ZCVB-U-CHM

CHEMISTRY

Paper – I

*Time Allowed : **Three** Hours*

*Maximum Marks : **200***

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.*

*Questions no. **1** and **5** are **compulsory**. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two Sections A and B.*

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Neat sketches may be drawn, wherever required.

*Answers must be written in **ENGLISH** only.*

$h = 6{\cdot}626 \times 10^{-34}$ Js

$R = 8{\cdot}314$ JK^{-1} mol^{-1}

$c = 3 \times 10^{8}$ ms^{-1}

$N_A = 6{\cdot}023 \times 10^{23}$ mol^{-1}

$m_e = 9{\cdot}1 \times 10^{-31}$ kg

$\varepsilon_0 = 8{\cdot}854 \times 10^{-12}$ $C^2J^{-1}m^{-1}$

$k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}

$\pi = 3{\cdot}14$

$F = 96500$ C mol^{-1}

1 atm = 101325 Pa

SECTION A

Q1. (a) (i) Does the Frenkel disorder in AgBr create vacancies of Ag^+, vacancies of Br^- or both ? Explain. The ionic radii are 1·15 Å for Ag^+ and 1·96 Å for Br^-.

(ii) Calculate the temperature at which the fraction of Frenkel defects in a crystal of AgBr exceeds 1 part per billion. The enthalpy of Frenkel defect formation, ΔH_f, has the value of 1·16 eV/defect, and the entropic prefactor, A, has a value of 3·091. *8*

(b) Does the enthalpy of formation of compounds containing a certain element change, if the enthalpy of formation of the element under standard state conditions is set equal to 100 kJ mol^{-1} rather than to zero ? If it changes, how will it change for the compound A_nB_m, if the formation enthalpy of element A is set equal to 100 kJ mol^{-1} ? *8*

(c) Draw an energy level diagram (with energy on the y-axis and internuclear distance r, on the x-axis) plotting a C – F and C – I bond. You should include numbers on y-axis. No numbers are needed on x-axis, but relative distances should be correct. Bond dissociation energies are 238 kJ/mol and 484 kJ/mol for C – I and C – F, respectively. *8*

(d) Explain the application of phase rule in desilverization of lead. *8*

(e) Calculate the equilibrium constant of the cell reaction $2Ag^+ + Zn \longrightarrow 2Ag + Zn^{2+}$ occurring in the zinc-silver cell at 25°C when $[Zn^{2+}] = 0{\cdot}10$ M and $[Ag^+] = 10$ M. The e.m.f. of the cell is found to be 1·62 V. *8*

Q2. (a) Prove that for a particle in the box, the total energy eigenfunctions,

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

where $\phi(x)$ is a continuous function at the edges of the box. Is $d\phi_{(x)}$ a continuous function of x at the edges of the box ? The dimensions of the box are from x = 0 to x = L. *15*

(b) The ionic bond length for KF is 0·217 nm. Calculate the energy (in units of kJ/mol) required to dissociate a single molecule of KF into neutral atoms, K and F, using information provided below. Assume that potassium and fluorine ions are point charges. *10*

Element	Ionization Energy	Electron Affinity
Potassium (K)	418 kJ/mol	48 kJ/mol
Fluorine (F)	1680 kJ/mol	328 kJ/mol

(c) In a face-centred unit cell with all the positions occupied by A atoms, the body centred octahedral hole in it is occupied by an atom B of an appropriate size. Calculate the void space per unit volume of unit cell for such a crystal. *15*

Q3. (a) At what temperature does the slope of Z versus P curve as $P \rightarrow 0$ have its maximum value for a Van der Waals gas ? What is the value of the maximum slope ? *10*

(b) For the reaction,

$$Ag_2O\,(s) \longrightarrow 2Ag\,(s) + \frac{1}{2}O_2\,(g),$$

$\Delta_r H^0 = 30{\cdot}56$ kJ mol^{-1} and $\Delta_r S^0 = 6{\cdot}6$ JK^{-1} mol^{-1} at 1 bar. Calculate the temperature at which $\Delta_r G^0$ will be zero. What will be the direction of the reaction at this temperature ? Also, depict the direction of reaction above and below this temperature and why ? *15*

(c) What are ion-selective electrodes ? How can glass electrode be used to determine the pH of a given solution ? *15*

Q4. (a) How does Debye-Huckel theory of strong electrolytes explain the increase of molar conductance with dilution ? *15*

(b) Give the classical statistical mechanical definition of the canonical partition function, Q. What is the relationship between thermodynamic Helmholtz free energy, F, and Q ? Using these expressions show that heat capacity at constant volume, C_V, is given by *10*

$$C_V = kT\left[\frac{\partial^2}{\partial T^2}(T\,ln\,Q)\right]_V$$

(c) Derive Clausius–Clapeyron equation for a one component system at equilibrium, represented as *15*

$$\underset{\text{(liquid)}}{\text{water}} \rightleftharpoons \underset{\text{(vapour)}}{\text{water}}$$

SECTION B

Q5. (a) A reactant reacts 30% in 30 min. If the reaction follows a second order kinetics, find the rate constant and remaining concentration of the reactant after 60 min. *8*

(b) State and explain Stark–Einstein law of photochemical equivalence. *8*

(c) What are the different methods used for separation of lanthanides ? *8*

(d) What is EAN rule ? Is this rule followed by the complexes given below ? *8*

(i) $Cr(CO)_6$

(ii) $Ni(CO)_4$

(iii) $Fe(CO)_9$

(e) Acetic acid is a weak acid in aqueous solution and nitric acid a strong acid, but both behave as bases in sulphuric acid. Why ? *8*

Q6. (a) Derive rate equation for kinetics of a reversible reaction of type,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B.$$

15

(b) For the photochemical formation of ethylene from di-n-propyl ketone using a wavelength 313 nm, the quantum yield is 0·21. Calculate the number of moles of ethylene formed when the sample is irradiated with 50 watt of this radiation, assuming that all the radiation is absorbed by the same sample. *15*

(c) What is Stereoisomerism ? Explain isomerism in $[Co(NH_3)_4Cl_2]^+$ emphasizing on structure and colour of the complex. *10*

Q7. (a) Derive an expression for Langmuir's adsorption isotherm. Show that at normal pressures, Langmuir's unimolecular adsorption reduces to Freundlich adsorption isotherm. *15*

(b) What is Z-diagram ? Explain electron flow mechanism in photo system-I and II through Z-diagram. *15*

(c) How do π-donor and π-acceptor ligands affect the spectral properties of metal complexes ? Explain with MO diagram. *10*

Q8. (a) Draw the chemical structures of the following coordination compounds : *15*

(i) Potassium trans-dichlorodinitro platinate (II)

(ii) 1,6 dichloro-2,3-dinitro-ethylene diamine platinum (IV)

(iii) trans tetraammine dichloro cobalt (III) ion

(iv) Ammonium iron (II) sulphate (Mohr's salt)

(v) μ-amido-μ-superoxo bis (tetraammine) cobalt (III)

(b) How does Mg^{2+} state help in the conversion of glucose into pyruvate ? Explain it by proposing a mechanism for conversion. *15*

(c) Deduce the effective magnetic moment (μ_{eff}) for *10*

(i) Europium (Eu^{3+})

(ii) Samarium (Sm^{3+})

Given : $\mu_{eff} = g\sqrt{J(J+1)}$

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$