# **SAMPLE QUESTION PAPER**



### **BLUEPRINT**

Time Allowed : 3 hours

#### Maximum Marks: 70

S. No.	Chapter	MCQs, A & R (1 mark)	VSA (2 marks)	SA (3 marks)	Case Based (4 marks)	LA (5 marks)	Total
1.	Solutions	2(2)	1(2)	1(3)	_	_	4(7)
2.	Electrochemistry	2(2)	_	1(3)	1(4)*	_	4(9)
3.	Chemical Kinetics	2(2)	_	_	_	1(5)*	3(7)
4.	The <i>d</i> - and <i>f</i> -Block Elements	_	_	1(3)*	1(4)*	_	2(7)
5.	Coordination Compounds	2(2)	_	_	_	1(5)*	3(7)
6.	Haloalkanes and Haloarenes	1(1)	1(2)	1(3)	_	_	3(6)
7.	Alcohols, Phenols and Ethers	1(1)	_	_	_	1(5)*	2(6)
8.	Aldehydes, Ketones and Carboxylic Acids	3(3)	1(2)	1(3)	_	_	5(8)
9.	Amines	1(1)	1(2)	1(3)	_	_	3(6)
10.	Biomolecules	2(2)	1(2)*	1(3)	_	_	4(7)
	Total	16(16)	5(10)	7(21)	2(8)	3(15)	33(70)

\*It is a choice based question.

### Subject Code : 043

### CHEMISTRY

Time Allowed : 3 Hours

### General Instructions :

### Read the following instructions carefully.

- (a) There are 33 questions in this question paper with internal choice.
- (b) SECTION A consists of 16 multiple-choice questions carrying 1 mark each.
- (c) SECTION B consists of 5 short answer questions carrying 2 marks each.
- (d) SECTION C consists of 7 short answer questions carrying 3 marks each.
- (e) SECTION D consists of 2 case-based questions carrying 4 marks each.
- (f) SECTION E consists of 3 long answer questions carrying 5 marks each.
- (g) All questions are compulsory.
- (*h*) Use of log tables and calculators is not allowed.

### SECTION A

### The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

- 1. Which one of the following compounds is more reactive towards  $S_N1$  reaction?
  - (a)  $CH_2 = CHCH_2Br$
  - (b) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br
  - (c)  $C_6H_5CH(C_6H_5)Br$
  - (d) C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)Br
- 2. Which radioactive isotope would have the longer half-life <sup>15</sup>O or <sup>19</sup>O? (Given rate constants (*k*) for <sup>15</sup>O and <sup>19</sup>O are  $5.63 \times 10^{-3}$  s<sup>-1</sup> and  $2.38 \times 10^{-2}$  s<sup>-1</sup> respectively.)
  - (a) <sup>15</sup>O
  - (b) <sup>19</sup>O

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- (c) Both will have the same half-life.
- (d) None of the above, information given is insufficient.
- 3. The oxidation of toluene to benzaldehyde by chromyl chloride is called
  - (a) Etard reaction (b) Riemer-Tiemann reaction
  - (c) Stephen reaction (d) Cannizzaro reaction.
- 4. What will be the molality of a solution of glucose in water which is 10% w/W?
  - (a) 0.01 m (b) 0.617 m (c) 0.668 m (d) 1.623 m
- 5. What is the molar conductance at infinite dilution for sodium chloride if the molar conductance at infinite dilution of Na<sup>+</sup> and Cl<sup>-</sup> ions are  $51.12 \times 10^{-4}$  S cm<sup>2</sup>/mol and  $73.54 \times 10^{-4}$  S cm<sup>2</sup>/mol respectively?
  - (a)  $124.66 \text{ S cm}^2/\text{mol}$  (b)  $22.42 \text{ S cm}^2/\text{mol}$
  - (c)  $198.20 \text{ S cm}^2/\text{mol}$  (d)  $175.78 \text{ S cm}^2/\text{mol}$
- 6. The major product of acid catalysed dehydration of 1-methylcyclohexanol is
  - (a) 1-methylcyclohexane (b)
  - (c) 1-cyclohexylmethanol
- (b) 1-methylcyclohexene
- (d) 1-methylenecyclohexane.

Maximum Marks : 70

SOP-4

7.	The	CFSE of [CoCl <sub>6</sub> ] <sup>3–</sup> is	s 1800	$00 \text{ cm}^{-1}$ , the CFSE for	[Co	$Cl_4]^-$ will be		
	(a)	$18000 \text{ cm}^{-1}$	(b)	$8000 \text{ cm}^{-1}$	(c)	$2000 \text{ cm}^{-1}$	(d)	$16000 \text{ cm}^{-1}$

- 8. Which of the following is a non-reducing sugar?
  - (a) Glucose (b) Sucrose
  - (c) Maltose (d) Lactose

**9.** Arrange the following in the increasing order of their boiling points :

- A: Butanamine, B: N,N-Dimethylethanamine, C: N-Ethylethanamine
- (a) C < B < A (b) A < B < C
- (c) A < C < B (d) B < C < A
- 10. A 5% solution (*w*/*W*) of cane sugar (molar mass = 342 g mol<sup>-1</sup>) has freezing point 271 K. What will be the freezing point of 5% glucose (molar mass = 18 g mol<sup>-1</sup>) in water if freezing point of pure water is 273.15 K?
  (a) 273.07 K
  (b) 269.07 K
  - (c) 273.15 K (d) 260.09 K
- 11.  $\alpha$ -Hydroxypropanoic acid can be prepared from ethanal by following the steps given in the sequence.
  - (a) Treat with HCN followed by acidic hydrolysis.
  - (b) Treat with NaHSO<sub>3</sub> followed by reaction with Na<sub>2</sub>CO<sub>3</sub>.
  - (c) Treat with  $H_2SO_4$  followed by hydrolysis.
  - (d) Treat with  $K_2Cr_2O_7$  in presence of sulphuric acid.
- 12. The molar conductivity of  $CH_3COOH$  at infinite dilution is 390 S cm<sup>2</sup>/mol. Using the graph and given information, the molar conductivity of  $CH_3COOK$  will be



13. Given below are two statements labelled as Assertion (A) and Reason (R).Assertion (A) : Proteins are found to have two different types of secondary structures *viz*. alpha-helix and beta-pleated sheet structure.

**Reason** (**R**) : The secondary structure of proteins is stabilized by hydrogen bonding.

Select the most appropriate answer from the options given below :

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- 14. Given below are two statements labelled as Assertion (A) and Reason (R).
   Assertion (A): Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
   Reason (P): Those aldehydes which have G H atom undergo Cannizzaro reaction.

**Reason** (R) : Those aldehydes which have  $\alpha$ -H atom undergo Cannizzaro reaction.

Select the most appropriate answer from the options given below :

- (a) Both A and R are true and R is the correct explanation of A.
- (b) Both A and R are true but R is not the correct explanation of A.
- (c) A is true but R is false.
- (d) A is false but R is true.
- 15. Given below are two statements labelled as Assertion (A) and Reason (R).
  Assertion (A): [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> gives white precipitate with barium chloride.
  Reason (R): The given complex dissociates in the solution to give Br<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. Select the most appropriate answer from the options given below:
  - (a) Both A and R are true and R is the correct explanation of A.
  - (b) Both A and R are true but R is not the correct explanation of A.
  - (c) A is true but R is false.
  - (d) A is false but R is true.
- 16. Given below are two statements labelled as Assertion (A) and Reason (R).Assertion (A): The rate of a reaction sometimes does not depend on concentrations.Reason (R): Lower the activation energy faster is the reaction.Select the most appropriate answer from the options given below:
  - (a) Both A and R are true and R is the correct explanation of A.
  - (b) Both A and R are true but R is not the correct explanation of A.
  - (c) A is true but R is false.
  - (d) A is false but R is true.

### SECTION B

### This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

- 17. Compare the basicity of the following compounds and arranged them in decreasing order.
  - (i)  $H_2C = CHCH_2NH_2$
  - (ii) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>
  - (iii)  $HC \equiv CCH_2NH_2$
- **18.** (i) Why is freezing point depression of 0.1 M sodium chloride solution nearly twice that of 0.1 M glucose solution?
  - (ii) At 300 K, 36 g of glucose present per litre in its solution has an osmotic pressure of 4.98 bar. If osmotic pressure of solution is 1.52 bar at the same temperature, what would be its concentration?
- **19.** Write the reaction and IUPAC name of the product formed when 2-methylpropanal (isobutyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis.
- **20.** Give reason for the following :
  - (a) During the electrophilic substitution reaction of haloarenes, *para*-substituted derivative is the major product.
  - (b) The product formed during  $S_N 1$  reaction is a racemic mixture.
- **21.** Account for the following :
  - (a) There are five -OH groups in glucose.
  - (b) Glucose is a reducing sugar.

### OR

What happens when D-glucose is treated with the following reagents?

- (a) Bromine water
- (b) HNO<sub>3</sub>

### **SECTION C**

### This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each.

- 22. (i) Write the structures of main products when benzenediazonium chloride  $(C_6H_5N_2^+Cl^-)$  reacts with the following reagents :
  - (a)  $HBF_4/\Delta$  (b) Cu/HBr
  - (ii) Write the structures of *A*, *B* and *C* in the following reactions :

(a) 
$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2/HCl} B \xrightarrow{C_6H_5OH} C$$

(b) 
$$CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$$

- 23. (a) Why does the cell voltage of a mercury cell remain constant during its lifetime?
  - (b) Write the reaction occurring at anode and cathode and the products of electrolysis of aq. NaCl.
  - (c) What is the pH of HCl solution when the hydrogen gas electrode shows a potential of -0.59 V at standard temperature and pressure?
- **24.** (a) How are vitamins classified? Give examples.
  - (b) Name the vitamin whose deficiency causes
    - (i) night blindness
    - (ii) pernicious anaemia.
- **25.** (a) State Henry's law and explain why are the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
  - (b) Assume that argon exerts a partial pressure of 6 bar. Calculate the mol fraction of argon gas in water. (Given Henry's law constant for argon dissolved in water,  $K_{\rm H} = 40$  kbar)
- 26. Answer the following questions (any 2) :
  - (a) What is the effect of pH on dichromate ion solution?
  - (b) Why Cu<sup>+</sup> ion is not stable in aqueous solution?
  - (c) Why Scandium (at. no. 21) salts are white in colour?
- 27. (a) Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction.
  - (b) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes and vinylic halides?



- **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?

### SECTION D

### The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

**29.** Most of the transition metal compounds are coloured due to the presence of incomplete *d*-subshell in transition metal ions.

In free isolated gaseous ion the five *d* orbitals are degenerate, *i.e.* they are identical in energy. In real life situations, the ion will be surrounded by solvent molecules if it is in solution; by other ligands if it is in a complex; or by other ions if it is in crystal lattice. The surrounding groups affect the energy of some *d* orbitals more than others. Thus the *d* orbitals are no longer degenerate, and they form two groups of orbitals of different energies. Thus in transition element ions with a partly filled *d* shell, it is possible to promote electrons from *d* level to another *d* level of higher energy. This corresponds to a fairly small energy difference and so light is absorbed in the visible region. The colour of a transition meltal complex is dependent on how big the energy difference is between the two *d* levels. This in turn depends on the nature of the ligand, and on the type of complex formed. Thus the octahedral complex [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> is blue, [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> is green and [Ni(NO<sub>2</sub>)<sub>6</sub>]<sup>4-</sup> is brown-red. The colour also depends on the number of ligands and the shape of the complex formed.

### Answer the following questions :

(a) Copper(I) compounds are white whereas copper(II) compounds are coloured. Give reason.

#### OR

How would you account for the following : Transition metals form coloured compounds?

- (b)  $K_2Cr_2O_7$  is orange coloured though Cr(VI) has  $d^0$  configuration. Explain.
- (c) Which of following cations are coloured in aqueous solutions and why? Sc<sup>3+</sup>, V<sup>3+</sup>, Ti<sup>4+</sup>, Mn<sup>2+</sup>

(At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)

30. Consider the following table of standard reduction potentials :

Reduction half reactions	E° values (V)			
$A^{3+} + 2e^{-} \longrightarrow A^{+}$	1.47			
$B^{2+} + 2e^- \longrightarrow B$	0.60			

$C^{2+} + 2e^{-}$	$\rightarrow C$	-0.21
$D^{+} + e^{-}$	$\rightarrow D$	-1.38

### Answer the following questions :

- (a) Name the strongest reducing agent.
- (b) Name the substance(s) that can be oxidised by  $A^{3+}$  ions easily.
- (c) Calculate the value of  $E^{\circ}$  for the possible overall cell reaction that delivers the highest voltage.

### OR

Name the substance(s) that can be oxidised by  $B^{2+}$ .

### **SECTION E**

### The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

- 31. Attempt any five of the following :
  - (a) What will be the magnetic moment of complex, Cs[FeCl<sub>4</sub>]?
  - (b) What is meant by chelate effect?

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- (c) Which of the following is more stable complex and why?  $[Co(NH_3)_6]^{3+}$  and  $[Co(en)_3]^{3+}$
- (d) NH<sub>2</sub>.NH<sub>2</sub> although possesses two electron pairs for donation but does not act as chelating agent, why?
- (e) Out of NH<sub>3</sub> and CO, which ligand forms a more stable complex with a transition metal and why?
- (f) Arrange the following complexes in the increasing order of conductivity of their solution :  $[Co(NH_3)_3Cl_3], [Co(NH_3)_4Cl_2]Cl, [Co(NH_3)_6]Cl_3, [Cr(NH_3)_5Cl]Cl_2$
- (g) What is the magnetic behaviour of the complex  $[Fe(en)_2Cl_2]Cl$ ?
- **32.** An ether  $A(C_5H_{12}O)$  when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis forms compounds *B* and *C*. Oxidation of *B* gives an acid *D* whereas oxidation of *C* gives a ketone *E*. Deduce the structures of *A*, *B*, *C*, *D* and *E*.

### OR

Compound (*A*) gives positive Lucas test in 5 minutes. When 6.0 g of (*A*) is treated with Na metal, 1120 mL of  $H_2$  is evolved at STP. Assuming (*A*) to contain one oxygen per molecule, write structural formula of (*A*). Compound (*A*) when treated with PBr<sub>3</sub> gives (*B*) which when treated with benzene in presence of anhydrous AlCl<sub>3</sub> gives (*C*). What are (*B*) and (*C*)?

- **33.** (a) A reaction is first order with respect to *A* and second order with respect to *B*.
  - (i) Write the differential rate equation.
  - (ii) How is the rate affected on increasing the concentration of *B* three times keeping concentration of *A* constant?
  - (iii) How is the rate affected when the concentrations of both *A* and *B* are doubled?
  - (b) With the help of an example explain what is meant by pseudo first order reaction.

OR

The initial rate of reaction :

 $A + 5B + 6C \longrightarrow 3D + 3E$ 

has been determined by measuring the rate of disappearance of A under the following conditions :

Expt. No.	[A] <sub>0</sub> (M)	[ <i>B</i> ] <sub>0</sub> (M)	[C] <sub>0</sub> (M)	Initial rate (M min <sup>-1</sup> )
1.	0.02	0.02	0.02	$2.08 \times 10^{-3}$
2.	0.01	0.02	0.02	$1.04 \times 10^{-3}$
3.	0.02	0.04	0.02	$4.16 \times 10^{-3}$
4.	0.02	0.02	0.04	$8.32 \times 10^{-3}$

- (i) Determine the order of reaction with respect to each reactant.
- (ii) What is the rate constant?
- (iii) Calculate the initial rate of the reaction when the concentration of all the reactants is 0.01 M.

## **Self Evaluation Sheet**

Once you complete **SQP-4**, check your answers with the given solutions and fill your marks in the marks obtained column according to the marking scheme. Performance Analysis Table given at the bottom will help you to check your readiness.



Q.No.	Chapter	Marks Per Question	Marks Obtained
1	Haloalkanes and Haloarenes	1	
2	Chemical Kinetics	1	
3	Aldehydes, Ketones and Carboxylic Acids	1	
4	Solutions	1	
5	Electrochemistry	1	
6	Alcohols, Phenols and Ethers	1	
7	Coordination Compounds	1	
8	Biomolecules	1	
9	Amines	1	
10	Solutions	1	
11	Aldehydes, Ketones and Carboxylic Acids	1	
12	Electrochemistry	1	
13	Biomolecules	1	
14	Aldehydes, Ketones and Carboxylic Acids	1	
15	Coordination Compounds	1	
16	Chemical Kinetics	1	
17	Amines	2	
18	Solutions	2	
19	Aldehydes, Ketones and Carboxylic Acids	2	
20	Haloalkanes and Haloarenes	2	
21	Biomolecules	2	
22	Amines	3	
23	Electrochemistry	3	
24	Biomolecules	3	
25	Solutions	3	
26	The <i>d</i> - and <i>f</i> -Block Elements	3	
27	Haloalkanes and Haloarenes	3	
28	Aldehydes, Ketones and Carboxylic Acids	3	
29	The <i>d-</i> and <i>f-</i> Block Elements	1 + 1 + 2	
30	Electrochemistry	1 + 1 + 2	
31	Coordination Compounds	5	
32	Alcohols, Phenols and Ethers	5	
33	Chemical Kinetics	5	
L	Total	70	
		Percentage	%

### **Performance Analysis Table**

- If your marks is
- Section 2000 TREMENDOUS!
- 81-90% EXCELLENT!
- 71-80% VERY GOOD!
- (C) 61-70% GOOD!
- **51-60%** FAIR PERFORMANCE!
- (AVERAGE!
- > You are done! Keep on revising to maintain the position.
- > You have to take only one more step to reach the top of the ladder. Practise more.
- > A little bit of more effort is required to reach the 'Excellent' bench mark.
- Revise thoroughly and strengthen your concepts.
- Need to work hard to get through this stage.
- > Try hard to boost your average score.



### 1. (c) : $C_6H_5CH(C_6H_5)Br \longrightarrow [C_6H_5CH(C_6H_5)]$

Here, carbocation formed is more stable through resonance with two benzene rings.

**2.** (a) : The rate constant for the decay of O-15 is less than that for O-19. Therefore, the rate of decay of O-15 will be slower and will have a longer half life.

3. (a)

4. (b): Mass of solution = 100 gMass of glucose = 10 g, Mass of water = 90 g

No. of moles of glucose =  $\frac{10}{180}$  = 0.0555 mol

Molality =  $\frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0555 \text{ mol}}{0.090 \text{ kg}} = 0.617 \text{ m}$ 

5. (a) : Molar conductance of NaCl =  $\lambda_{Na}^{+} + \lambda_{Cl}^{-}$ 

= 
$$51.12 \times 10^{-4} + 73.54 \times 10^{-4}$$
  
=  $124.66 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$   
H<sub>3</sub>C  
H<sub>3</sub>C  
OH  
H<sub>2</sub>SO<sub>4</sub>/ $\Delta$   
(b):  $H_2SO_4/\Delta$ 

According to Saytzeff rule, highly substituted alkene is major product. Here, dehydration reaction takes place, alkene is formed due to the removal of a water molecule.

7. **(b)**: Using equation, 
$$\Delta_t = \frac{4}{2} \Delta_a$$

 $\Delta_t = (4/9) \times 18000 \text{ cm}^{-1} = 8000 \text{ cm}^{-1}$ 

8. (b): Disaccharides such as sucrose in which the two monosaccharides units are linked through their reducing centres, *i.e.*, aldehydic or ketonic groups are non-reducing sugars.

9. (d): B < C < A

In primary amine, intermolecular association due to H-Bonding is maximum while in tertiary, it is minimum.

**10.** (**b**): 
$$\Delta T_f = \frac{K_f \times W_B}{M_B \times W_A}$$

For cane sugar solution, 2.15 K =  $\frac{K_f \times 5}{342 \times 0.095}$ (95 g of water = 0.095 kg)

For glucose solution,  $\Delta T_f = \frac{K_f \times 5}{180 \times 0.095}$ 

$$\frac{\Delta T_f}{2.15} = \frac{K_f \times 5}{180 \times 0.095} \times \frac{342 \times 0.095}{K_f \times 5}$$
$$\Delta T_f = \frac{342}{180} \times 2.15 = 4.085 \text{ K}$$

Freezing point of glucose solution = 273.15 - 4.085= 269.07 K 11. (a):



12. (b):  $\Lambda^{\circ}_{CH_{3}COOK} = \Lambda^{\circ}_{CH_{3}COOH} + \Lambda^{\circ}_{KCl} - \Lambda^{\circ}_{HCl}$ = 390 + 150 - 425 = 115 S cm<sup>2</sup>/mol

13. (b)

14. (c) : The aldehydes which have  $\alpha$ -H atoms, undergo aldol condensation. Those aldehydes which do not contain  $\alpha$ -H atoms undergo Cannizzaro reaction.

**15.** (c) : The complex dissociates to give  $[Co(NH_3)_5Br]^{2+}$  and  $SO_4^{2-}$  ions.  $SO_4^{2-}$  ion reacts with barium chloride to give white ppt. of BaSO<sub>4</sub>.

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 + 2Cl^-$$
  
(while ppt.)

16. (b)

17. The significant difference among these three bases depends on hybridisation of  $\beta$ -carbon atom. The compounds containing carbon with more *s*-character show more electron withdrawing nature and hence least basic. Thus, decreasing order of basicity is (ii) > (i) > (ii).

**18.** (i) Sodium chloride being a strong electrolyte completely dissociates in the solution while glucose does not dissociate. The number of particles in sodium chloride solution becomes double than that of glucose solution. Hence, freezing point depression of sodium chloride is nearly twice that of glucose solution of same molarity, because it is a colligative property.

(ii)  $\pi = CRT$ 

R and T are same in both cases hence

$$\frac{\pi_1}{\pi_2} = \frac{C_1}{C_2}$$
 or,  $C_2 = \frac{\pi_2 C_1}{\pi_1}$ 

Molarity of first solution

$$\stackrel{\text{H}^{+}/\text{H}_{2}\text{O}}{\longrightarrow} (CH_{3})_{2}CHCH-CH_{2}CH_{3} \longleftarrow (CH_{3})_{2}CHCH(C_{2}H_{5})(OH)$$
2-Methylpentan-3-ol

**20.** (a) At the *ortho* position, higher steric hindrance is present, hence *para* isomer is usually predominant and is obtained in the major amount.

(b) During the  $S_N 1$  mechanism, intermediate carbocation formed is  $sp^2$  hybridized and planar in nature. This allows the

attack of nucleophile from either side of the plane resulting in a racemic mixture.

**21.** (a) Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five —OH groups. Since it exists as a stable compound, five —OH groups should be attached to different carbon atoms.



(b) 
$$CH_3Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$
  
 $A \xrightarrow{B}$   
 $CH_3CH_2OH \xleftarrow{HNO_2}$ 

**23.** (a) The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its lifetime. (b) NaCl<sub>(a)</sub>  $\rightleftharpoons$  Na<sup>+</sup><sub>(a)</sub> + Cl<sup>-</sup><sub>(a)</sub>

Cathode : 
$$H_2O_{(l)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$$
  
Anode :  $Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$   
Net reaction :  $NaCl_{(aq)} + H_2O_{(l)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(q)} + \frac{1}{2}H_{$ 

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$$

(c) Given, potential of hydrogen gas electrode = -0.59 V

2

Electrode reaction: 
$$H^+ + e^- \longrightarrow \frac{1}{2}H$$
  
Applying Nernst equation,

$$E_{(H^+/H_2)} = E_{(H^+/H_2)}^{\circ} - \frac{0.059}{n} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$E_{(H^+/H_2)}^{\circ} = 0 V$$

$$E_{(H^+/H_2)} = -0.59 V$$

$$n = 1$$

$$[H_2] = 1 \text{ bar}$$

$$-0.59 = 0 - 0.059 (-\log [H^+])$$

$$-0.59 = -0.059 \text{ pH}$$

$$\therefore \text{ pH} = 10$$

**24.** (a) Vitamins are classified into two groups depending upon their solubility in water or fat.

**Fat soluble vitamins :** Vitamins which are soluble in fat and oils but insoluble in water are kept in this group. These are vitamins A, D, E and K.

**Water soluble vitamins :** These vitamins are soluble in water but insoluble in fat. B group vitamins and vitamin C are the examples. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (except vitamin  $B_{12}$ ) in our body.

(b) (i) Vitamin A (ii) Vitamin  $B_{12}$ 

**25.** (a) Henry's law : The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

The pressure underwater is high, so the solubility of gases in blood increases. When the diver comes to surface, the pressure decreases and so does the solubility, causing bubbles of nitrogen in blood. To avoid this situation the dilution of air is done.

(b) Using equation 
$$p = K_{\rm H} \times x$$

mole fraction of argon in water,  $x = p/K_{\rm H} = 6/40 \times 10^3$ =  $1.5 \times 10^{-4}$ 

**26.** (a) The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution) of dichromate ions

(p-Hydroxyazobenzene)

a colour change from orange to yellow is observed as dichromate ions change to chromate ions.

(b) In aqueous solutions,  $Cu^+$  undergoes disproportionation to form a more stable  $Cu^{2+}$  ion.

$$2\mathrm{Cu}^+_{(aq)} \longrightarrow \mathrm{Cu}^{2+}_{(aq)} + \mathrm{Cu}_{(s)}$$

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

(c) Only those ions are coloured which have partially filled d-orbitals facilitating d-d transitions.

However, in case of  $Sc^{3+}$  salts, as the *d*-orbital is empty after the formation of compound, there is no *d*-*d* transition. Thus, the compounds appear white.

**27.** (a) The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1-cyclohexylethene. The reagent which is used to carry out the reaction is ethanolic KOH.

(b) Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character of C-*X* bond in haloarenes and vinylic halides. Hence, they do not undergo nucleophilic reactions easily.

(c) The IUPAC name of the given compound is 3-bromo-1-chlorocyclohexene.



**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.

$$CH_{3}CH_{2}CH_{2} - CH_{2} + NaOH + I_{2} \rightarrow CHI_{3} + CH_{3}CH_{2}CH_{2}COONa$$

$$(HI_{3}) + CH_{3}CH_{2}CH_{2}COONa$$

$$(HI_{3}) + CH_{3}CH_{2}CH_{2}COONa$$

CH<sub>3</sub>CH<sub>2</sub> $-C-CH_2CH_3 \xrightarrow{I_2 /NaOH}$  No yellow ppt.of CHI<sub>3</sub> (b) (*A*) is a carboxylic acid, (*B*) is an alcohol and (*C*) is an ester.

$$RCH_{2}OH \xrightarrow{\text{alk. KMnO}_{4}} RCOOH$$

$$(B) \qquad (A)$$

$$RCOOH \xrightarrow{\text{LiAlH}_{4}} RCH_{2}OH$$

$$(B) \qquad (B)$$

$$RCOOH \xrightarrow{\text{RCOOH}} RCH_{4}OH \xrightarrow{\text{H}_{2}SO_{4}} RCOOH$$

**29.** (a) Cu(I) compounds have completely filled *d*-orbitals and there are no vacant *d*-orbitals for promotion of electrons whereas Cu(II) compounds have one unpaired electron which is responsible for colour formation.

#### OR

Due to presence of vacant *d*-orbitals and *d*-*d* transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

(b) The orange colour of  $Cr_2O_7^{2-}$  ion or  $K_2Cr_2O_7$  is not due to *d*-*d* transition but due to charge transfer, *i.e.*, momentary transfer of charge from oxygen atom to metal atom thereby changing  $O^{2-}$  ion momentarily to  $O^{-}$  ion and reducing the oxidation state of Cr from + 6 to + 5.

(c) Only those ions will be coloured which have partially filled *d*-orbitals. Ions with  $d^0$  and  $d^{10}$  will be colourless.

From electronic configuration of the ions,  $V^{3+}(3d^2)$  and  $Mn^{2+}(3d^5)$  are coloured. Ti<sup>4+</sup>(3d<sup>0</sup>) and Sc<sup>3+</sup>(3d<sup>0</sup>) are colourless.

**30.** (a) *D* is strongest reducing agent having the minimum reduction potential.

(b) B, C and D can be oxidised by  $A^{3+}$  ions. (c) At cathode:  $A^{3+} + 2e^- \longrightarrow A^+$  $E_{\rm red}^{\circ} = 1.47$ ; highest reduction potential. At anode :  $D \longrightarrow D^+ + e^ E_{\text{oxid}}^{\circ} = 1.38$ ; highest oxidation potential.  $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxid}}^{\circ} = 1.47 + 1.38 = 2.85 \text{ V}$ OR  $B^{2+} + 2e^{-} \longrightarrow B \text{ (reduction)}, E^{\circ}_{\text{red}} = 0.60 \text{ V}$   $C \longrightarrow C^{2+} + 2e^{-} \text{ (oxidation)}, E^{\circ}_{\text{oxid}} = 0.21 \text{ V}$  $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxid}}^{\circ} = 0.60 + 0.21 = 0.81 \text{ V}$  $E_{cell}^{o}$  is positive, spontaneous.  $D \longrightarrow D^+ + e^-$  (oxidation),  $E_{\text{oxid}}^\circ = 1.38 \text{ V}$  $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxid}}^{\circ} = 0.60 + 1.38 = 1.98 \text{ V}$  $E_{\text{cell}}^{\circ}$  is positive, spontaneous.  $A^+$  cannot be oxidised;  $A^+ \longrightarrow A^{3+} + 2e^-$ ;  $E_{\text{oxid}}^\circ = -1.47 \text{ V}$  $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{oxid}}^{\circ} = 0.60 - 1.47 = -0.87 \text{ V}$  $E^{\circ}_{cell}$  is negative, non-spontaneous. Only *C* and *D* can be oxidised by  $B^{2+}$  ion.

**31.** (a) Cs[FeCl<sub>4</sub>] Electronic configuration of Fe<sup>3+</sup> :  $3d^5$ Magnetic moment :

$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.92$$
 B.M.

(b) When a bidentate or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a chelating ligand. Chelating ligands form more stable complexes than monodentate analogs. This is called chelate effect.

(c)  $[Co(en)_3]^{3+}$  is more stable complex than  $[Co(NH_3)_6]^{3+}$  due to chelate effect as it forms rings.

(d)  $\ddot{N}H_2$ — $\ddot{N}H_2$  have two donor atoms, it can form three membered ring which is very strained, thus it can not act as chelating agent.

(e) In CO both lone pair of electrons and vacant  $\pi^*$  orbitals are present. Hence, it acts as electron pair  $\sigma$  donor as well as  $\pi$ 

acceptor by back bonding. Hence, M-CO bond is stronger.

$$M \stackrel{\pi}{\overleftarrow{\phantom{a}\sigma}} CO$$

NH<sub>3</sub> is electron pair donor only. Accumulation of negative charge on the metal ion takes place, hence M-NH<sub>3</sub> bond is weaker.

$$M \leftarrow \mathrm{NH}_3$$

(f)  $[Co(NH_3)_3Cl_3] < [Cr(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2$  $< [Co(NH_3)_6]Cl_3$ 

Conductivity depends on the number of ions produced in the solution. In the order given above the complexes, produce 1, 2, 3 and 4 ions respectively.

(g) Paramagnetic due to presence of one unpaired electron.

 $-CH \frac{Conc. HI ga}{Conc. HI ga}$ CH<sub>3</sub>CH<sub>2</sub>—O-→CH₃CH₂I + CH₃· CH<sub>3</sub> Hydrolysis (A)Hydrolysis CH<sub>3</sub>CH<sub>2</sub>OH CH<sub>3</sub>-CH-CH<sub>3</sub> Primary alcohol I Secondary OH alcohol (B)[0] [O] (C) C--CH<sub>3</sub> CH<sub>3</sub>COOH CH<sub>3</sub>-(D)Ô (E)R

(A) gives Lucas test within 5 minutes which shows that (A)is a secondary alcohol.

(A) contains one O-atom and thus, only one -OH group is present in (A). Thus, (A) is  $C_n H_{2n+1}$  OH.

1120 mL of  $H_2$  is evolved when 6 g (A) is treated with Na metal.

11200 mL of H<sub>2</sub> is evolved when

 $(6 \times 11200)/1120 = 60 \text{ g}(A)$  is treated with Na metal.

Since one mole of alcohol having one -OH group gives 11200 mL H<sub>2</sub> at STP with Na hence, molecular mass of (A) is 60. *i.e.*, molecular mass of  $C_n H_{2n+1}OH = 60$ ; n = 3

or (A) is  $C_3H_7OH$ ; being secondary alcohol its formula is CH<sub>3</sub>CHOHCH<sub>3</sub>.

Reactions involved :



**33.** (a) (i) Reaction is first order in *A* and second order in *B*, hence differential rate equation is

 $= k[A][B]^2$ dt (ii) Rate =  $k[A][B]^2$ If [*B*] is tripled, Rate =  $k[A][3B]^2 = 9[A][B]^2$  Thus, rate of reaction increases 9 times. (iii) If both [A] and [B] a

(iii) If both [*A*] and [*B*] are doubled,  
Rate = 
$$k [2A][2B]^2 = 8[A][B]^2$$

Thus, rate of reaction increases 8 times.

(b) The reactions which are of second order but behave like first order reactions are called pseudo first order reactions e.g., during hydrolysis of ethyl acetate (ester) with water, the concentration of water does not alter much during the reaction. So, in the rate equation the concentration of water (the reactant which is in excess) can be taken as constant hence, the reaction behaves as first order reaction.

 $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$ Rate = k'[CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>][H<sub>2</sub>O], the term [H<sub>2</sub>O] can be taken as constant. Hence, the rate equation becomes Rate = k[CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>] where k = k'[H<sub>2</sub>O]

#### OR

(i) Rate law may be written as : Rate =  $k[A]^a[B]^b[C]^c$ Comparing experiments 1 and 2,  $(\text{Rate})_1 = k(0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-3}$ ...(i)  $(\text{Rate})_2 = k(0.01)^a (0.02)^b (0.02)^c = 1.04 \times 10^{-3}$ ...(ii) Dividing eq. (i) by eq. (ii) we get,

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{(0.02)^a}{(0.01)^a} = \frac{2.08 \times 10^{-3}}{1.04 \times 10^{-3}} = 2$$

or 
$$2^{a} = 2$$
  $\therefore$   $a = 1$   
Comparing experiments 1 and 3,

$$(\text{Rate})_1 = k(0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-3}$$
 ...(iii)

$$(\text{Rate})_3 = k(0.02)^a (0.04)^b (0.02)^c = 4.16 \times 10^{-3}$$
 ...(iv)  
Dividing eq. (iv) by eq. (iii) we get,

$$\frac{(\text{Rate})_3}{(\text{Rate})_1} = \frac{(0.04)^b}{(0.02)^b} = \frac{4.16 \times 10^{-3}}{2.08 \times 10^{-3}} = 2$$
  
$$2^b = 2 \quad \therefore \quad b = 1$$

Comparing experiments 1 and 4, ->a/- ->h/- ->C 1 /

$$(\text{Rate})_1 = k(0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-5}$$
 ...(v)

$$(\text{Rate})_4 = k(0.02)^u (0.02)^v (0.04)^v = 8.32 \times 10^{-5} \qquad \dots \text{(vi)}$$

Dividing eq. (vi) by eq. (v), we get

$$\frac{(\text{Rate})_4}{(\text{Rate})_1} = \frac{(0.04)^c}{(0.02)^c} = \frac{8.32 \times 10^{-3}}{2.08 \times 10^{-3}} = 4$$

or  $2^c = 2^2$  : c = 2Therefore, the order of the reaction with respect to A, B and C are 1, 1 and 2 respectively.

Rate =  $k[A][B][C]^2$ 

(ii) Substituting the values from expt. 1, we get

2.08 × 10<sup>-3</sup> = k × 0.02 × 0.02 × (0.02)<sup>2</sup>  
∴ 
$$k = \frac{2.08 \times 10^{-3}}{(0.02)^4} = \frac{2.08 \times 10^{-3}}{16 \times 10^{-8}} = 1.3 \times 10^4 \,\mathrm{M^{-3}\,min^{-1}}$$

(iii) Rate of reaction when concentration of all reactants is 0.01 M,

Rate =  $1.3 \times 10^4 \times (0.01) \times (0.01) \times (0.01)^2$  $= 1.3 \times 10^{-4} \text{ M min}^{-1}$ 

 $\odot$ 

Chemistry