740092

CHEMISTRY

Paper-II

Time: 3 Hours   Full Marks: 100

Insturctions :   (1)   *Answer **all** questions.*

(2)   *The figures in the right-hand margin indicate full marks for the questions.*

1.   Answer any **ten** questions :   2×10=20

(a)   What is PDI? What is the main difference between biopolymers and synthetic polymers from PDI point of view?

(b)   State the Schulze-Hardy rule. If the arsenious sol is negatively charged, arrange the following ions in the order of precipitating power :

(i) Na_3PO_4

(ii) $AlCl_3$

(iii) $Mg(NO_3)_2$

(c)   Write the expression for the Maxwell-Boltzmann distribution of speeds.

(d)   Explain why viscosity of glycerol is much more than that of ether.

(e)   At Boyle temperature a real gas behaves as an ideal gas. Explain why.

(f)   What is ultraviolet catastrophe?

(g)   Distinguish between basicity and nucleophilicity.

(h)   Explain why dipole moments of phenol (1.7D) and methanol (1.6D) are in opposite directions.

(i)   Acid catalysed dehydration of 2-methylbutan-2-ol gives rise to two products. Predict the structure of the products.

(j)   Draw secondary or β-structure of protein.

(k)   Draw resonance structures of tropylium ion and predict its aromaticity.

2.   Answer any **six** questions :   2×6=12

(a)   Three spin allowed transitions are expected for d^2 configuration in octahedral field. Assign the transitions with the help of an Orgel diagram.

(b)   Discuss the CO stretching frequencies of the following transition metal complexes :

$[Ni(CO)_4]$ 2060 cm^{-1}, $[Mn(CO)_6]^+$ 2090 cm^{-1} and $[V(CO)_6]^-$ 1860 cm^{-1}

(c)   How does greenhouse gas, CO_2 affect environment?

(d)   How could Green Chemistry principles be applied to treat CO_2?

(e) The first ionization energies of C and Ge are 1086 kJ mol^{-1} and 760 kJ mol^{-1}, respectively. Explain the reason.

(f) The electron affinities of Be and Mg are zero. Why?

(g) Account for the very high boiling point of HF (19.9°C) compared to HBr (–66.7°C).

3. Answer any **six** questions :   3×6=18

(a) State the principles of corresponding states. What are the physical significance of reduced variables?

(b) Explain the role of salt bridge in electrochemical cell.

(c) Devise the electrochemical cell diagram in which the cell reaction is

$$Mn(s) + Cl_2(g) \rightarrow MnCl_2(aq \ d)$$

(d) Water can form bubbles, cavity and droplet. Write the expression of the pressure difference across the surface for each case.

(e) Write the Gibbs-Duhem equation. State the physical significance of the expression.

(f) How over alkylation in the synthesis of amine from alkyl halide can be stopped?

(g) How will you convert benzene into aniline? Write reactions involved in the conversion.

(h) Distinguish 1°, 2°, 3° alcohols by oxidation reaction with chromic acid.

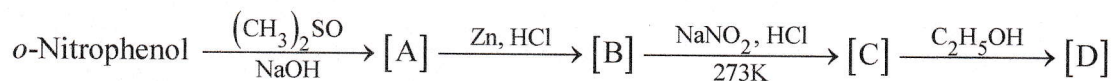4. Answer any **six** questions :   4×6=24

(a) At 90°C the vapour pressure of benzene is 20 kPa and that of toluene is 18 kPa. What is the composition of the vapour when the liquid mixture has the composition $x_{benzene} = 0.33$ and $x_{toluene} = 0.67$?

(b) Define $C_{P, m}$ and $C_{V, m}$ and derive the relation between them for n moles of an ideal gas.

(c) At a total pressure of 2 atmospheres and 673K the equilibrium constant K_P for the reaction $N_2O_4 (g) \leftrightarrow 2\,NO_2 (g)$ is 1.64×10^{-4}. Calculate K_C and K_X.

(d) Describe the activated complex theory. Show that it leads to the rate constant

$$= \left(\frac{RT}{h N_A} \right) e^{\left(\frac{\Delta H^{\neq}}{RT} \right)} e^{\left(\frac{\Delta S^{\neq}}{R} \right)}, \text{ where the symbols have their own meanings.}$$

(e) State Kohlrausch's Law of independent migration of ions. How does it help in determination of molar conductance at infinite dilution of weak electrolytes?

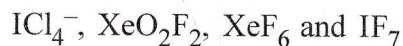(f) Propose a reaction mechanism by which carbon chain length of an aliphatic carboxylic acid can be increased.

(g) Identify compounds A, B, C and D in the following sequence of reactions :

$$o\text{-Nitrophenol} \xrightarrow[\text{NaOH}]{(CH_3)_2SO} [A] \xrightarrow{Zn, HCl} [B] \xrightarrow[273K]{NaNO_2, HCl} [C] \xrightarrow{C_2H_5OH} [D]$$

5. Answer any **four** questions : 4×4=16

(a) Use VSEPR model to predict the probable structures of the following :

ICl_4^-, XeO_2F_2, XeF_6 and IF_7

(b) How is H_2O_2 prepared industrially? Describe the structure of H_2O_2.

(c) Explain the structure and bonding of XeF_2 with the help of molecular orbital theory.

(d) How boric acid can be produced from borax? Give reaction. Describe the structure of boric acid and its origin of acidity.

(e) Choose the correct catalytic processes for the following transition metal catalysts :

Catalyst	Catalytic process
Pt/Pd supported on CeO_2	Photocatalysis
TiO_2	Propylene hydrogenation
$TiCl_4/Et_3Al$	Three-way catalysis
$[RhCl(PPh_3)_3]$	Production of H_2SO_4 Ethylene polymerization Methanol synthesis

6. Propose reaction mechanisms of the following (any **two**) : 5×2=10
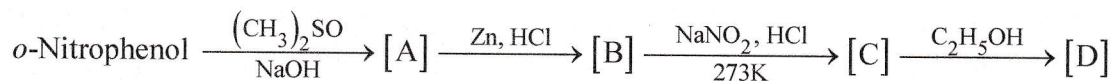
(a) Kiliani-Fischer synthesis of monosaccharides

(b) Synthesis of Nylon 66

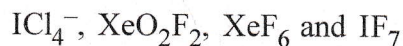(c) Mutarotation

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