2021

CHEMISTRY — HONOURS

Paper : CC-14

(Physical Chemistry-5)

Full Marks : 50

The figures in the margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

Answer ***question number 1*** and ***any eight*** from the rest.

1. Answer ***any ten*** questions: 1×10

(a) The infrared and Raman spectra of a triatomic molecule of the type MX_2 show two infrared frequencies and one Raman frequency. Determine whether the molecule is linear or non-linear.

(b) The adsorption of a gas follows Langmuir isotherm with $K = 1{\cdot}25\ Pa^{-1}$ at 298 *K*. Find the pressure (in Pa) at which surface coverage is 0·2.

(c) A solution absorbs 300 nm radiation at the rate of 1W. What does this correspond to in amount of photons absorbed per second?

(d) If γ is the surface tension of a soap solution, then calculate the amount of work done in blowing a soap bubble from diameter *d* to a diameter 2*d*.

(e) Why phosphorescence of aromatic hydrocarbon is usually observed at low temperature in rigid matrix?

(f) Why Debye equation for the dipole moment should be applicable to gases and vapours only?

(g) How many normal modes of vibration are there for benzene molecule?— Explain.

(h) Adsorption of a gas by solid is an exothermic process— justify or criticize.

(i) Excitation to the first vibrational excited state of $H^{35}Cl$ occurs with infrared radiation of frequency 2900 cm^{-1}. Calculate the expected position of the same absorption in the case of $D^{35}Cl$. (assuming force constant to be same).

(j) The photochemical dissociation of molecular chlorine reaches a steady state as a result of the recombination of atoms.

$$Cl_2 + h\nu \underset{K_{-1}}{\overset{I_a}{\rightleftharpoons}} 2Cl$$

Obtain the steady state concentration of chlorine atoms.

(k) Find the C.G.S. unit of μ^2/kT, where μ is the permanent dipole moment of a molecule.

(l) What is the physical basis of separation of electronic and nuclear motion in molecules?

2. (a) Write down the principle involved in determining the bond length of a homonuclear diatomic molecule by spectroscopic method.

(b) The Pt-catalyzed decomposition of HI obeys the rate law $dP_{HI}/dt = k_1$, at high pressures, with k_1 = 500 mm Hg. s^{-1} at 100°C. At low pressure, the rate law becomes $dP_{HI}/dt = k_2P_{HI}$, with k_2 = 50 s^{-1} at 100°C. Calculate the HI pressure at which the value of dP_{HI}/dt should be 250 mmHgs^{-1} at 100°C. Assume Langmuir adsorption isotherm. 2+3

3. (a) How a lyophilic colloid help in stabilizing a lyophobic colloid? Explain what do you mean by the term 'gold number'.

(b) In the vibration-rotation spectrum (v = 0 to v = 1) of CO, the rotational constant for ground state and first excited vibrational states are found to be B_0 = 1·915 cm^{-1} and B_1 = 1·898 cm^{-1}. Calculate the percentage increase in bond length on going from v = 0 to v = 1. What effect does this lengthening of the bond have on spacings of the rotational lines in the fundamental band for $\Delta J = \pm 1$? 2+3

4. (a) What is the quantitative version of the Franck-Condon principle? Define Franck-Condon factor.

(b) A capillary tube of radius 0·001 cm is inclined at an angle 45° to the surface of liquid. The liquid wets the wall. It has a density of 0·85 g cm^{-3} and surface tension of 36 dyne cm^{-1}. Calculate d, the distance along the capillary to the meniscus. 2+3

5. (a) Show that a diatomic molecule dissociates into atoms if it is present in the vibration state of vibrational quantum number,

$$v = \frac{1}{2x_e} - \frac{1}{2}$$

where, x_e is the anharmonicity constant.

(b) The surface tension of a 1% by weight solution of a surfactant is 70 dyne cm^{-1}, and that of a 2% solution is 68 dyne cm^{-1} (water is 72 dyne cm^{-1}). Show that the adsorbed film obeys the two-dimensional ideal gas law, and calculate the molecular weight of the surfactant, if it is known that the 2% solution had 20 × 10^{-9}g of surface excess of surfactant per cm^2. Assume 298K temperature. 2+3

6. (a) Define Zeta potential using Stern double layer theory.

(b) 52·48 ml of the quartz container was filled up with CH_3COCH_3 vapour at 47°C at 780 mm of Hg. The vapour was irradiated with radiation of wavelength 300 nm and intensity 2·1 × 10^{18} photons s^{-1} for 30 minutes. Find out the increase in pressure. (Given, quantum yield = 0·1 and the dissociation reaction is $CH_3COCH_3 \rightarrow C_2H_6 + CO$, and ideal behaviour of the vapour.) 2+3

7. (a) Explain why band centre is missing in roto–vibronic spectra? Is there any exception?

(b) For $^{1}H^{35}Cl$, rotational constant $B_0 = 10{\cdot}44\ cm^{-1}$ and $B_1 = 10{\cdot}13\ cm^{-1}$ for the $v = 0$ and $v = 1$ vibrational levels, respectively, and the separation of these vibrational levels, w_0, is $2886{\cdot}04\ cm^{-1}$. Calculate the wavenumbers of the first two members of each of the O and S branches in the Raman vibration-rotation spectrum. 2+3

8. (a) How can you experimentally determine that lyophobic colloid particles are charged?

(b) The absorbance of a solution in which B_i^{3+} was very large and SCN^- was $5{\cdot}0 \times 10^{-5}$ mol dm^{-3} in a cell of 1·0 cm thickness was found to be 0·286. The reaction which occurs is,

$$Bi(SCN)^{2+} \rightleftharpoons B_i^{3+} + SCN^-$$

What was the absorption coefficient of $Bi(SCN)^{2+}$? In another experiment, absorbance was found to be 0·24 when the initial $[Bi^{3+}]$ was 0·50 mol dm^{-3}. What is the value of K_c of the above equilibrium? 2+3

9. (a) The vibrational wavenumbers of the following molecules in their $v = 0$ states are :
HCl : 2885 cm^{-1}, DCl : 1990 cm^{-1}, D_2 : 2990 cm^{-1} and HD : 3627 cm^{-1}. Calculate the energy change, in kJ mol^{-1} of the reaction

$$HCl + D_2 \rightarrow DCl + HD$$

and determine whether energy is liberated on absorbed.

(b) The gas phase reaction

$$2A \rightarrow B + C$$

is bimolecular with an activation energy of 24000 cal mol^{-1}. The molecular weight and diameter of A are, respectively, 60 and 3·5 Å. After deducing the necessary equation using the Collision theory of reaction rate, calculate the value of the rate constant at 300K. (Assuming steric factor = 1) 2+3

10. (a) A time-lag is essential between the moment of energization and the moment of decomposition in the Lindemann mechanism — justify or criticize.

(b) The photochemical combination of hydrogen and chlorine gas takes place according to the following mechanism,

$$Cl_2 + h\nu \rightarrow Cl + Cl$$
$$Cl + H_2 \rightarrow HCl + H$$
$$H + Cl_2 \rightarrow HCl + Cl$$
.....
and so on.

What happen when,

(i) a third body such as an unreactive molecule is introduced into the reaction vessel. Obtain the expression for the rate of formation of hydrogen chloride in presence of an unreactive molecule or a wall.

(ii) O_2 gas is introduced into the reaction vessel. 2+3

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11. (a) Explain why the polarizability of a polar molecule decreases at high frequencies.

(b) A diatomic gas at high temperature shows a series of vibrational absorptions. By accident, some of the data are lost, but it is known that the absorption included 5600, 11200 and 14000 wavenumbers. Explain what the probable quantum number assignments are for these three transitions (The values are hypothetical, no deviation from the simple parabolic potential energy curve is assumed, and selection rule restrictions are ignored. 2+3

12. (a) Calculate the relative permitivity (ε_r) of HCl(g) at 1 atm and 273 K.
Given : dipolemoment (μ) of HCl(g) = $3{\cdot}60 \times 10^{-30}$ C.m.
distortion polarizability (α) of HCl(g) = $2{\cdot}93 \times 10^{-40}$ $C^2m^2\ J^{-1}$
permitivity of vacuum (ϵ_0) = $8{\cdot}854 \times 10^{-12}$ $C^2N^{-1}m^{-2}$

(b) The mechanism of quenching fluorescence is

$$A + h\nu \rightarrow A^*,\ I_a$$
$$A^* + Q \rightarrow A + Q,\ k_q$$
$$A^* \rightarrow A + h\nu_f,\ k_f = I_f/[A^*]$$

where I_a is the amount of exciting radiation absorbed per liter of solution per second, k_q is the rate constant for quenching, k_f is the rate constant for fluorescence, and I_f is the amount of fluorescence radiation per liter per second. Assuming a steady state is reached, derive the equation for the intensity of fluorescence radiation I_f as a function of [Q]. Describe how the data should be plotted to determine the rate constant for quenching. 2+3

13. (i) The value of the rotational constant B_0 obtained from the rotational Raman spectrum of $^{14}N^{15}N$ is $1{\cdot}923604\ cm^{-1}$. Calculate the bond length r_0.

(ii) Why does it differ from $r_0 = 1{\cdot}100105$Å for $^{14}N_2$?

(iii) Would the values of r_e (equilibrium internuclear bond length) differ?

(iv) Would there be an intensity alteration in the spectrum of $^{14}N^{15}N$?

(v) Would $^{14}N^{15}N$ show a rotational infrared spectrum? 5
