181002

COMBINED COMPETITIVE EXAMINATION (MAIN)

CHEMISTRY

Paper–I

Time : 3 Hours *Full Marks* : 200

Note : *(1) The figures in the right-hand margin indicate full marks for the questions.*

*(2) Attempt **five** questions in all.*

(3) Question No. 1 is compulsory.

1. Give your justification for any ***ten*** of the following statements or facts : 4×10=40

(a) Electron affinity of fluorine is less than that of chlorine.

(b) The solutions and compounds of U^{3+} ions are deep orange in colour.

(c) The rate of a first order reaction decreases exponentially with time.

(d) Ionic solids are hard and brittle while metals are hard, malleable and ductile.

(e) Both $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ are diamagnetic but they have different geometries.

(f) Mixing of ideal gases is purely an entropy effect.

(g) ΔG is used more compared to ΔA to express spontaneity of the chemical reactions.

(h) Usually a saturated solution of KCI or NH_4NO_3 is used in the salt bridge.

(i) IR stretching frequency of CO for metal carbonyl complexes are in the order

$$M\text{–}CO > M_2\text{–}CO > M_3\text{–}CO$$

(j) Although sodium ion has smaller ionic radii than potassium ion, ionic mobility of sodium ion is less than that of potassium ion in water.

(k) Adsorption is genereally exothermic.

(l) Joule-Thomson experiment is isoenthalpic.

(m) The quantum yield of H_2-Cl_2 photochemical reaction is 10^6 which is much higher than H_2-Br_2 reaction.

2. Answer any ***eight*** questions from the following : 5×8=40

(a) How are Cartesian coordinates related to polar coordinates? Give relevant diagrams.

(b) Show that the molar heat capacity ($C_{V,m}$) of a monoatomic perfect gas is 12.47 $J.K^{-1}.mol^{-1}$.

(c) A sparingly soluble electrolyte M_2X ionizes as $M_2X \leftrightarrow 2M^+ + X^{2-}$. Deduce the relationship among solubility product (K_{sp}), molal solubility (S) and molal activity coefficients ($\gamma_\pm$)

(d) Draw the shapes of $3d_{xy}$ and $3d_{x^2-y^2}$. Give all the values of n,l and m for these orbitals.

(e) Solid A is insulator in the solid state but conductor in the molten state and in aqueous solution. What type of solid is it? Justify your answer.

(f) Describe what happens and write the chemical reactions involved–

(i) when metallic potassium is dissolved in ammonia to form dilute solution;

(ii) when more potassium is added to form concentrated solution.

(g) Distinguish between the rate (r) and the rate constant (k) of a chemical reaction with respect to concentration of the species involved in the reaction and time.

(h) If both NaCl and CsCl adopt same crystal structure, which one will have high lattice energy and why?

(i) State Fajan's rule. Explain why Ag_2S is much less soluble than Ag_2O in water.

(j) The dipole moment of HI is 0.384 D and bond distance is 1.60 Å. What will be the percentage of ionic character of HI?

(k) Predict the shape of PCl_5 and explain why the axial and equatorial bond lengths in PCl_5 are not equal.

(l) Draw the resonating structures for CO_3^{2-} and NO_2.

3. Answer any ***eight*** questions from the following : 5×8=40

(a) Consider two H-like atoms. In atom A, the electron is in $n = 1$ state while in atom B, it is in $n = 4$ state. (i) Which atom has the ground state configuration? (ii) In which atom the electron moves faster? (iii) Which atom has larger ionization energy? (iv) Which atom has the lower potential energy?

(b) Show that for a first order reaction with rate constant k, half life time is

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

(c) What is activated complex theory? Write the expression of rate constant in terms of entropy of activation ($\Delta^{\pm} S^0$) and enthalpy of activation ($\Delta^{\pm} H^0$).

(d) For the electrochemical half reaction Cu^{2+} (aq) + e $\rightarrow$ Cu^{+} (aq), state how the electrode potential varies with concentration of the ions in solution.

(e) Predict the bond order and magnetic property in B_2 and N_2.

(f) Sketch the η^2 and η^4 interaction of 1,4-butadiene with a metal atom.

(g) Explain the effect on the *d*-orbital energies upon compression of an octahedral complex along the *z*-axis.

(h) How is the magnetic behaviour of Gd^{3+} and Lu^{3+} different from the rest of the lanthanides?

(i) Show that $\Delta G = W_{non-PV}$ at constant T and P.

(j) What is the coordination number of CCP and BCC or cubic-I structure? What is the amount of the unfilled or unoccupied space in the above structures?

(k) Calculate the entropy of mixing per mole of air with 79% N_2, 20% O_2 and 1% He.

(l) Using VSEPR theory, predict the geometry and shape of the following molecules : XeF_4 and ICl_2^-

4. Answer any ***five*** questions from the following : 8×5=40

(a) Discuss why in square planar complexes, the crystal field splitting of the d-orbital energies of a central metal ion decrease in the sequence $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$

(b) Draw the structure of Zeise's salt. Discuss the Dewar-Chatt-Duncanson description of bonding of Zeise's salt.

(c) Write a short note on Joule-Thomson experiment.

(d) Predict the bond order of metal-metal bond in the following complexes : $[Mo_2Cl_8]^{4-}$ and $[Re_2Cl_8]^{2-}$

(e) Describe the physical significance of ψ and ψ^2. What is eigenvalue equation? Explain with the help of an example. Deduce the expression for the linear momentum and Hamiltonian operator.

(f) What is intrinsic point defect? Discuss how the number of Schottky and Frenkel or intrinsic point defects vary with temperature and enthalpy.

(g) What are exact and inexact differentials? Show that *dW* is an inexact differential.

(h) What is a reference electrode? Give three examples of reference electrode (Write their IUPAC notations). What is the importance of a reference electrode?

5. Answer any ***five*** questions from the following : 8×5=40

(a) Show that for an infinitesimal reversible process, $dS_{system} + dS_{surrounding} = 0$.

(b) Draw the molar conductivity vs. concentration plot for strong electrolytes. Write the physical significance of the limiting molar conductivity (Λ_m^0). State the Kohlrausch's law and the Kohlrausch's law of independent migration of ions.

(c) What are the mathematical expressions for normalized and orthogonal wave functions? Write the expression of the normalized wave function for the particle in a box system.

(d) Describe the structure of AgCl and ZnS. Write their coordination and the formula unit.

(e) What are allowed and forbidden transitions? It is observed that solutions of $[Fe(CN)_6]^{4-}$ is yellow and $[Fe(H_2O)]^{2+}$ is green. Explain and characterize the origin of the transitions in these complexes.

(f) How would you expect the first and second ionization energies of the lanthanoids to vary across the series?

(g) What are degenerate orbitals? Comment upon the degeneracy of 3*s*, 3*p* and 3*d* for H-atom and multielectron system.

(h) The rate law for the reaction $A + B \rightarrow P$ is $r = k[A]^2[B]$. *(i)* By what factor is the initial rate multiplied if the initial concentration of A is multiplied by 1.5 and the initial concentration of B is tripled? (ii) If tripling the initial A concentration multiples the initial rate by 27, what is the order with respect to A?

6. Answer any ***five*** questions from the following : 8×5=40

(a) If $\Delta H_{sublimation}$ (Li) = 161 kJmol^{-1}, $\Delta H_{dissociation}$ (F_2) = 79 kJmol^{-1}, $\Delta H_{ionization}$ (Li) = 531 kJmol^{-1}, $\Delta H_{electron\ affinity}$ (F) = –328 kjmol^{-1}, $\Delta H_{lattice\ enthalpy}$ (LiF(s)) = 1239 kJmol^{-1}, calculate the enthalpy of formation of LiF (s).

(b) The ligand field splitting parameter (Δ_0) between t_{2g} and e_g orbital for the octahedral complexes $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$ are 15800 cm^{-1} and 38500 cm^{-1} respectively. The electron pairing energy *(P)* for Mn^{3+} ions is about 2800 cm^{-1}. Do these complexes have high spin or low spin? Write their *d*-electron configuration.

(c) What are Miller indices? Determine the indices of a plane that intersects the axes at $\frac{a}{2}, \frac{b}{2}, \frac{c}{2}$. Calculate the separations of the (1 1 2) planes in a crystal in which the cubic unit cell has side 562 pm.

(d) The standard cell potential for the reaction $Cu^{2+}(aq) + Fe^{2+}(aq) + I^-(aq) \rightleftharpoons CuI(s) + Fe^{3+}(aq)$ is + 0.090 V. Use the Nernst equation to calculate the electrochemical potential at 298.15 K for the cell Pt(s) | CuI_2 (aq, 0.010 mol dm^{-3}) CuI(s) || $FeSO_4$(aq, 0.010 mol dm^{-3}), $Fe_2(SO_4)_3$ (aq), 0.020 mol dm^{-3}) | Pt(s).

(e) Absorption of UV radiations decomposes acetone according to the reaction

$$(CH_3)_2CO + h\nu \rightarrow C_2H_6 + CO$$

The quantum yield for the reaction at 280 nm is 0.2. A sample of acetone absorbs radiation at 280 nm at the rate of 7.5×10^{-3} Js^{-1}. Calculate the rate of formation of CO.

(f) Find the activation energy of a reaction whose rate constant is multiplied by 6.50 when temperature is increased from 300.0 K to 310.0 K.

(g) The conductivity of KCl (aq) at 25°C is 14.668 mS m^{-1} when c = 1 mmol dm^{-3} and 71.740 mS m^{-1} when c = 5 mmol dm^{-3}. Determine the values of the limiting molar conductivity Λ_m^0 and the Kohlrausch's constant (κ).

(h) The equilibrium constant K_P for the reaction Cl_2 (g) ↔ 2Cl (g) is 0.57 bar at 2000 K. Suppose that 0.1 mole of chlorine is present in a volume of 5 L at that temperature. What will be the degree of dissociation?

7. Answer any ***five*** questions from the following : 8×5=40

(a) Discuss the separation of lanthanoids by cation exchange chromatography.

(b) State Franck-Condon principle. Discuss the fate of the excited states with the help of Jablonski diagram.

(c) The expression for the change in the equilibrium constant (K) for an equilibrium $A \leftrightarrow B$ with temperature (T) is given by $\frac{dlnK}{dT} = \frac{\Delta rH^\circ}{RT^2}$. State and explain the direction of shift of the equilibrium with increase in temperature when *(i)* the reaction is exothermic. and *(ii)* the reaction is endothermic.

(d) Show that the variation of Gibb's free energy G with T and P is

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

(e) How do a solution of weak acid and its salt behave as a buffer? Derive Henderson-Hasselbalch equation to calculate pH of the solution.

(f) Draw the MO diagram for CO molecule. Explain which end in CO forms organometallic compounds.

(g) Explain how you will determine the solubility product of AgCl with the help of an electrochemical cell. Write the corresponding cell diagram.

(h) Write the Arrhenius equation. Write the significance of activation energy. What is Arrhenius plot? State what information can be retrieved from the Arrhenius plot.

8. Answer any ***four*** questions from the following : 10×4=40

(a) Write the Schrodinger equation for particles in a one-dimensional box and write the solution of this equation. Show that the separation between adjacent energy levels with quantum numbers n and $n + 1$ decreases as the length of the box increases. Calculate the probability that a particle will be found between $0.49L$ and $0.51L$ in a box of length L for $n = 1$ state.

(b) Derive Bragg's equation for reflection of X-rays from the faces of a crystal and explain the physical significance of n in the equation. The angle of a Bragg reflection from a set of crystal planes separated by 99.3 pm is 20.85°. Calculate the wavelength of the X-rays.

(c) Define rate law of a reaction. Define integrated and differential rate laws. Discuss three experimental methods of determining the order of a chemical reaction. Explain how rate constant can be evaluated from the integrated rate law plot for first and second order reaction.

(d) Show the following :

(i) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(ii) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(iii) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

(iv) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

(e) Derive the Gibbs-Helmholtz equation. Discuss its physical significance.

(f) Derive the Kelvin equation ($P = P^{\circ} e^{\frac{2\gamma \bar{V} m}{rRT}}$, where all the symbols have their usual meanings) for the vapour pressure of water droplet.

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