2015

CHEMISTRY

[Honours]

PAPER – VII

Full Marks : 45

Time : 2 hours

The figures in the right hand margin indicate marks

GROUP – A

Answer any **one** question from the following : 15 × 1

1. (*a*) Consider the following two competing irreversible first order reactions : $A \rightarrow B$ (rate constant k_1) and $A \rightarrow C$ (rate constant k_2). Show that

(*i*) $[A] = [A]_0 e^{-(k_1+k_2)t}$

(*ii*) $t_{1/2} = \frac{0 \cdot 693}{k_1 + k_2}$

(*iii*) $\frac{[B]}{[C]} = \frac{k_1}{k_2}$ at any time during the reaction.

(*iv*) For the set of initial conditions $[B]_0 = [C]_0 = 0$, and $k_1/k_2 = 2$, plot $[A]$, $[B]$ and $[C]$ as a function of time on the same graph. 1 + 1 +1 + 2

(*b*) KCl has an f.c.c. lattice but from X-ray diffraction experiment if appears to be a simple cube. Explain. 3

(*c*) Plot γ (surface tension) vs. concentration plot for (*i*) Acetic acid (*ii*) SD S (sodium dodecyl sulphate). 1

(*d*) Derive Einstein equation for heat capacity of elemental solids, $\bar{C}_v$, stating the assumption (s) and hence deduce the limiting value of $\bar{C}_v$ at $T \rightarrow OK$ and $T \rightarrow \infty$. 4 + 2

2. (*a*) (*i*) Derive Langmuir adsorption isotherm stating the postulates.

(*ii*) Show that when a diatomic gas adsorbs as atoms on the surface of a solid, the Langmuir adsorption isotherm becomes

$$\theta = (kP)^{1/2} \Big/ \left(1 + (kP)^{1/2}\right)$$

where the symbols have their usual significance. 3 + 2

(*b*) The index of refraction of gaseous paraffin C_nH_{2n+2} is found to be 1·00 139 when the gas is at STP. Given the molar refractions as 1·1 and 2·42 cm^3mol^{-1} for H and C respectively, determine the formula of the hydrocarbon. 3

(*c*) Write down the principle involved in determining the A—A bond distance in a homonuclear molecule (A_2) by spectroscopic method. 3

(*d*) Consider a particle with quantum number '*n*' moving in a one dimensional box of length '*l*'.

(*i*) Determine the probability of finding the particle in the region $0 \leq x \leq l/4$.

(*ii*) For what value of '*n*' the above determined probability is a maximum ?

2 + 2

GROUP – B

Answer any **two** questions from the following : 10×2

3. (*a*) Derive the Michaelis-Menten equation for an enzyme catalysed reaction and show that the reaction is zero order with respect to substrate, at large substrate concentration. 4

(*b*) A molecule on proper excitation undergoes photochemical dissociation. Draw the potential energy curves for the ground state and the excited state of the molecule. 3

(*c*) The rate constant for the decomposition of N_2O_3 in the gas phase

$$2N_2O_3 \rightarrow 4NO_2 + O_2$$

is $2 \times 10^{-4}\ s^{-1}$. Find out the total pressure after 5 min when the initial pressure was 500 mm of Hg. 3

4. (*a*) Classify the following operators as linear or not : Give reasons.

$$d^2/dx^2,\ \int(\ )dx,\ (\ )^2$$ 3

(*b*) The fundamental frequency and anharmonicity constant for $H^{35}Cl$ are respectively 2990·6 cm^{-1} and 0·0174. Find out, (*i*) The force constant and (*ii*) the first overtone. 2 + 2

(*c*) At 292 K, the surface tensions of solutions of butyric acid in water, γ can be represented accurately by the equation, $\gamma = \gamma_0 - a \ln(1 + b\,c)$, where c is the concentration of butyric acid, γ_0 is the surface tension of water, '*a*' and '*b*' are two

constants. Set up the expression for the excess concentration of solute per sq cm of surface as a function of c. 3

5. (*a*) Evaluate the commutator $\left[\hat{A}, \hat{B}\right]$ where

$$\hat{A} = \frac{d}{dx} - x \text{ and } \hat{B} = \frac{d}{dx} + x .$$ 3

(*b*) Show that if the reactant '*A*' undergoes two simultaneous reactions to produce *B* and *C* according to the reaction : $A \rightarrow B$ (rate constant k_1) and $A \rightarrow C$ (rate constant k_2), then the observed activation energy for the disappearance of A (E_a) is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

(where E_1 and E_2 is the activation energy of the first and second reaction, respectively). 3

(*c*) Write short notes on : 2 + 2

(*i*) Hot band

(*ii*) Rule of mutual exclusion.

6. (*a*) In the photochemical combination of $H_2(g)$ and $Cl_2(g)$ a quantum yield of 1×10^6 is obtained with light of wavelength 4800 Å. How many moles of HCl (g) would be produced under these conditions per calorie of light energy absorbed ? 3

(*b*) Determine the highest order that can be observed in Bragg's reflection from a solid by X-ray ? 2

(*c*) The reaction $2NO + O_2 \rightarrow 2NO_2$ may occur through the following mechanism

$$NO + NO \rightleftharpoons N_2O_2$$

$$N_2O_2 + O_2 \rightarrow 2NO_2$$

(*i*) Derive the differential rate equation and mention the condition under which the reaction would become 3rd order.

(*ii*) Show that the dependence on temperature of the overall rate constant of the reaction can be given by

$$k = Ae^{-(E_a + \Delta H)/RT}$$

where ΔH is the enthalpy change of first reaction. 3 + 1 + 1

GROUP –C

Answer any **five** questions from the following : 2×5

7. (*a*) If the activation energy for the reaction

$$H_2 + I_2 \rightarrow 2HI$$

is 167 KJ and ΔH for the reaction is – 8·2 KJ, what is the activation energy for the decomposition of HI ?

(*b*) Find the de Broglie wavelength of electrons that have been accelerated through a potential difference of 1 kV. [Given mass of electron $9{\cdot}11 \times 10^{-31}$ kg].

(*c*) What are the SI units of rate constant for $\frac{1}{2}$ order and 3rd order reaction ?

(*d*) Calculate the degeneracy of the energy level with energy equal to $\frac{11h^2}{8ma^2}$ for a particle in a cubical box.

(*e*) What is the essential condition for a molecule to exhibit pure vibrational spectra ?

(*f*) State and explain Frank-Condon principle.

(*g*) Colloidal solutions are thermodynamically unstable—Comment.

(*h*) Explain whether X-ray of wavelength 1000 pm is suitable for studying Bragg reflection of a cubic crystal with $a = 450$ pm.
