2022

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 no. 1** and **any eight** from the rest.

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

    (a) What will be the nature of the plot of total polarization (P_T) vs. $1/T$ for benzene?

    (b) Will there be any rotational energy at absolute zero?

    (c) What are the possible maximum and minimum values of optical density?

    (d) Low temperature and viscous medium are suitable for observing phosphorescence— Explain.

    (e) What are hot bands?

    (f) Can a molecule undergoing harmonic oscillations only dissociate?— Justify or criticize.

    (g) Dipole moment of HI is 0.3 Debye. Express its dipole moment in S.I. unit.

    (h) Why are strong electrolytes negatively adsorbed in aqueous medium?

    (i) Gold number of albumin and gelatine are 0.08 and 0.005. Which one is a better protective colloid?

    (j) Draw the graph which represents the variation of amount of chemisorption of a gas by a solid with temperature under constant pressure.

    (k) Colloid solution of gold prepared by different methods are of different colour.— Explain.

    (l) Surface tension of water around 293 K decreases by 0.16 dyne $cm^{-1}K^{-1}$. Calculate total surface energy per sq. cm. area at 293 K. [Given : $\gamma_{H_2O} = 72.75$ dyne cm^{-1} at 293 K].

2. (a) In methyl alcohol $C - O - H$ bond angle is 110°. Using the geometry and bond and group moments, calculate the dipole moment of methanol.

    Given : $\mu_{CH_3} = 0.4D$ and it acts along $C - O$ bond.

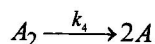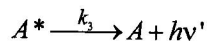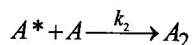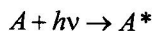 $\mu_{CO} = 0.7D, \mu_{O-H} = 1.6D$

    (b) C–H stretching vibration in an organic compound occur at 2900 cm^{-1}. At what wave no. would C–D stretching vibration occur? 3+2

Please Turn Over

3. (a) A plausible mechanism for the dimerisation of anthracene (A) is :

$$A + h\nu \rightarrow A*$$

$$A* + A \xrightarrow{k_2} A_2$$

$$A* \xrightarrow{k_3} A + h\nu'$$

$$A_2 \xrightarrow{k_4} 2A$$

Show that the maximum concentration of A_2 is determined only by the intensity of light absorbed. Compare this with that expected in the absence of light.

(b) Derive Laplace equation for the pressure difference across a spherical curved surface. (2+1)+2

4. (a) Indicate all the photophysical processes occuring from an excited electronic state with the help of Jablonski diagram.

(b) Calculate the percentage ionic character of H–I bond where the bond length of H–I bond is 1.60 Å and its dipole moment is 0.38 D. 3+2

5. (a) Pure rotational spectrum of $C^{12}O^{16}$ has two successive lines at 7.72 cm^{-1} and 11.58 cm^{-1}. Determine the 'J' values between which transitions occur in each case.

(b) The kinetics of the reaction $[Co(NH_3)_5Br]^{++} + OH^- \rightarrow [Co(NH_3)_5OH]^{++} + Br^-$ was studied in aquous solution of (A) 0.15(N) KCl and (B) 0.3(N) KCl. State with reason whether the rate constant of the reaction in the case (A) would be greater than, less than or equal to in the case of (B). 3+2

6. (a) A unimolecular gaseous reaction show 2nd order kinetics at low pressure.— Explain using Lindemann mechanism.

(b) Absorption and fluorescence spectra hold a mirror image relationship.— Comment. 3+2

7. (a) Predict the structure of NO_2^+ ion based on the following spectroscopic data. It exhibits one vibrational frequency at 1400 cm^{-1} which is Raman active but IR inactive and two frequencies at 2360 cm^{-1} and 540 cm^{-1} which are IR-active but Raman inactive. To which vibrational modes do these frequencies correspond?

(b) The density of $SiHBr_3$(MWt 269) is 2.690 gm/cc. At 25°C its refractive index is 1.578 and dielectric constant is 3.570. Estimate its dipole moment in Debyes. (neglecting atomic polarisation). (2+1)+2

8. (a) Find the number of normal modes of vibration of H_2O molecule and explain which of these vibrations are IR and Raman active.

(b) From the following data for adsorption of N_2 gas on a solid surface, calculate the constant involved in the Langmuir isotherm.

$P = \infty$, V = 180 cc/gm, P = 3.5 atm

V = 100 cc/gm. [V = volume of gas adsorbed]. 3+2

9. (a) A mixture of dichromate and permanganate ions was analyzed spectrophotometrically at 440 nm and 545 nm. The absorbance values were 0.385 and 0.653 respectively at each wavelength for a 1 cm cell. Calculate concentration of dichromate and permanganate in the unknown mixture.

Given : $Cr_2O_7^{2-}$: $\epsilon_{440} = 370\,M^{-1}cm^{-1}$

$\epsilon_{545} = 10.8\,M^{-1}cm^{-1}$

MnO_4^- : $\epsilon_{440} = 92.8\,M^{-1}cm^{-1}$

$\epsilon_{545} = 2350\,M^{-1}cm^{-1}$

(b) Give mathematical expression for Gibbs' surface excess. Justify that it can take up both positive and negative values.   3+2

10. (a) The surface tension of dilute solution of a certain surfactant decreases linearly with concentration. At 10^{-4}(M) surfactant the surface tension has decreased by 3 dynes cm^{-1}. Calculate Γ, the surface excess at 298 K.

(b) Exlpain the term 'Tyndall effect' using a labelled diagram. How does the wavelength of the scattered light depend on the size of the colloidal particle?   3+2

11. (a) Write down the differences between the Collision theory of reaction rate and transition state theory of reaction rate.

(b) 5g of a catalyst adsorbs 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å?   3+2

12. (a) An actinometer contains 20 cm^3 of a 0.05(M) oxalic acid through which radiation of wavelength 3500 Å was passed for 2 hrs. After exposure the solution required 34 cm^3 of $KMnO_4$ to titrate the undecomposed oxalic acid. The same volume i.e. 20 cm^3 solution required 40 cm^3 $KMnO_4$ before exposure. Calculate the energy absorbed in Joules/s if quantum efficiency is 0.53.

(b) The fundamental and first overtone for $^{14}N^{16}O$ are centred at 1876.06 cm^{-1} and 3724.0 cm^{-1} respectively. Calculate the exact zero point energy of the molecule.   3+2

13. (a) How can you justify the temperature dependence of Arrhenius frequency factor (A) using the collision theory of reaction rate?

(b) Discuss briefly the discrete lines and the continuous band in case of predissociation spectra.   3+2

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