2016

CHEMISTRY

(*Physical*)

[Honours]

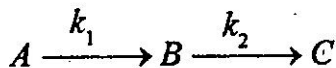## PAPER — VII

Full Marks : 45

Time : 2 hours

The figures in the right hand margin indicate marks

GROUP — A

Answer any **one** question from the following :

1. (*a*) Consider a consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where both the steps are first order. If at time t_m, concentration of B is maximum,

show that

$$t_m = \frac{\ln k_1 - \ln k_2}{k_1 - k_2}$$

Draw the plot of $[A]$, $[B]$ and $[C]$ vs. t for the above reaction. 4 + 1

(b) A 1×10^{-3} M solution of a dye (X) shows an absorbance of 0·20 at 450 nm and absorbance of 0·05 at 620 nm. A 1×10^{-4} M solution of another dye (Y) shows 0·00 absorbance at 450 nm and an absorbance of 0·42 at 620 nm. Calculate the concentration of each dye present together in a solution, which exhibit an absorbance of 0·38 and 0·71 at 450 nm and 620 nm respectively. The same cell is used in all measurements and its thickness is 1·00 cm. 5

(c) Show that the wavefunctions $\psi_1 = \sin\frac{\pi x}{a}$

and $\psi_2 = \cos\frac{\pi x}{a}$ are orthogonal in the interval $0 < x < a$. 3

(d) The distance between two successive planes of a cubic lattice cannot be $\dfrac{a}{\sqrt{7}}$ where a is the edge length of the cube. Explain.　　2

2. (a) Use the Lindemann hypothesis, to show that a unimolecular decomposition may follow a first order kinetics.　　4

(b) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the bond length of the molecule.　　4

(c) Under what condition

$$(\hat{A} + \hat{B})^2 = \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2 ?$$　　3

(d) 100 c.c. of a silver sol contains 3×10^{10} particles, each of diameter 100 nm. If the solution requires 2.7×10^{-4} gm of Al^{3+} to attain iso-electric point, calculate the surface charge density on silver particles.　　4

(4)

GROUP – B

Answer any **two** questions from the following :

3. (a) Show that in a crystal lattice there cannot be five fold rotational axis of symmetry.　　4

   (b) The reaction $A \longrightarrow$ Product gives a linear plot of $\dfrac{1}{[A]}$ vs. t of intercept 100 mol l^{-1} and slope 3×10^{-2} lit $mol^{-1}s^{-1}$. What is the order of the reaction ? Calculate $t_{1/2}$ of this reaction.　　$2 + 2$

   (c) Define chemiluminescence with example.　2

4. (a) What are 'Stokes' and 'anti-stokes' lines in Raman spectrum ? Why 'Stokes' lines are more intense than 'anti-stokes' lines ?　$2 + 2$

   (b) Define micelle and critical micelle concentration (CMC). On which factors CMC of surfactants depend and how ?　$2 + 2$

(c) The rate of hydrolysis of an ester catalysed by strong acid is almost doubled when the pH is changed from 0·80 to 0·50. Justify whether this is an example of homogeneous catalysis or not.　　　　2

5. (a) A light of wavelength λ having an intensity I_0 falls on a solution of concentration C and pathlength l. Write an expression for the intensity of light absorbed.　　　3

(b) Show that linear momentum operator p_x is hermitian.　　　3

(c) The molar polarisation of fluorobenzene vapour is 70·62 cm³ mol⁻¹ at 351 K and 62·47 cm³ mol⁻¹ at 423 K. Calculate the dipole moment of the molecule.　　　4

6. (a) Verify that the function $Ae^{-\frac{1}{2}Bx^2}$ is the ground state eigenfunction of linear harmonic oscillator, where $B = \dfrac{\sqrt{mk}}{\hbar}$. Hence show that eigenvalue $E = \dfrac{1}{2}h\nu$.　　　4

(b) Define catalyst poison. How catalyst poisons inhibit rate of heterogeneous catalytic reaction ?   1 + 2

(c) Discuss briefly how the BET adsorption equation may be used to determine the surface area of an adsorbent.   3

GROUP – C

7. Answer any five questions :   2 × 5

(a) Determine the Miller indices of the planes that intersect the crystal axis at (i) $a, 2b, 3c$ and (ii) $a, b, -c$.

(b) The rate constant of the reaction between $K_2S_2O_8$ and KI in aqueous medium is affected by ionic strength. Justify with the help of an appropriate equation.

(c) A first order reaction can be studied even when the initial concentration of the reactants are not known. Explain.

(*Continued*)

(d) 0.1 M $AlCl_3$ is more effective than 0.1 M NaCl solution in coagulating an As_2S_3 sol while 0.1 M $AlCl_3$ is less effective than 0.1 M Na_3PO_4 in coagulating Fe_2O_3 sol. Explain.

(e) Draw the plot of $\log k$ vs. pH for a homogeneous acid catalysed reaction. Comment on the intercept on $\log k$ axis.

(f) Symmetric stretch mode of vibration of carbon dioxids molecule is Raman active but infrared inactive. Explain.

(g) Define gold number of a lyophilic colloid.

(h) Calculate the deBroglie wavelength of an electron that has been accelerated through a potential difference of 300 volts.