West Bengal State University

B.A./B.Sc./B.Com (Honours, Major, General) Examinations, 2014

PART – II

CHEMISTRY — HONOURS

PHYSICAL CHEMISTRY, CEMAT 24PA, 24PB

Paper – IV

(NEW & OLD SYLLABUS)

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.

(NEW SYLLABUS)

(Use separate answer-script for answering CEMAT-24PA and CEMAT-24PB)

CEMAT-24PA

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

UNIT – I

1. a) Find the value of the commutators $[\hat{x}, \hat{p}_x]$ and $[\hat{x}, \hat{p}_y]$. 3

b) Calculate the probability that a particle in the ground state will be found between 0·65 L and 0·67 L in a one dimensional box of length L ($0 \le x \le L$). [Given : $\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$] 3

c) Show that the wave function , $\psi_0(x)$, defined below, is the eigenfunction of the Hamiltonian operator of a one dimensional harmonic oscillator.

[Given : Potential energy, $u(x) = \frac{1}{2}kx^2$,

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \text{ where, } \alpha = \frac{(km)^{1/2}}{\hbar}$$

other terms have their usual meaning.] 4

d) Find the de Broglie wavelength of the electrons that have been accelerated from rest through a potential difference of 40 kV.

[Given : electronic charge, $e = 1{\cdot}602 \times 10^{-19}$ C , $m_e = 9{\cdot}109 \times 10^{-31}$ kg] 3

2. a) What do you mean by zero point energy of a particle executing simple harmonic motion ? The occurrence of zero point energy for such a particle is consistent with the Heisenberg Uncertainty Principle. Explain. 2 + 2

b) Show the schematic plots for each of following cases of photoelectric effect :

i) Photoelectric current versus potential difference for two different intensities of UV-light.

ii) Maximum photoelectron kinetic energy versus frequency of incident UV-light for two different metal surfaces having different work functions.

Give reason for each case. 4

c) If $\hat{H}\psi_1 = E_1\psi_1$ and $\hat{H}\psi_2 = E_2\psi_2$, then under what conditions, $\psi = C_1\psi_1 + C_2\psi_2$ will be an eigenfunction of the operator, $\hat{H}$? What will be the eigenvalue ? Justify your answer.
[Given : E_1 and E_2 are eigenvalues, C_1 & C_2 are arbitrary constants.] 3

d) Write down Wien's displacement law indicating the quantities involved. 2

UNIT – II

3. a) Show that in the photochemical decomposition of HI, the rate of disappearance of HI does not depend on the concentration of HI. What is the quantum yield of this reaction ? 3 + 1

b) The radial wavefunction for 2s orbital of a hydrogen atom is given by $R_{2,0} = N(2 - r/a_0)\, e^{-r/2a_0}$, N = constant.

i) Determine the number of location of node(s) in the 2s wavefunction.

ii) Write down the corresponding radial distribution function. Give the diagram of the distribution function. 2 + 2

c) Find the average value of the distance in terms of a_0 of an electron from the nucleus in the 1s state of hydrogen atom.

[Given : $R_{1s}(r) = \frac{2}{a_0^{3/2}} e^{-\rho/2}$ where $\rho = \frac{2r}{na_0}$, a_0 = Bohr radius,

$\int_0^\infty x^n \exp(-ax)dx = n!/a^{n+1}$] 4

4. a) What do you mean by photosensitization ? Give one example. 2 + 1

b) Calculate the number of photons of wavelength 350 nm that have the same energy content of 1 kcal. 2

c) Find the point at which the probability density of the $3d_{z^2}$ orbital of the hydrogen atom will be highest.

[Given : $\psi_{320} = cr^2 \exp(-r/3)(3\cos^2\theta - 1)$ where c contains all the constants of the wavefunction and ψ_{320} is expressed in atomic units.] 4

d) If the molar absorption coefficient of a solution is 475 m^2/mol, how thick a layer must be used to reduce the intensity of the transmitted beam to 20% of its initial value ? The concentration is 0·126 mol dm^{-3}. 3

CEMAT-24PB

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

UNIT – I

5. a) Find the criterion for a spontaneous process in a system at constant temperature and volume and hence apply this to explain that mixing of two ideal gases at constant temperature and volume should be spontaneous. [Consider mechanical work only] 2 + 2

b) Show that $\mu_i = \left(\frac{\partial H}{\partial x_i}\right)_{S,P,x_{j\neq i}} = \left(\frac{\partial A}{\partial x_i}\right)_{T,V,x_{j\neq i}}$. 3

c) Prove that $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{RT}{p_i}$

Consider the system as a mixture of ideal gases, p_i = partial pressure of i^{th} constituent and other terms have usual meaning. 3

d) Consider the association of potassium atoms in the vapour phase to form dimers

$2\kappa(g) \rightleftharpoons \kappa_2(g)$

Suppose we start with 2 moles of $\kappa(g)$ and no dimers. Derive an expression for $\kappa_p(T)$ in terms of ξ_{eq}, the extent of reaction at equilibrium and the pressure, P, and hence show that if P increases ξ_{eq} should increase. 3

6. a) Starting from van't Hoff equation for a solid-vapour equilibrium arrive at the Clausius-Clapeyron equation. 4

b) The equilibrium constant for the reaction described by

$2\ HBr\ (g) \rightleftharpoons H_2\ (g) + Br_2\ (g)$

can be expressed by the empirical formula

$$\ln \kappa = -6 \cdot 375 + 0 \cdot 6415 \ln (T/\kappa) - \frac{11790\,\kappa}{T}.$$

Find $\Delta H°$ at 25°C for the reaction. 3

c) At constant temperature and pressure 1 mol of a solute is dissolved in n_1 moles of a solvent of molecular weight M_1. If the total volume of the solution be V litres and ρ be its density in g cm^{-3}, then show that

$$\overline{V_1} = \frac{M_1}{1000\left[\rho + V\frac{dp}{dv}\right]}$$

where $\overline{V_1}$ = partial molar volume of solvent. 3

d) One mol of toluene (latent heat of vaporisation = 33·42 kJ mol^{-1}) is vaporised at its boiling point (111°C) and at a pressure of 101·3 k Pa. Calculate ΔG and ΔA for this process.

[Given : G = Gibbs free energy, A = Helmholtz free energy] 3

UNIT – II

7. a) Define molar conductivity of an ion. For a $z : z$ valent electrolyte, find the relation between the ion's mobility and its molar conductivity. 4

b) The ratio of the slopes of the linear portions in the plots of $ln\ \gamma_{\pm}$ versus $C^{1/2}$ for NaCl (aq) and $CaCl_2$ (aq) at 25°C is approximately 2 : 7. Justify / criticise the statement.

[C = molar concentration, $\gamma \pm$ = mean ionic activity coefficient] 4

c) Consider the electrochemical cell whose cell diagram is Cd (s) | $CdCl_2$ (m) | AgCl (s) | Ag (s). Given that $\gamma_{\pm}$ = 0·0669 for 1·00 molal $CdCl_2$ (aq). Calculate the value of the *emf* of the cell at 298·15 K.

[Given : standard reduction potentials at 25°C for Cd^{2+}(aq)/ Cd (s) and AgCl (s) | Ag (s), Cl^- (aq) are – 0·403 and + 0·2224 V respectively.] 4

8. a) Consider a suitable concentration cell without transference. Give the cell diagram. Find the net cell reaction and hence using Nernst equation on the net cell reaction find the expression of *emf* of the cell. 6

b) "For the hydrolysis of a salt of weak acid and strong base, the weaker the acid, the greater is the hydrolysis of the salt." Justify/criticise the statement. 2

c) Give the schematic conductometric titration plots of conductance versus volume of titrant for the following cases :

i) H_2SO_4 (aq) *vs.* NaOH (aq)

ii) NH_4Cl (aq) *vs.* NaOH (aq).

Give explanation for each case. 4

(OLD SYLLABUS)

Group – A

(PHYSICAL CHEMISTRY)

Answer any *one* question from each Unit.

UNIT – I

1. a) "Zero point energy of a simple harmonic oscillator does not violate Heisenberg's uncertainty principle." Justify. 2

b) State the conditions of "acceptability of wave functions" in quantum mechanics with explanation. 3

c) Evaluate the commutator $[\hat{A}, \hat{B}]$ where $\hat{A} = \frac{\partial}{\partial x} - x$ and $\hat{B} = \frac{\partial}{\partial x} + x$. 3

d) *X*-rays of wavelength 10 pm are scattered from a target. (i) Find the wavelength of the *X*-ray scattered through 45°. (ii) Find the maximum wavelength present in the scattered *X*-rays. (iii) Find the maximum kinetic energy of the recoil electron. 1 + 1 + 1

e) Show that $< p_x >$ is zero for all the stationary states of a particle in a one-dimensional box of length *L*. 2

f) Find $\left\langle \frac{1}{r} \right\rangle$ for 1s orbital of hydrogen atom.

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

[$\int_0^\infty x^n e^{-qx} dx = \frac{n!}{q^{n+1}}, n > -1; q > 0$] 3

2. a) Show that the average displacement of a harmonic oscillator, $< x >$, is zero for all the quantum states of a harmonic oscillator. 2

b) State with explanation whether $i\frac{\partial}{\partial x}$ is a Hermitian operator or not. 3

c) Given $\hat{A} = x + \frac{\partial}{\partial x}$. Find the value of $\hat{A}^2$. 2

d) Benzene may be regarded as a two-dimensional square box of side 3·5 Å and containing 6 π-electrons. What wavelength of light should be required to promote an electron from the ground state to the first excited state ? [Given, $m_e = 9 \cdot 11 \times 10^{-31}$ kg] 3

e) A microparticle can be found anywhere with equal probability within a length *L*. Find roughly its uncertainty in momentum. If the latter is the minimum possible value of its momentum, find also the minimum kinetic energy. 2

f) The radial wavefunction for 2s orbital of hydrogen atom is given by the following expression : $R_{2,0} = N\left(2 - \frac{r}{a_0}\right)\exp(-r/2a_0)$, N is a constant.

i) Determine the number and location of node(s) in the 2s wavefunction.

ii) Write down the expression for the radial distribution function of a 2s electron and sketch the radial distribution curve. 2 + 2

UNIT – II

3. a) Show that $\sum n_i d\mu_i = 0$. 2

b) Elucidate the concept of chemical potential as escaping tendency and mention the significance with respect to the equilibrium state of the system. 3

c) Using Clausius inequality derive the criteria for equilibrium and spontaneity in terms of G and A. 2 + 2

d) Calculate K_p for the reaction $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$, if at equilibrium the total pressure is 1 atm and partial pressure of NOCl is 0·7 atm at 200°C. Calculate $\Delta H°$, if K_p increases by 1·5% per degree around 200°C. 4

e) With the help of Gibbs-Helmholtz equation, obtain an expression of temperature coefficient of $E°$ of a cell at constant pressure and hence suggest how the standard enthalpy change of a cell reaction can be determined. 2 + 2

f) Represent a cell whose overall cell reaction is following : 1

$Ag^+\,(aq) + Cl^-\,(aq) \rightarrow AgCl\,(s)$

4. a) Show that $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{V_i}$. 2

b) Plot the following :
$ln\ K_p$ *vs.* $1/T$ (for exothermic and endothermic reaction) 1

c) Derive Clausius-Clapeyron equation thermodynamically for liquid $\rightleftharpoons$ vapour equilibrium. 3

d) In a study of the water-gas shift reaction,
$CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$; a mixture of CO_2 and H_2 initially containing 42·4 mol% H_2 was brought to equilibrium in a closed vessel at 1259K. The system was then found to contain 15·2 mol% H_2. Calculate K_p and $\Delta G°$ for the reaction at 1259K. 3

e) Does the equilibrium constant of a chemical reaction depend on the following ?

i) Standard states chosen for the reactants and products;

ii) The stoichiometric representation of the reaction.

Justify your answer. 2 + 2

f) What is meant by liquid junction potential ? Why is KCl used in salt bridge to eliminate liquid junction potential ? 2 + 1

g) What do you mean by a concentration cell ? 2

UNIT – III

5. a) Plot the following :

i) λ *vs.* $\sqrt{C}$ for acetic acid;

ii) $\frac{1}{\lambda}$ *vs.* $\lambda.C$ for acetic acid. 2

b) State how the law of independent migration of ions can be utilized to determine the λ_0 of a weak acid, *e.g.* acetic acid. 2

c) Discuss the effect of temperature on the surface tension of the liquid. 3

d) Describe the "moving boundary method" for the determination of transport number of an ion. 4

e) Specific conductance of pure water is $38 \cdot 4 \times 10^{-9}$ $ohm^{-1}cm^{-1}$ at 18°C. The equivalent conductance at infinite dilution of H^+ and OH^- are 315·2 $ohm^{-1}cm^2$ gm $eqv^{-1}$and 173·8 $ohm^{-1}cm^2$ gm eqv^{-1}, respectively. Calculate the ionic product of water at 18°C. 3

f) The speed ratio of Ag^+ and NO_3^- ions in an aqueous solution of $AgNO_3$ has been found to be 0·92. Calculate the transport number of each of them. 2

6. a) Describe a process for the determination of relative viscosity of a liquid. 4

b) The equivalent conductance at infinite dilution of HCl, NaCl and NaOAc are 426·2 $ohm^{-1}cm^2$, 126·5 $ohm^{-1}cm^2$ and 91·0 $ohm^{-1}cm^2$, respectively at 25°C. Calculate $\lambda°$ 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 the resistance 508·6 ohms. Calculate the dissociation constant of CH_3COOH.

[Given specific conductance for 0·01(M) KCl is $1 \cdot 41 \times 10^{-3}$ $ohm^{-1}cm^{-1}$]. 3

c) Write the unit and dimension of the surface tension. 2

d) Explain why the mobility of Li^+ in water is less than that of K^+ ? 1

e) A gas bubble of diameter 2 cm rises steadily through a solution of density 1·75 gm/c.c. at the rate of 0·35 cm/sec. Calculate the coefficient of viscosity of the solution neglecting the density of the gas. 3

f) State and explain the effect of dilution on the magnitude of (i) conductance; (ii) specific conductance and (iii) equivalent conductance of a strong electrolyte. 3