $Cu^+$  ion because hydration enthalpy of  $Cu^{2+}$  is higher than that of  $Cu^+$ . It compensates the second ionisation enthalpy of Cu involved in the formation of  $Cu^{2+}$  ions.

(ii) This is due to the presence of maximum number of unpaired electrons in  $Mn^{2+}$  (3 $d^5$ ).

(iii) Greater the number of unpaired electrons, stronger is the metallic bond and therefore, higher is the enthalpy of atomisation. Since, iron has greater number of unpaired electrons than copper hence iron has higher enthalpy of atomisation.

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**29.** (a)  $Cr^{2+}$  is reducing as its configuration changes from  $d^4$  to  $d^3$ , a more stable half filled  $t_{2g}$  configuration.



 $Mn^{3+}$  is oxidising because its configuration also changes from  $d^4$  to  $d^5$  (which is half-filled) and has extra-stability.

(b) In  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , titanium has  $3d^1 4s^0$  configuration. In Ti<sup>3+</sup> ion, the *d*-orbitals split up into two parts  $t_{2g}$  and  $e_g$ . The  $t_{2g}$  part has three out of five *d*-orbitals  $(d_{xy}, d_{yz}, d_{zx})$  with energy lower than the atomic orbitals whereas  $e_g$  have two orbitals  $(d_{x^2-y^2}$  and  $d_{z^2})$  having energy more than the atomic orbitals. Due to less energy difference between  $t_{2g}$  and  $e_g$  orbitals, the electrons transit between these two orbital groups (called *d*-*d* transition). The energy required for this purpose is sufficiently available in the visible region. The *d*-*d* transition absorbs yellow region light and therefore colour observed is purple (complementary colour).



30. (a) In sucrose carbon no. 1 of α-D-glucose is joined together with carbon no. 2 of β-D-fructose.
(b) Adenine, guanine and cytosine are the bases common in DNA and RNA both.

(c) Although, glucose in its open chain structure contains free aldehydic group yet it does not give 2, 4-DNP test a characteristic reaction of aldehyde, *i.e.*, –CHO group. This is because glucose actually exists in the cyclic hemiacetal form with only a small amount of the open chain form in equilibrium. Since the concentration of open chain form is very low and its reaction with 2, 4-DNP is reversible thus, its 2, 4-DNP adduct is not observed.

#### OR

In  $\alpha$ -D-Glucose, the –OH group at C<sub>1</sub> is towards right whereas in  $\beta$ -D-glucose, the –OH group at C<sub>1</sub> is towards left. Such a pair of stereoisomers which differ in the configuration only at C<sub>1</sub> are called anomers.

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The six membered cyclic structure of glucose is called pyranose structure ( $\alpha$ - or  $\beta$ -), in analogy with heterocyclic compound pyran.



**31.** (a) (i) 
$$\Lambda_m = \frac{\kappa \times 10^3}{M}$$

where *M* is the concentration of solution in molarity. (ii) Electrolytic conductivity,  $\kappa = 3.72 \times 10^{-2} \text{ S cm}^{-1}$ Molar conductivity,

$$\Lambda_m = \frac{\kappa(\text{S cm}^{-1}) \times 1000 (\text{cm}^3 \text{ L}^{-1})}{M (\text{mol L}^{-1})}$$
$$= \frac{3.72 \times 10^{-2} \times 1000}{0.30} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

(b) (i) For strong electrolytes,  $\Lambda_m$  increases slowly with dilution. Since there is no wide effect on  $\Lambda_m$  value of electrolyte 'B' on dilution. Thus, 'B' is a strong electrolyte.

(ii) If an external opposite potential is applied in the galvanic cell and increased slowly, reaction continues to take place till the opposing voltage reaches the value 1.1 V. After that reaction stops and no further chemical reaction takes place. Hence, no current flows through the cell.

(iii) The overall reaction for electrolysis of brine solution can be written as

$$\operatorname{NaCl}_{(aq)} + \operatorname{H}_2\operatorname{O}_{(l)} \longrightarrow \operatorname{NaOH}_{(aq)} + \frac{1}{2}\operatorname{H}_{2(g)} + \frac{1}{2}\operatorname{Cl}_{2(g)}$$

Hence, the pH of brine solution which is neutral will increase due to formation of NaOH.

#### OR

(a) 
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.403 - (-0.763)$$
  
= 0.36 V

The net cell reaction is  $\operatorname{Zn}_{(s)} + \operatorname{Cd}_{(aq)}^{2+} \rightarrow \operatorname{Zn}_{(aq)}^{2+} + \operatorname{Cd}_{(s)}$ Here, value of n = 2

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$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$
  
= 0.36 -  $\frac{0.0591}{2} \log \frac{0.0004}{0.2}$   
= 0.36 -  $\frac{0.0591}{2} (-2.69) = 0.36 + 0.08 = 0.44 \text{ V}$   
 $\therefore \quad \Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 0.44$   
 $= -84920 \text{ J/mol}$   
(b)  $\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightarrow \text{Cu}_{(s)}$   
 $E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$   
= 0.34 -  $\frac{0.059}{2} \log \frac{1}{0.1} = 0.34 - \frac{0.059}{2} \log 10$   
 $= 0.34 - \frac{0.059}{2} \times (1) = 0.34 - 0.0295 = 0.3105 \text{ V}$   
When the concentration of  $\text{Cu}^{2+}$  ions is decreased.

When the concentration of  $Cu^{2+}$  ions is decreased, the potential for copper electrode decreases.

**32.** (a) (i) Single O—O bond is weaker than S—S bond because of high interelectronic repulsions between the lone pair and bond pair of O—O bond, as a result catenation property is weaker in oxygen. (ii) In SF<sub>6</sub> molecule, sulphur is surrounded by six fluorine atoms which protect it from attack by reagents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. So,  $H_2O$  cannot attack SF<sub>6</sub> easily.

(iii) HF does not attack on wax but attacks sodium silicate which is the main constituent of glass. As a result, the glass bottles are slowly corroded or eaten up by HF.

 $Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$ 

(b) (i) Acidified  $K_2Cr_2O_7$  turns green due to formation of chromium sulphate.

$$\begin{array}{c} \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \\ \text{(Orange)} & \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \\ & \text{(Green)} \end{array}$$

(ii) Cl will replace I.  $2\text{NaI}_{(aq)} + \text{Cl}_{2(g)} \longrightarrow 2\text{NaCl}_{(aq)} + \text{I}_{2(s)}$ 

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#### OR

(a) The basic character decreases from  $NH_3$  to  $BiH_3$ . The basic nature is due to the presence of lone pair of electrons on the central atom.  $NH_3$  is the strongest electron pair donor due to its small size as the electron density of the electron pair is concentrated over a small region. As the size increases the electron

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density gets diffused over a large region and hence the ability to donate the electron pair (basic nature) decreases.

(b) (i)  $H_2O < H_2S < H_2Se < H_2Te$ 

As the atomic size increases down the group, the bond length increases and hence, the bond strength decreases. Consequently, the cleavage of E—H

bond (E = O, S, Se, Te, etc.) becomes easier. As a result, the tendency to release hydrogen as proton increases *i.e.*, acidic strength increases down the group.

(ii) The acidic strength of the hydrohalic acids in the order :

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

(c) (i) 
$$2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$
  
(ii)  $3Cu + 8HNO_3 (dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ 

**33.** (a) Formula of the compound 'C' indicates it is an amine. Since it is obtained by the reaction of  $Br_2$  and KOH with the compound 'B' so compound 'B' can be an amide. As 'B' is obtained from compound 'A' by reaction with ammonia followed by heating so, compound 'A' could be an aromatic acid. Formula of compound 'C' shows it to be aniline, then 'B' is benzamide and compound 'A' is benzoic acid. The sequence of reactions can be written as follows :



(b) (i) Aniline gives white or brown precipitate with bromine water.



Ethylamine does not react with bromine water. (ii) When heated with an alcoholic solution of KOH and CHCl<sub>3</sub>, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

OR

(a) (i) In Friedel — Crafts reaction,  $AlCl_3$  is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel — Crafts reaction.

$$\overset{\text{in}_2}{\bigcirc} + \text{AlCl}_3 \longrightarrow \overleftarrow{\bigcirc} - \overset{+}{\text{NH}_2 \text{AlCl}_3}$$

(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$$R - X \xrightarrow[-HX]{\text{NH}_3} R - \text{NH}_2 \xrightarrow[-HX]{R-X} R_2 \text{NH} \xrightarrow[-HX]{R-X} R_3 \text{N} \xrightarrow[-HX]{R-X} R_4 \text{N}^+ X^-$$

(b) (i) Amines like ammonia are good nucleophiles. This is because alkyl group in an amine shows electron releasing effect. This increases the electron density on 'N' of amino group and hence, makes the amines very good nucleophiles.

(ii) Due to resonance in aniline, the lone pair of electrons on nitrogen gets delocalised over the benzene ring and becomes less available for protonation.



In alkyl amine, alkyl group releases electrons and increases electron density on nitrogen, making it stronger base.

(c)  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ 

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

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