West Bengal State University

B.A./B.Sc./B.Com. (Honours, Major, General) Examinations, 2013

PART-II

CHEMISTRY — HONOURS

Paper - IV

(NEW & OLD SYLLABUS)

Duration : 2 Hours [Maximum Marks : 50

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

Marks will be deducted for spelling mistakes, untidiness and bad handwriting.

The figures in the margin indicate full marks.

Use separate answer script for each Group.

(NEW SYLLABUS)

Group – A

(Physical Chemistry)

CEMAT 24-PA

Attempt *two* questions taking *one* question from each Unit.

UNIT – I

1. a) Write down the Planck distribution law for black body radiation in one convenient form and hence show that the wavelength corresponding to the maximum energy density is inversely proportional to the absolute temperature. [Assume $hc/\lambda kT >> 1$, terms have their usual significance.] 1 + 3

   b) Show that for a particle in a cubical box, the energy level having energy three times to that of lowest energy level, is three fold degenerate. 3

   c) Determine the value of x at which the first excited wave function of the simple harmonic oscillator exhibits maximum or minimum.

   [Given : $\psi_1(x) = \left(\dfrac{\alpha}{4\pi}\right)^{\frac{1}{4}} (2\alpha^{1/2}x)e^{-\alpha x^2/2}$; $\alpha = (k\mu)^{1/2}/h$,

   k = force constant, μ = reduced mass.] 3

   d) When a metal surface is irradiated by light of wavelength 300 nm the stopping potential is found to be 0·5 V. Calculate the work function and the threshold wavelength. [Given : 1 eV = $1 \cdot 602 \times 10^{-19}$ J] 3

2. a) The classically allowed region for the simple quantum mechanical harmonic oscillator in its ground state is where $-\alpha^{-1/2} \le x \le \alpha^{-1/2}$. Justify.
[Given : x = displacement from equilibrium position of the oscillator (one dimensional), $\alpha = (k/\mu)^{1/2}/h$, k = force constant, μ = reduced mass.] 3

b) Prove that the differential operator, $\frac{d}{dx}$, is not Hermitian in nature. 3

c) Evaluate $\left[\hat{x}^n, \hat{P}_x\right]$, where n is positive integer. 3

d) A monochromatic X-ray beam whose wavelength is 0·0558 nm is scattered in Compton scattering through an angle 46°. Calculate the wavelength of the scattered beam. [Given : h (Plank's constant) = $6 \cdot 626 \times 10^{-34}$ Js, m_0 (rest mass of electron) = $9 \cdot 1 \times 10^{-31}$ kg, c (speed of light in vacuum) = $2 \cdot 998 \times 10^8$ ms^{-1}] 4

UNIT – II

3. a) The equation involving only ϕ, obtained on separation of the time-independent Schrödinger equation for the hydrogen atom is $\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$, where m^2 is constant and $\Phi(\phi)$ is single valued function of ϕ. The solution of the above equation is $\Phi_m = A\exp(im\phi)$, where A is normalisation constant. Find A and m. 4

b) With the help of Jablonski diagram show the various photophysical processes through which a molecule in excited singlet state (S_2^{υ}) can return to the ground singlet state (S_0). [υ indicates vibrational level, other terms have their usual significance.] 3

c) Show that the degree of degeneracy of a hydrogen atom at bound state level is equal to n^2. (Omit spin consideration, n = principal quantum number) 2

d) The quantum yield of CO in the photolysis of gaseous acetone ($P < 6$ kPa) at wavelengths between 250-320 nm is unity. After 20 min irradiation with light of 313 nm wavelength, 18·4 cm^3 of CO (measured at 1008 Pa and 22°C) is produced. Calculate the number of quanta absorbed and the absorbed intensity in joules per second. 3

4. a) "In the photostationary state of dimerisation of anthracene at its large concentration, the concentration of dimer is independent of the concentration of monomers." Based on suitable mechanism justify the statement. 4

b) Give schematic probability density plots of the following hydrogen atomic orbitals : 2

i) $3S$, ii) $3P_0$.

c) Describe the basic principle of measurement of intensity of radiation by uranyl oxalate actinometer. 3

d) Show that the most probable value of r in a 1st state of the hydrogen atom is a_0 (Bhor radius).

[Given : $R_{1s}(r) = \dfrac{2}{a_0^{3/2}} e^{-r/a_0}$, R_{1s} = radial factor in the hydrogen atom wave function, r = the distance between the electron and the proton.] 3

CEMAT 24-PB

Attempt *two* questions taking *one* question from each Unit.

UNIT – I

5. a) Show that the greatest decrease in Gibbs energy on mixing of two ideal gases at constant temperature and pressure is associated with the formation of the mixture having equal number of moles of the two constituents.

[Assume the expression for the Gibbs energy of mixing for an ideal mixture] 3

b) Prove that :

i) $\left[\dfrac{\partial(G/T)}{\partial(1/T)}\right]_P = H$

ii) $\dfrac{d\,ln\,K_p}{dT} = \dfrac{\Delta H^0}{RT^2}$.

[Terms have their usual significance.] 2 × 3

c) At 25°C, for the reaction

$Br_2(g) \rightleftharpoons 2\,Br(g)$

We have $\Delta G° = 161{\cdot}67$ kJ mol^{-1} and $\Delta H° = 192{\cdot}81$ kJ mol^{-1}.

At what temperature will the system contain 10 mol per cent bromine atoms in equilibrium with bromine vapour at $p = 1$ atm. 4

6. a) The decrease in Gibbs energy ($-\Delta G$) for a system, associated with a reversible change in state at constant temperature and pressure is equal to the maximum work over and above expansion work. Justify. 3

b) If ξ is degree of advancement of chemical reaction, then at equilibrium $\left(\dfrac{\partial G}{\partial \xi}\right)_{P,T} = 0$. Justify. 2

c) Establish the relation between K_p and K_x. 2

d) Prove that $\left(\dfrac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \mu_i$

[Terms have their usual significance.] 3

e) The mean heat of vaporisation of water in the temperature range between 90°C and 100°C is 542 cal g^{-1}. Calculate the vapour pressure of water at 90·0°C, the value at 100·0°C being 76·0 cm. 3

UNIT – II

7. a) For the concentration cell $Ag\,|\,AgCl(s)\,|\,HCl(a_1)\,|\,HCl(a_2)\,|\,AgCl(s)\,|\,Ag$

i) Write the various processes at the two electrodes and at the liquid junction

ii) Derive expression for ΔG of the cell. 4

b) Discuss the effect of addition of KCl and KNO_3 on solubility and concentration solubility product of AgCl in water. 3

c) Calculate any change in pH of one litre solution of 0·1 (M) in acetic acid and 0·1 (M) in sodium acetate at 25°C due to addition of 1 cc of 10 (N) HCl. [K_a (Acetic acid) = $1\cdot8\times10^{-5}$ at 25°C, neglect any volume change.] 2

d) In a moving-boundary experiment to determine the transference number of chloride ion in 0·010 mol lit $^{-1}$ sodium chloride solution, the chloride ion moved a distance of 3·0 cm in 976 s. The cross section of the tube was 0·427 cm^2 and the current $2\cdot08\times10^{-3}$ A. Calculate t. 3

8. a) Find an expression of the degree of hydrolysis (α) of a salt formed from a strong acid and a weak base in terms of concentration (c) of the salt and hence explain the nature of dependence of α on c. 3

b) Given that standard potentials of the Cu^{2+}/Cu and Cu^{+}/Cu couples are +0·340 V and + 0·522 V, respectively. Evaluate $\phi°(Cu^{2+}, Cu^{+})$.

[$\phi°(Cu^{2+}, Cu^{+})$ = standard potential of (Cu^{2+}, Cu^{+}) system.] 3

c) State the law of independent migration of ions. 2

d) Calculate the solubility of Ag_2CrO_4 in 0·2 (M) $NaNO_3$, assuming that the simple Debye-Hückel equation for activity coefficients applies. The thermodynamic solubility product is $4\cdot5\times10^{-12}$. The temperature is 25°C. 4

(OLD SYLLABUS)

Group – A

Attempt any *three* questions taking *one* question from each Unit.

UNIT – I

1. a) The solution of the Schrödinger equation for a particle of mass m free to move parallel to the x-axis with zero potential energy is of the form $\psi = Ae^{ikx}$. Find the linear momentum of the particle.

[Given : A is constant, $K = \frac{(2mE)^{1/2}}{h}$, E = energy of the particle.] 3

b) Determine the commutator of the operators $\frac{d}{dx}$ and $\frac{1}{x}$. 3

c) Calculate the most probable radius at which an electron will be found when it occupies $1s$ orbital of hydrogen atom.

[Given : Radial factor of the wave function associated with $1s$ state of hydrogen atom, $R_{1s}(r)$, $R_{1s}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$, where a_0 = Bohr radius] 4

d) Show that the probability of finding the particle in a one-dimensional box in the region $\frac{L}{4}$ and $\frac{3L}{4}$ is $\frac{1}{2}$ if n is even.

[Given : $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$, where n = 1, 2, 3, ... ; L is length of the box.] 3

e) A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0·1 Å. Calculate the uncertainty involved in the measurement of its velocity.

[Given : $m_e = 9 \cdot 1 \times 10^{-31}$ kg, $h = 6 \cdot 626 \times 10^{-34}$ Js] 3

2. a) An integral number of half wavelengths of a single particle can be fitted between the walls of a one-dimensional box. Use this fact and the de Broglie relation to derive the expression for the quantised energy levels of the one-dimensional box. 2

b) A nitrogen molecule is confined in a cubic box of volume 1·00 m³. Assuming that the molecule has an energy equal to $\frac{3}{2}$KT at T = 300 K, what is the value of $n = (n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}}$ for this molecule ? What is the energy separation between the levels n and $n + 1$?

[Terms have their usual significance.] 4

c) Give the schematic plots of radial factor of the wave function, radial distribution function and probability density for $2s$ state of hydrogen atom.

[Given : R_{2s} (radial factor) = $\frac{1}{\sqrt{2}} \frac{1}{a_0^{3/2}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$, where a_0 = Bohr radius.] 3

d) Calculate the percentage change of energy in a given energy level of a particle in a one-dimensional box when the length of the box is increased by 10 per cent. 3

e) Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a one-dimensional harmonic oscillator of effective mass equal to that of an oxygen atom (15·9949 m_u) and force constant 544 Nm^{-1}.

[Given : m_u = atomic mass constant = $1 \cdot 66054 \times 10^{-27}$ kg.] 4

UNIT – II

3. a) Show that for a pure real gas its fugacity (f) at moderate pressure can be expressed as, $F \cong \frac{P^2 \overline{V}}{RT}$. ($\overline{V}$ = molar volume of the gas) 4

b) The following reaction is studied starting from 3 mole of O_2 at a certain temperature :

$$3O_2 (g) \rightleftharpoons 2O_3 (g)$$

Assuming that the advancement (ξ) at equilibrium is very much less than unity, show that $\xi = \frac{3}{2}\sqrt{pK_p}$ (K_p = equilibrium constant). 3

c) Calculate the equilibrium constant of the following reaction at 25°C :

$$Cu^{2+} (aq) + Cu (s) \rightleftharpoons 2Cu^{+} (aq)$$

[Given : The standard electrode potentials ($\phi°$) at 25°C, $\phi°_{Cu^{2+},Cu^{+}}$ = 0·16 V and $\phi°_{Cu^{+}/Cu}$ = 0·52 V] 3

d) 'The temperature coefficient of the standard cell potential for a certain cell whose cell reaction is $AgBr(s) + \frac{1}{2}H_2(g) \longrightarrow Ag(s) + HBr(aq)$ is found to be negative.' Using suitable expression for temperature coefficient justify the statement. 2

e) The solubility product of $PbSO_4$ in aqueous medium is $1 \cdot 31 \times 10^{-8}$ at certain temperature. Calculate the number of moles of $PbSO_4$ that can be dissolved in 5 litres of $1 \cdot 0 \times 10^{-3}$ (M) Na_2SO_4 solution (aq). 2

f) Consider the cell, $Pt \mid H_2 (g, p°) \mid HCl(aq) \mid AgCl(s) \mid Ag$

for which the cell reaction is $2AgCl(s) + H_2(g) \rightarrow 2Ag(s) + 2HCl(aq)$. At 25°C and a molality of HCl of 0·010 mol kg^{-1}, E_{cell} = + 0·4658 V.

i) Calculate $\Delta_r G$ for the cell reaction

ii) Assuming that the Debye-Huckel limiting law holds at this concentration, calculate the standard electrode potential, $\phi°_{AgCl/Ag,Cl^-}$. 4

4. a) Give cell diagram of a suitable concentration cell with transference where the extreme electrode is reversible with respect to cation of the electrolyte and hence derive thermodynamically the expression for the cell potential. 1 + 4

b) Prove that,

i) $\mu_i = \left(\dfrac{\partial A}{\partial n_i}\right)_{T,V,n_j \neq i}$

ii) $\dfrac{\mathrm{d}\, ln\, K_c^{\circ}}{\mathrm{d}T} = \dfrac{\Delta_r U^{\circ}}{RT^2}$ (Assume Van't Hoff equation).

[Terms have their usual meaning.] 3 + 3

c) Show that for homogeneous reaction $\Delta_r G = \left(\dfrac{\partial G}{\partial \xi}\right)_{T,P}$ and hence give a schematic plot of G versus ξ.

[ξ = advancement of the reaction.] 2 + 1

d) Molecular bromine is 24 per cent dissociated at 1600 K and 1·00 bar in the equilibrium, $Br_2\,(g) \rightleftharpoons 2\,Br\,(g)$. Calculate k at (i) 1600 K and (ii) 2000 K.

[Given : Standard reaction enthalpy, $\Delta_r H^{\circ} = +112$ kJ mol^{-1} over the temperature range.] 4

UNIT – III

5. a) Define molar conductivity of an ion. Find a relation between molar conductivity of an ion and its ionic mobility. 1 + 4

b) If there is 1% error in the value of r, the radius of the capillary, find the error in the viscosity coefficient value calculated by using Poiseuille equation. 3

c) How does the viscosity coefficient of a liquid vary with temperature ? Find a suitable equation to explain the nature of variation. 1 + 2

d) The surface tension of a liquid is equal, both numerically and dimensionally to the surface energy. Justify / criticise. 2

e) Find the change in surface energy when two identical mercury droplets of diameter 2 mm merged isothermally to form 1 drop. (γ_{Hg} = 49·0 dynes cm^{-1}). 3

6. a) Give a schematic plot of logarithm of vapour pressure of an ideal liquid against reciprocal of the absolute temperature. Derive a suitable equation to justify the plot. 1 + 3

b) State the characteristics of Newtonian fluid. 2

c) Give schematic conductometric titration curve for each of the following systems :

i) Aqueous sodium acetate solution by hydrochloric acid solution.

ii) Aqueous silver nitrate solution by potassium chloride solution. 2 + 2

d) The limiting molar conductivities of NaI, $NaCH_3CO_2$ and Mg $(CH_3CO_2)_2$ are 12·69, 9·10 and 18·78 ms m^2 mol^{-1}, respectively (all at 25°C). What is the limiting molar conductivity of MgI_2 at this temperature ? 3

e) A steel ball of density 7·9 g/cc and 4 mm diameter requires 55 sec to fall a distance of 1 metre through a liquid of density 1·10 g/cc. Calculate the coefficient of viscosity of the liquid. 3