Time Allowed : 3 Hours **Maximum Marks : 70**

General Instructions:

(I) *All questions are compulsory.*

(II) ***Section A:*** *Q.no.* ***1 to 20*** *are very short answer questions (objective type) and carry* ***1*** *mark each.*

(III) ***Section B:*** *Q.no.* ***21 to 27*** *are short answer questions and carry* ***2*** *marks each.*

(IV) ***Section C:*** *Q.no.* ***28 to 34*** *are long answer questions and carry* ***3*** *marks each.*

(V) ***Section D:*** *Q.no.* ***35 to 37*** *are also long answer questions and carry* ***5*** *marks each.*

(VI) *There is no overall choice. However an internal choice has been provided in two questions of two marks, two questions of* ***3*** *marks and all the* ***3*** *questions of five marks weightage. You have to attempt only one of the choices in such questions.*

(VII) *Use log tables if necessary, use of calculators is not allowed.*

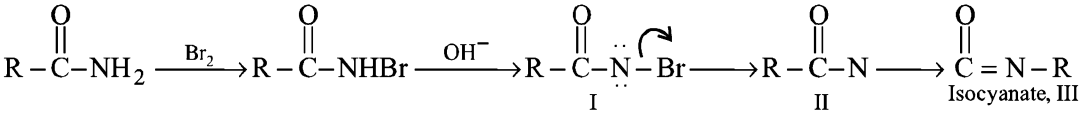
SECTION - A

Read the given passage and answer the questions 1 to 5 that follow :

The conversion of an amide to an amine with one carbon atom less by the action of alkaline hypohalite is known as Hoffmann degradation.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2$$

The most important feature of the reaction is the rearrangement of N-bromamide anion to isocyanate :



$$\xrightarrow{H_2O} H_2N - R + CO_2$$

Hoffmann reaction is accelerated if the migrating group is more electron-releasing.

1. Which step is the driving force in the above reaction to proceed in right direction?

2. What is the change in carbon chain during Hoffman reaction?

3. Which type of amine is produced by Hoffman reaction?

4. Mention the gas evolved along with amine in Hoffman reaction.

5. Among the migrating groups $-CH_3$, $-NO_2$, $-C_2H_5$, $-OR$; which will not accelerate Hoffman reaction?

Questions 6 to 10 are one word answers:

6. Out of bromine and oxygen, with which chromium will exhibit its highest oxidation state?

7. The rate of a reaction becomes eight times when the concentration of the single reactant X is made twice. Write is rate law of reaction.

8. Why is frenkel defect found in AgCl?

9. Arrange the following in order of increasing boiling point:

$CH_3CH_2CH_2CH_2Br$; $(CH_3)_3CBr$; $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2Br$

10. In complex iron hexacyano ferrate (II) how many ions will be formed when 1 mole of the complex is taken into aqueous solution (assume complete dissociation)?

Questions 11 to 15 are multiple choice questions :

11. The volume of gases NH_3, CO_2 and H_2 adsorbed by one gram of charcoal at 300 K are in order of :

(a) $H_2 > CO_2 > NH_3$ (b) $NH_3 > H_2 > CO_2$ (c) $NH_3 > CO_2 > H_2$ (d) $CO_2 > NH_3 > H_2$

12. The type of isomerism present in pentamminenitrochromium (III) chloride is

(a) optical (b) linkage (c) ionisation (d) polymerisation

13. 'If temperature increases, solubility of gas decreases'. For this situation which of the following statement(s) is/are correct ?

(i) Reaction is endothermic. (ii) Le-chatelier's principle can be applied.

(a) Statement (i) and (ii) both are correct (b) Statement (i) is correct only

(c) Statement (ii) is correct only (d) Both statement(s) (i) and (ii) are incorrect

14. Chloro compound of vanadium has only spin magnetic moment of 1.73 BM. This vanadium chloride has the formula:

(a) VCl_2 (b) VCl_4 (c) VCl_3 (d) VCl_5

15. An organic compound A (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then A is

(a) tert-butyl chloride (b) sec-butyl chloride (c) isobutyl chloride (d) n-butyl chloride

Questions 16 to 20 :

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

16. **Assertion :** Isobutanal does not give iodoform test.

Reason : It does not have α-hydrogen.

17. **Assertion :** The kinetics of the reaction $mA + nB + pC \longrightarrow m'X + n'Y + p'Z$

obey the rate expression as $\frac{dX}{dt} = k[A]^m[B]^n$.

Reason : The rate of the reaction does not depend upon the concentration of *C*.

18. **Assertion:** *ter*-butyl methyl ether is not prepared by the reaction of *ter*-butyl bromide with sodium methoxide.

Reason: Sodium methoxide is a strong nucleophile.

19. **Assertion :** Reaction of SO_2 and H_2S in the presence of Fe_2O_3 catalyst gives elemental sulphur.

Reason : SO_2 is a reducing agent.

20. **Assertion:** 2, 2-dimethylpropanal undergoes Cannizzaro reaction with conc. NaOH.

Reason: Cannizzaro reaction is a disproportionation reaction.

SECTION - B

21. The resistance of a 0.01 N solution of an electrolyte was found to be 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1}. Calculate specific conductance and equivalent conductance of solution.

OR

(a) A solution containing one mole per litre of each $Cu(NO_3)_2$, $AgNO_3$, $Hg_2(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are :

$Ag^+/Ag = +0.80\ V$, $2Hg_2^{2+}/Hg = +0.79\ V$

$Cu^{2+}/Cu = +0.34\ V$, $Mg^{2+}/Mg = -2.37\ V$

With increasing voltage, what will be the sequence of deposition of metals on the cathode?

(b) The value of Λ^∞ for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 $ohm^{-1}cm^2mol^{-1}$ respectively. Calculate Λ^∞ for NH_4OH solution.

22. The following values for the first order rate constant were obtained in a reaction :

$T_1 = 298\ K$, $k_1 = 3{\cdot}5 \times 10^{-5}\ s^{-1}$, $T_2 = 308\ K$, $k_2 = 14{\cdot}0 \times 10^{-5}\ s^{-1}$. What is E_a of reaction?

OR

Following reaction takes place in one step :

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

How will be the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume?

23. Write down the structures and names of the products obtained when D–glucose is treated with

(i) acetic anhydride (ii) hydrocyanic acid

24. In a compound AX, the radius of A^+ ion is 95 pm and that of X^- ion is 181 pm. Predict the crystal structure of AX and write the coordination numbers of each of the ions.

25. Give a chemical test to distinguish 1-propanol and 2-propanol.

26. Give suitable reasons for following statements:

(a) Two complexes of nickel $\left[Ni(CN)_4\right]^{2-}$ and $\left[Ni(CO)_4\right]$ have different structures but do not differ in magnetic behaviour.

(b) Square planar complexes of MX_2L_2 type with co-ordination number of 4 exhibit geometrical isomerism while tetrahedral complexes with similar composition do not.

27. Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

SECTION - C

28. Resistance of a conductivity cell filled with 0.1 M KCl is 100 ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. Conductivity of 0.1 M KCl solution is 1.29×10^{-2} ohm^{-1} cm^{-1}.

29. (a) Show graphically, how the amount of a gas adsorbed on a solid in physical adsorption varies with
(i) pressure, and (ii) temperature?

(b) Name a substance which can adsorb polluting gases present in air.

30. Among $Ag(NH_3)_2Cl$, $[Ni(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$, which

(a) has square planar geometry?

(b) remains colourless in aqueous solution and why?
[Ag (Z = 47), Ni (Z = 28), Cu (Z = 29)].

31. (a) Give suitable reasons for following statements:
(i) HF is not stored in glass bottles but is kept in wax bottles.
(ii) Interhalogen compounds are more reactive than halogens.

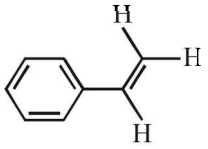
(b) Complete the following reaction : $I^-(aq) + H_2O(l) + O_3(g) \longrightarrow$

32. Distinguish between primary and secondary structure of a protein.

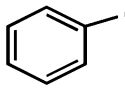
OR

What are nucleotides? Name two classes of nitrogen containing bases found in nucleotide.

33. Write the products of the following reactions:

(a)  $+ HBr \longrightarrow$

(b) $CH_3CH_2CH=CH_2 + HCl \longrightarrow$

(c)  $+ HBr \xrightarrow{\text{Peroxide}}$

OR

(a) Which compound in the following pairs will react faster in S_N2 reaction?
(i) CH_3Br or CH_3I
(ii) CH_3Br or $(CH_3)_3CBr$

(b) Why does ammonolysis of alkyl halides not yield pure amines?

34. Write reaction(s) of phenol involving

(a) the cleavage of O — H bond.

(b) the cleavage of C — OH bond.

(c) the phenol molecule as a whole.

SECTION - D

35. (a) The vapour pressures of pure liquids A and B are 70 mm and 90mm Hg respectively at 25 °C. The mole fraction of 'A' in a solution of two is 0.3. Assuming that A and B form an ideal solution, calculate the partial pressure of each component is equilibrium with the solution.

(b) (i) Two liquids A and B oil at 145 °C and 190 °C respectively. Which of them has a higher vapour pressure at 80 °C?

(ii) Why is the vapour pressure of a solution of glucose in water lower than that of water?

OR

(a) Vapour pressure of pure water at 35°C is 31.82 mm Hg. When 27.0 g of solute is dissolved in 100 g of water (at the same temperature) vapour pressure of the solution, thus formed is 30.95 mm Hg. Calculate the molecular mass of solute.

(b) (i) What are non-ideal solutions ?

(ii) What role does the molecular interaction play in deciding the vapour pressure of following solutions?

(1) Alcohol and acetone (2) Chloroform and acetone

36. (a) (i) Which of the following oxides in basic: V_2O_5 or CrO_3?

(ii) What is most stable oxidation state of Ti (Z = 22) is aqueous solution?

(iii) Why is copper sulphate pentahydrate coloured?

(b) Explain why

(i) E° for Mn^{3+}/Mn^{2+} couple is more positive than that for Fe^{3+}/Fe^{2+}.
[Atomic numbers of Mn = 25, Fe = 26]

(ii) Ce^{3+} can be easily oxidised to Ce^{4+}. [Atomic number of Ce = 58]

OR

(a) Complete the following :

(i) Why do *d*-block elements have greater tendency to form complexes that *f*-block elements?

(ii) Name the element which finds use in X-ray tube.

(b) Explain why ?

(i) *d*-Block elements have greater tendency to form complexes than *f*-block elements.

(ii) As compared to other transition elements Zn, Cd and Hg have very low melting point.

37. (a) Explain why :

(i) During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled.

(ii) Carboxylic acids do not form oximes.

(b) Write chemical equations to illustrate each of the following reactions:

(i) Gatterman – Koch reaction

(ii) Cannizzaro reaction

OR

(a) Formic acid reduces Tollen's reagent while other carboxylic acids do not. Justify.

(b) Why are boiling points of aldehydes and ketones lower than those of the corresponding acids?

(c) Why is benzoic acid a stronger acid than acetic acid?

(d) Give IUPAC names of the following:

(i) $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COCl$

(ii) $(CH_3CO)(CH_3CH_2CO)O$