

7281

D-VSF-L-PUA

## CHEMISTRY

### Paper I

Time Allowed : Three Hours

Maximum Marks : 200

#### INSTRUCTIONS

*Candidates should attempt Questions No. 1 and 5 which are compulsory, and any THREE of the remaining questions, selecting at least ONE question from each Section.*

*All questions carry equal marks.*

*Marks allotted to parts of a question are indicated against each.*

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

*Answers must be written in ENGLISH only.*

*Unless otherwise indicated, symbols and notations have their usual meanings.*

#### SECTION A

1. Attempt any *four* of the following :

- (a) The vapour pressures of water at 298 K and 308 K are 3167 Pa and 5599 Pa respectively. Calculate the molar enthalpy of vaporisation of water.

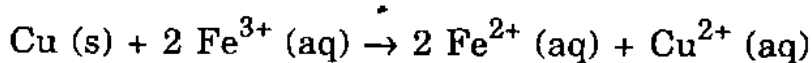
10

- (b) Derive Bragg's equation. How do you calculate the spacings between the planes ? 10
- (c) Define eigenfunction and eigenvalue. Determine the eigenvalue of the function  $\psi = e^{ikx}$  with operator  $\frac{d}{dx}$ . 10
- (d) Absorption spectra of actinide elements comprises of very sharp lines. Assign the transition(s) responsible. 10
- (e) Calculate radial distance from the nucleus of hydrogen atom at which the given radial wave function ( $R_{2,0}$ ) for 2s orbital is zero.  
(Given,  $a_0 = 52.9 \times 10^{-12}$  m)

$$R_{2,0}(2s) = \frac{1}{2\sqrt{2} \cdot a_0^{3/2}} \left( 2 - \frac{r}{a_0} \right) \cdot e^{-\frac{r}{2a_0}} \quad 10$$

2. (a) State and explain the law of photochemical equivalence. How are the discrepancies of this law explained ? 20
- (b) Volume of nitrogen gas at 1 atm and 273 K required to cover 1 g of silica gel is  $0.129 \text{ dm}^3$ . Calculate the surface area of the gel if each nitrogen molecule occupies an area of  $16.2 \times 10^{-10} \text{ m}^2$ . 20

3. (a) Consider a galvanic cell that uses the following reaction :



Given :

$$E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = + 0.77 \text{ V}$$

$$E^0_{\text{Cu}^{2+}/\text{Cu}} = + 0.34 \text{ V}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

- (i) Calculate the standard cell potential and comment on your result. 10
- (ii) Calculate the cell potential at 25°C that has the following concentration values :

$$[\text{Fe}^{3+}] = 1.0 \times 10^{-4} \text{ M}; [\text{Cu}^{2+}] = 0.25 \text{ M};$$

$$[\text{Fe}^{2+}] = 0.2 \text{ M} \quad \text{10}$$

- (b) Explain the differences between homogeneous and heterogeneous catalysis with examples. Enumerate the steps involved in Langmuir - Hinshelwood catalysis. 20

4. (a) What are "excess-functions" ? Show that

$$\Delta H^E_{\text{mix}} = \Delta G^E_{\text{mix}} - \left( \frac{\partial \Delta G^E_{\text{mix}}}{\partial T} \right)_{P, x}$$

where symbols have their usual meanings. 20

- (b) Equation for probability density,  $F(v)$ , for the Maxwell distribution of speed is

$$F(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$$

From the above equation, derive the expression for the most probable speed. Show how distribution varies with the temperature. 20

## SECTION B

5. Attempt any *four* of the following :

(a) Give 'spin only' formula for calculating magnetic moment. How is this parameter affected by variation of temperature ? Comment. 10

(b) What is residual entropy ? Why are certain substances like CO and N<sub>2</sub>O associated with residual entropy even at 0 K ? 10

(c) What are orthonormal wave-functions ? Normalise the following wave-function for a particle in one-dimensional box :

$$\psi_n(x) = B \sin \frac{n\pi x}{a} \quad 10$$

(d) The overall rate constant for a complex reaction

is  $\left(\frac{k_1 k_2}{k_3}\right)^{1/2}$ , where  $k_1$ ,  $k_2$  and  $k_3$  are the rate

constants, and  $E_1$ ,  $E_2$  and  $E_3$  are the corresponding energies of activation. Obtain the expression for the overall energy of activation of this reaction. 10

(e) What is a superacid ? Explain protonating action of a superacid, giving suitable example(s). 10

6. (a) What are semiconductors ? Explain n-type and p-type semiconductors. How does variation of temperature affect their conductivity ? 20
- (b) (i) Carbon dioxide has a linear structure whereas sulphur dioxide is a bent molecule. Explain, giving reason. 10
- (ii) Explain lanthanide contraction. How are properties of elements of 5d series following lanthanides affected by this contraction ? Explain. 10
7. (a) How does acid catalysis differ from proton catalysis ? Illustrate giving mechanistic pathways, the role of a metal ion acting as a Lewis acid catalyst in a biological reaction. 20
- (b) Aqueous solutions containing  $Ti^{3+}$  ions are reddish violet in colour; a single broad peak with a maximum is observed at  $20300\text{ cm}^{-1}$ . Assign the transition(s) taking place and explain the observation. 20
8. (a) Starting with  $[PtCl_4]^{2-}$ , prepare diamminedichloroplatinum (II). Name the isomer formed. 20
- Choose the relevant starting material and write all steps to get the other geometrical isomer of the above product.

(b) When any alkali metal is dissolved in liquid ammonia, a blue coloured, conducting and paramagnetic solution is obtained.

Explain, giving reason, each of the above observations.

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