*General Instructions :*

Read the following instructions very carefully and follow them :

(i) This question paper contains 35 questions. All questions are compulsory.

(ii) Question paper is divided into FIVE sections – Section A, B, C, D and E.

(iii) *In section – A :* Question Numbers 1 to 18 are Multiple Choice (MCQ) type Questions carrying 1 mark each.

(iv) *In section – B :* Question Numbers 19 to 25 are Very Short Answer (VSA) type questions carrying 2 marks each.

(v) *In section – C :* Question Numbers 26 to 30 are Short Answer (SA) type questions carrying 3 marks each.

(vi) *In section – D :* Question Numbers 31 and 32 are case based questions carrying 4 marks each.

(vii) *In section – E :* Question Numbers 33 to 35 are Long Answer (LA) type questions carrying 5 marks each.

(viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section – B, 2 questions in Section – C, 2 questions in Section – D and 2 questions in Section – E.

(ix) Use of calculators is NOT allowed.

## SECTION – A

1. Which of the following molecules has a chiral centre correctly labelled with an asterisk (*) ? 1

   (a) $CH_3C^*HBrCH_3$      (b) $CH_3C^*HClCH_2Br$

   (c) $HOCH_2C^*H(OH)CH_2OH$      (d) $CH_3C^*Br_2CH_3$

2. Which of the following alcohols will not undergo oxidation ? 1
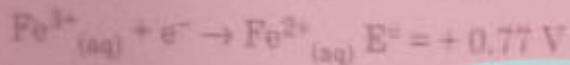
   (a) Butanol      (b) Butan-2-ol

   (c) 2-Methylbutan-2-ol      (d) 3-Methylbutan-2-ol

3. A voltaic cell is made by connecting two half cells represented by half equations below : 1

$$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)} \quad E^\circ = -0.14 \text{ V}$$

$$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)} \quad E^\circ = +0.77 \text{ V}$$
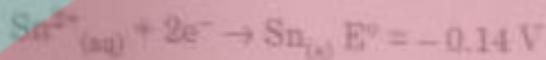
Which statement is correct about this voltaic cell ?

(a) $Fe^{2+}$ is oxidised and the voltage of the cell is $-0.91$ V

(b) Sn is oxidised and the voltage of the cell is $0.91$ V

(c) $Fe^{2+}$ is oxidised and the voltage of the cell is $0.91$ V

(d) Sn is oxidised and the voltage of the cell is $0.63$ V

4. Four half reactions I to IV are shown below : 1

I. $2Cl^- \rightarrow Cl_2 + 2e^-$

II. $4OH^- \rightarrow O_2 + 2H_2O + 2e^-$

III. $Na^+ + e^- \rightarrow Na$

IV. $2H^+ + 2e^- \rightarrow H_2$
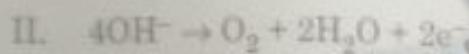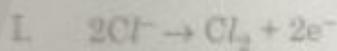
Which two of these reactions are most likely to occur when concentrated brine is electrolysed ?

(a) I and III                    (b) I and IV

(c) II and III                   (d) II and IV

5. Which property of transition metals enables them to behave as catalysts ? 1

(a) High melting point           (b) High ionisation enthalpy

(c) Alloy formation              (d) Variable oxidation states

6. In the two tetrahedral structures of dichromate ion 1

(a) 4 Cr – O bonds are equivalent in length.

(b) 6 Cr – O bonds are equivalent in length.

(c) All Cr – O bonds are equivalent in length.

(d) All Cr – O bonds are non-equivalent.

7. 1 mole of liquid A and 2 moles of liquid B make a solution having a total vapour pressure 40 torr. The vapour pressure of pure A and pure B are 45 torr and 30 torr respectively. The above solution    1

(a)   is an ideal solution.

(b)   shows positive deviation.

(c)   shows negative deviation.

(d)   is a maximum boiling azeotrope.

8. Which of the following would not be a good choice for reducing nitrobenzene to aniline ?    1

(a)   $LiAlH_4$              (b)   $H_2/Ni$

(c)   Fe and HCl           (d)   Sn and HCl

9. If molality of a dilute solution is doubled, the value of the molal elevation constant ($K_b$) will be    1

(a)   halved              (b)   doubled

(c)   tripled              (d)   unchanged

10. Hydrolysis of sucrose is called    1

(a)   inversion            (b)   hydration

(c)   esterification        (d)   saponification

11. Which one of the following has lowest $pK_a$ value ?    1

(a)   $CH_3 - COOH$            (b)   $O_2N - CH_2 - COOH$

(c)   $Cl - CH_2 - COOH$        (d)   HCOOH

12. Which of the following cell was used in Apollo space programme ?    1

(a)   Mercury cell           (b)   Daniel cell

(c)   $H_2-O_2$ Fuel cell       (d)   Dry cell

13. The following experimental rate data were obtained for a reaction carried out at 25 °C :

$$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$$

| Initial $[A_{(g)}]$/mol dm$^{-3}$ | Initial $[B_{(g)}]$/mol dm$^{-3}$ | Initial rate/mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|
| $3.0 \times 10^{-2}$ | $2.0 \times 10^{-2}$ | $1.89 \times 10^{-4}$ |
| $3.0 \times 10^{-2}$ | $4.0 \times 10^{-2}$ | $1.89 \times 10^{-4}$ |
| $6.0 \times 10^{-2}$ | $4.0 \times 10^{-2}$ | $7.56 \times 10^{-4}$ |

What are the orders with respect to $A_{(g)}$ and $B_{(g)}$ ?

| | Order with respect to $A_{(g)}$ | Order with respect to $B_{(g)}$ |
|---|---|---|
| (a) | Zero | Second |
| (b) | First | Zero |
| (c) | Second | Zero |
| (d) | Second | First |

14. The magnetic moment of $[NiCl_4]^{2-}$

   (a)  1.82 BM              (b)  2.82 BM

   (c)  4.42 BM              (d)  5.46 BM

   [Atomic number : Ni = 28]

For questions number 15 to 18, two statements are given – one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below :

(a)   Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(b)   Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(c)   Assertion (A) is true, but Reason (R) is false.

(d)   Assertion (A) is false, but Reason (R) is true.

15. **Assertion (A)** : Proteins are polymers of $\alpha$-amino acids connected by a peptide bond.

**Reason (R)** : A tetrapeptide contains 4 amino acids linked by 4 peptide bonds. 1

16. **Assertion (A)** : For a zero order reaction the unit of rate constant and rate of reaction are same.

**Reason (R)** : Rate of reaction for zero order reaction is independent of concentration of reactant. 1

17. **Assertion (A)** : Acetic acid but not formic acid can be halogenated in presence of red P and $Cl_2$.

**Reason (R)** : Acetic acid is a weaker acid than formic acid. 1

18. **Assertion (A)** : Trans $[Cr\ Cl_2(ox)_2]^{2-}$ shows optical isomerism. 1

**Reason (R)** : Optical isomerism is common in octahedral complexes involving didentate ligands.

## SECTION – B

19. (a) (i) What should be the signs (positive/negative) for $E°_{Cell}$ and $\Delta G°$ for a spontaneous redox reaction occurring under standard conditions ?

     (ii) State Faraday's first law of electrolysis. $2 \times 1 = 2$

### OR

    (b) Calculate the emf of the following cell at 298 K :

    $Fe_{(s)} \mid Fe^{2+} (0.01M) \parallel H^+_{(1M)} \mid H_{2(g)}$ (1 bar), $Pt_{(s)}$
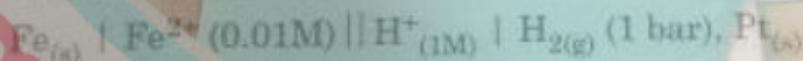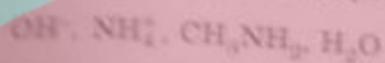
    Given $E°_{Cell} = 0.44$ V. 2

20. What happens to the rate constant k and activation energy $E_a$ as the temperature of a chemical reaction is increased ? Justify. 2

21. (a) Which of the following species cannot act as a ligand ? Give reason.

   $OH^-$, $NH_4^+$, $CH_3NH_2$, $H_2O$                                2 × 1 = 2

   (b) The complex $[Co(NH_3)_5(NO_2)]Cl_2$ is red in colour. Give IUPAC name of its linkage isomer.

22. Why is boiling point of o-dichlorobenzene higher than p-dichlorobenzene but melting point of para isomer is higher than ortho isomer ?                                2

23. For the pair phenol and cyclohexanol, answer the following :                                2 × 1 = 2

   (a) Why is phenol more acidic than cyclohexanol ?

   (b) Give one chemical test to distinguish between the two.

24. (a) (i) Draw the zwitter ion structure for sulphanilic acid.                                2 × 1 = 2

   (ii) How can the activating effect of $-NH_2$ group in aniline be controlled ?

OR

   (b) (i) Complete the reaction with the main product formed :                                2 × 1 = 2

   $N_2^+Cl^-$

   ⬡ $\xrightarrow{CH_3CH_2OH}$
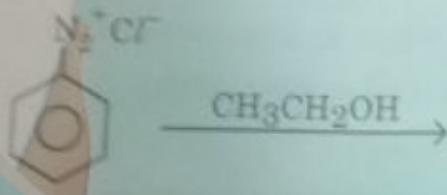
   (ii) Convert Bromoethane to Propanamine.

25. Give the reaction of glucose with hydrogen cyanide. Presence of which group is confirmed by this reaction ?                                2

## SECTION – C

26. (a) For the reaction $1 + 2 = 3$

$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$ at 318 K

calculate the rate of reaction if rate of disappearance of $N_2O_{5(g)}$ is $1.4 \times 10^{-3}$ m s$^{-1}$.

(b) For a first order reaction derive the relationship $t_{99\%} = 2t_{90\%}$.

27. (a) On the basis of crystal field theory write the electronic configuration for $d^5$ ion with a strong field ligand for which $\Delta_0 > P$. $1 + 2 = 3$

(b) $[Ni(CO)_4]$ has tetrahedral geometry while $[Ni(CN)_4]^{2-}$ has square planar yet both exhibit diamagnetism. Explain.
[Atomic number : Ni = 28]

28. (a) Illustrate Sandmeyer's reaction with an equation. $1 + 2 = 3$

(b) Explain, why $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in aqueous solution.

29. Give reasons for any 3 of the following observations : $3 \times 1 = 3$

(a) Penta-acetate of glucose does not react with hydroxylamine.

(b) Amino acids behave like salts.

(c) Water soluble vitamins must be taken regularly in diet.

(d) The two strands in DNA are complimentary to each other.

30. (a) (i) Why is the C – O bond length in phenols less than that in methanol ?

$3 \times 1 = 3$

(ii) Arrange the following in order of increasing boiling point :
Ethoxyethane, Butanal, Butanol, n-butane

(iii) How can phenol be prepared from anisole ? Give reaction.

### OR

(b) (i) Give mechanism of the following reaction : $2 + 1 = 3$

$$CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} CH_3CH_2 - O - CH_2CH_3 + H_2O$$

(ii) Illustrate hydroboration – oxidation reaction with an example.

## SECTION – D

31.

### Nucleophilic Substitution

Nucleophilic Substitution reaction of haloalkane can be conducted according to both $S_N1$ and $S_N2$ mechanisms. $S_N1$ is a two step reaction while $S_N2$ is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity : In $S_N1$ reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In $S_N2$ reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate ($S_N1$) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate ($S_N2$) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both $S_N1$ and $S_N2$ reaction, but with different results. Generally speaking weak polar solvent is favourable for $S_N2$ reaction, while strong polar solvent is favourable for $S_N1$. Generally speaking the substitution reaction of tertiary haloalkane is based on $S_N1$ mechanism in solvents with a strong polarity (for example ethanol containing water).

Answer the following questions :

(a) Why racemisation occurs in $S_N1$ ?     1

(b) Why is ethanol less polar than water ?     1

(c) Which one of the following in each pair is more reactive towards $S_N2$ reaction ?

   (i)    $CH_3 - CH_2 - I$ or $CH_3CH_2 - Cl$

                                          $2 \times 1$

   (ii) ⬡—$Cl$ or ⬡—$CH_2 - Cl$

### OR

(c) Arrange the following in the increasing order of their reactivity towards $S_N1$ reactions :

   (i)    2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

   (ii)   1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane     $2 \times 1$

32. Rahul set-up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity K and molar conductivity $\wedge_m$ and recorded his readings in tabular form.

| S.No. | Conc.(M) | $k$ S cm$^{-1}$ | $\wedge_m$ S cm$^2$ mol$^{-1}$ |
|-------|----------|-----------------|---------------------------------|
| 1. | 1.00 | $111.3 \times 10^{-3}$ | 111.3 |
| 2. | 0.10 | $12.9 \times 10^{-3}$ | 129.0 |
| 3. | 0.01 | $1.41 \times 10^{-3}$ | 141.0 |

Answer the following questions :

(a) Why does conductivity decrease with dilution ?     1

(b) If $\wedge_m^\circ$ of KCl is 150.0 S cm$^2$ mol$^{-1}$, calculate the degree of dissociation of 0.01 M KCl.     1

(c) If Rahul had used HCl instead to KCl then would you expect the $\wedge_m$ values to be more or less than those per KCl for a given concentration. Justify.     $2 \times 1$

### OR

(c) Amit, a classmate of Rahul repeated the same experiment with $CH_3COOH$ solution instead of $KCl$ solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul.

$2 \times 1$

## SECTION – E

33. (a) (i) Why is boiling point of 1M NaCl solution more than that of 1M glucose solution ?

$1 + 2 + 2 = 5$

(ii) A non-volatile solute 'X' (molar mass = 50 g mol$^{-1}$) when dissolved in 78g of benzene reduced its vapour pressure to 90%. Calculate the mass of X dissolved in the solution.

(iii) Calculate the boiling point elevation for a solution prepared by adding 10g of $MgCl_2$ to 200g of water assuming $MgCl_2$ is completely dissociated.

($K_b$ for Water = 0.512 K kg mol$^{-1}$, Molar mass $MgCl_2$ = 95g mol$^{-1}$)

OR

(b) (i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5 ?

$1 + 2 + 2 = 5$

(ii) Determine the osmotic pressure of a solution prepared by dissolving $2.32 \times 10^{-2}$g of $K_2SO_4$ in 2L of solution at 25 °C, assuming that $K_2SO_4$ is completely dissociated.

(R = 0.082 L atm K$^{-1}$ mol$^{-1}$, Molar mass $K_2SO_4$ = 174g mol$^{-1}$)

(iii) When 25.6g of Sulphur was dissolved in 1000g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of Sulphur ($S_x$).

($K_f$ for benzene = 5.12 K kg mol$^{-1}$, Atomic mass of Sulphur = 32g mol$^{-1}$)

34. (a) (i) Write the reaction involved in Cannizaro's reaction.

$1 + 1 + 3 = 5$

(ii) Why are the boiling point of aldehydes and ketones lower than that of corresponding carboxylic acids ?

(iii) An organic compound 'A' with molecular formula $C_5H_8O_2$ is reduced to n-pentane with hydrazine followed by heating with NaOH and Glycol. 'A' forms a dioxime with hydroxylamine and gives a positive Iodoform and Tollen's test. Identify 'A' and give its reaction for Iodoform and Tollen's test.

OR

(c) Amit, a classmate of Rahul repeated the same experiment with $CH_3COOH$ solution instead of $KCl$ solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul.                                                         2 × 1

## SECTION – E

33. (a) (i) Why is boiling point of 1M $NaCl$ solution more than that of 1M glucose solution ?                                                         1 + 2 + 2 = 5

   (ii) A non-volatile solute 'X' (molar mass = 50 g $mol^{-1}$) when dissolved in 78g of benzene reduced its vapour pressure to 90%. Calculate the mass of X dissolved in the solution.

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   **OR**

   (b) (i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5 ?                                                         1 + 2 + 2 = 5

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   **OR**

(b) (i) Give a chemical test to distinguish between ethanal acid and ethanoic acid. $1+1+3=5$

(ii) Why is the α-hydrogens of aldehydes and ketones are acidic in nature ?

(iii) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.
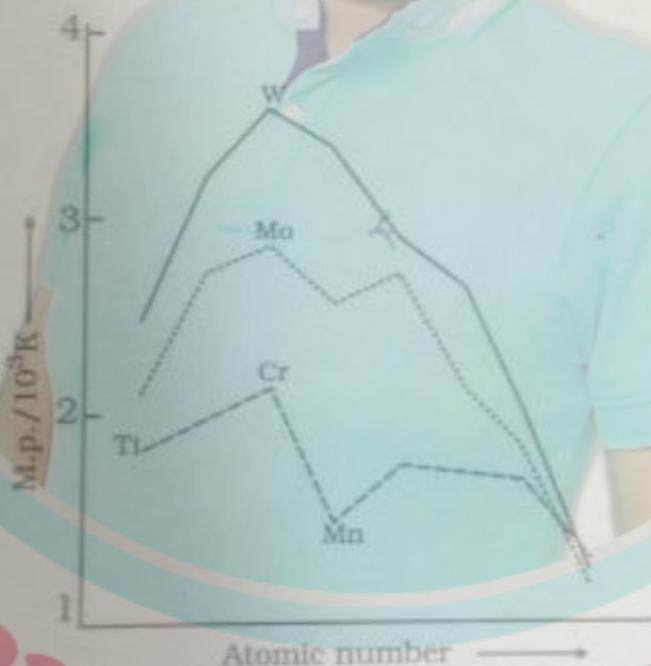
(1) Identify 'A', 'B' and 'C'.

(2) Out of 'B' and 'C', which will have higher boiling point ? Give reason.

35. (a) Why is chemistry of actinoids complicated as compared to lanthanoids ?
$1+2+2=5$

(b) Complete the following reaction and justify that it is a disproportionation reaction :

$3\,MnO_4^{2-} + 4H^+ \rightarrow$ \_\_\_\_ + \_\_\_\_ + $2\,H_2O$.
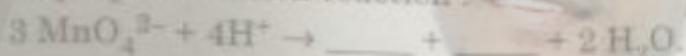
(c) The given graph shows the trends in melting points of transition metals :



Explain the reason why Cr has highest melting point and manganese (Mn) a lower melting point.