

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

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

(Turn Over)

$$(ii) \quad t_{1/2} = \frac{0.693}{k_1 + k_2}$$

(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 it 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 $T \rightarrow 0K$ 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

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

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 $\text{cm}^3\text{mol}^{-1}$ 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



is $2 \times 10^{-4} \text{ s}^{-1}$. 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.

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

- (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, $\gamma = \gamma_0 - a \ln(1 + bc)$, 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 $[\hat{A}, \hat{B}]$ where

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

(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

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

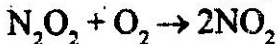
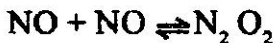
(where E_1 and E_2 is the activation energy of the first and second reaction, respectively). 3

(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 \AA . 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



- (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

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

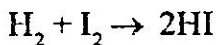
where ΔH is the enthalpy change of first reaction. 3 + 1 + 1

GROUP -C

Answer any five questions from the following :

2 × 5

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



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 9.11×10^{-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.
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