West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2010

PART – II (Honours)

CHEMISTRY

Paper – IV (A)

Duration : 2 Hours Full Marks : 50

Candidates are required to give their answers in their own words as far as practicable.

The figures in the margin indicate full marks.

Answer any *three* questions taking *one* from each Unit.

UNIT - I

1. a) State the acceptability conditions imposed on the wavefunction. Verify the acceptability of the following functions as wavefunction : 3 + 2

   i) $F(x) = e^{-x^2/2}, \{-\infty \le x \le +\infty\}$

   ii) $F(\theta) = e^{i\theta}, \{0 \le \theta \le 2\pi\}$

   b) Derive the expression for energy levels of a particle in a one-dimensional box from the de Broglie relation. 4

   c) Find the eigenfunctions and eigenvalues of the operator d/dx. If the eigenfunctions are to remain finite for $x \to \pm \infty$, find the eigenvalues. 2 + 3

   d) Sketch the probability density function for a quantum mechanical harmonic oscillator for $\upsilon = 0$ and $\upsilon = 1$ levels. 2

2. a) Consider a quantum particle of mass m confined in a zero potential energy region between impenetrable walls at $x = 0$ and $x = a$. For this system :

   i) write the time-independent Schrödinger equation.

ii) solve the equation for the wavefunction of the system.

iii) find out the expectation value of momentum, $\langle p_x \rangle$, for the system and comment on the result. 1 + 3 + 2 + 1

b) Evaluate the commutator $\left[\hat{x}, \hat{H}\right]$ for a particle in a one-dimensiional space.

The lifetime of an excited state of a molecule is 2×10^{-9} sec. What is the uncertainty in its energy in J and in cm^{-1} ? 3 + 1 + 1

c) Calculate the mean radius of a 1s orbital for the hydrogen atom.

Given : $\psi_{1s} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$. 4

UNIT - II

3. a) Show that the chemical potential of any ideal gas in a mixture is always less than the chemical potential of the pure ideal gas under the same total pressure.

Derive the relation, $\overline{S}_i = \overline{S}_{i(pure)} - R \ln x_i$ 2 + 2

b) For the reaction $A \rightarrow B$ at equilibrium show that $\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 0$ where ξ is the degree of advancement of the reaction.

Does the equilibrium constant of a reaction depend upon its stoichiometry ?

Under what condition does the equilibrium constant of a reaction become independent of temperature ? Explain briefly. $3 + 1\frac{1}{2} + 1\frac{1}{2}$

c) Calculate the mean ionic activity coefficient of 0·001 (M) aqueous solution of $K_3\left[Fe(CN)_6\right]$. Debye-Hückel constant is 0·51. 3

d) Show that $\frac{\partial\left(E^0/T\right)}{\partial(1/T)} = \frac{\Delta H^0}{nF}$ 3

e) Show that $\mu_i = \left(\frac{\partial H}{\partial x_i}\right)_{s,p,x_{j\neq i}} = \left(\frac{\partial A}{\partial x_i}\right)_{T,V,x_{j\neq i}}$ 2

a) Write down the cell reaction and calculate the *e.m.f.*, the free energy change and the equilibrium constant of the reaction taking place at 25° C of the following cell :

$H_2(1\text{ atm})|HBr\ (a \pm = 0{\cdot}2), Hg_2Br_2(s)|Hg$

Given : $E^0_{Hg/Hg_2Br_2(s),\,Br} = -0{\cdot}1385$ V 1 + 2 + 1 + 2

b) Deduce van't Hoff reaction isotherm. 4

c) Discuss the effect of addition of KCl and KNO_3 on the solubility and solubility product of AgCl in water. 2 + 2

d) For the reaction $HgO(s) \rightleftharpoons Hg\ (l) + \frac{1}{2} O_2\ (g)$ at 30°C $\Delta G^\circ = 14$ kcal mol^{-1}. What will be the value of K_P and pressure of oxygen gas at the equilibrium (assume ideal behaviour) ? 4

UNIT - III

a) Define work of cohesion and work of adhesion. At 20°C for CH_2I_2, γ is 50 N/m and for pure water it is 72 N/m and the interfacial tension is 46 N/m. Calculate the spreading coefficient of CH_2I_2 on water. (γ = surface tension).

$1\frac{1}{2} + 1\frac{1}{2} + 3$

b) A steel ball of density 10·0 gm/c.c. having diameter of 4 mm is dropped into a column of liquid. It takes 5 seconds to fall through a distance of 10 cm. Calculate the viscosity coefficient of the liquid given density of liquid = 3·8 gm/c.c. 3

c) Why is alternating current used for the measurement of conductance ? 2

d) The equivalent conductance at infinite dilution of HCl, NaCl and NaOAc are 426·2, 126·5 and 91·0 $ohm^{-1} cm^2$ respectively at 25° C. Calculate Λ° for CH_3COOH. A conductance cell filled with 0·01 (M) KCl has a resistance of 257·3 ohms at 25° C. The same cell filled with 0·2 (N) CH_3COOH has a resistance of 508·6 ohms. Calculate the dissociation constant of CH_3COOH.

[Specific conductance of 0·01 (M) KCl = $1·41 \times 10^{-3}$ $ohm^{-1} cm^{-1}$] 2 + 3

6. a) Define coefficient of viscosity of a liquid. Find the dimension of the viscosity coefficient. How would you determine the activation energy for the laminar flow of a liquid ? 2 + 2

b) A spherical air bubble is created within a liquid of surface tension 72 dynes/cm. If the volume of the bubble is $\frac{\pi}{6}$ cm^3, calculate the excess pressure inside the bubble. 3

c) How would you explain the abnormality high ion conductance of a proton in water ? 2

d) Show that for dilute aqueous solutions of the weak acid HA, $1/\wedge$ *vs* $\wedge c$ plot is a straight line with positive intercept. 3

e) Define ionic mobility and state its unit. Calculate the ionic mobility of the cation in an infinitely dilute KCl at 25°C.

[Given : Transport number of K^+ is 0·49, the equivalent conductance of KCl at infinite dilution is 150 $ohm^{-1} cm^2$] 2 + 2