2011

Indian Forest Service

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, $a_0 = 52{\cdot}9 \times 10^{-12}$ m)

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

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 $0{\cdot}129$ dm^3. Calculate the surface area of the gel if each nitrogen molecule occupies an area of $16{\cdot}2 \times 10^{-10}$ m^2. *20*

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

$Cu\ (s) + 2\ Fe^{3+}\ (aq) \rightarrow 2\ Fe^{2+}\ (aq) + Cu^{2+}\ (aq)$

Given :

$E^0_{Fe^{3+}/Fe^{2+}} = + 0{\cdot}77\ V$

$E^0_{Cu^{2+}/Cu} = + 0{\cdot}34\ V$

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

(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 :

$[Fe^{3+}] = 1{\cdot}0 \times 10^{-4}$ M; $[Cu^{2+}] = 0{\cdot}25$ M; $[Fe^{2+}] = 0{\cdot}2$ M *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

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

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_2O 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 :

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

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 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.

Choose the relevant starting material and write all steps to get the other geometrical isomer of the above product. *20*

(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. 20