2015

CHEMISTRY

(Major)

Paper : 5.2

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer in brief : 1×7=7

(a) State what is meant by quantum yield for photochemical reactions.

(b) What would be the ratio (σ / A) of the collision cross-section σ of a spherical molecule B, undergoing B-B type collisions in gas phase and of its surface area $A = \pi r^2$, where r is the molecular radius?

(c) Under what condition would the Lindemann theory of unimolecular gaseous reactions show second-order kinetics?

(d) How does the rate of the ionic reaction

$$S_2O_8^{2-} + 2I^- \rightarrow \text{products}$$

performed in aq. NaCl solutions would change with the increasing concentration of NaCl in water? Explain.

(e) How is the glow of fireflies explained in chemistry?

(f) Find the degree of freedom for an equilibrium mixture of gaseous ammonium chloride, ammonia and hydrogen chloride at 200 °C (a temperature at which all these substances remain at gas phase), given that the ammonia and hydrogen chloride gases there formed only from decomposition of the ammonium chloride introduced into the system.

(g) What is the relation between the surface area S of the solid adsorbent, the number of adsorbate gas molecules N_m forming a completely occupied monolayer, and the surface area ($A = \pi r^2$) of each adsorbate gas molecule?

2. Answer the following questions : 2×4=8

(a) What is meant by a molecular beam? In what way is a molecular beam used?

(b) What is the relation between adsorption and heterogeneous catalysis caused by solid catalyst surfaces? Why does the catalytic activity of solid catalysts become more pronounced when they are powdered?

(c) Explain how one may calculate the surface area of an adsorbent, provided the monolayer volume V_m of the adsorbate gas was determined using either the BET or the Langmuir isotherm.

(d) Obtain an expression for the Gibbs free energy of mixing $\Delta_{mix}G$ for an ideal binary liquid solution in terms of the mole amounts n_1 and n_2 of the two liquids, the mole fractions x_1 and x_2 and the temperature T.

3. Answer any *three* of the following : $5 \times 3 = 15$

(a) Show that for bimolecular collision of structureless particles, the transition state theory reduces to the simple collision theory.

(b) On the basis of the postulates of Langmuir adsorption theory, deduce the Langmuir adsorption isotherm. How can the monolayer volume V_m be obtained from this isotherm?

(c) The decomposition of HI takes place by the following mechanism :

$$HI + h\nu \rightarrow \dot{H} + \dot{I}$$

$$\dot{H} + HI \rightarrow H_2 + \dot{I}$$

$$\dot{I} + \dot{I} \rightarrow I_2$$

Find an expression for the rate of the reaction. Also find the quantum efficiency of the reaction.

(d) Draw and interpret the phase diagram of a binary condensed-phase system with the formation of a eutectic solid. Mention a real-life example of such a system. Why is a eutectic mixture not considered as a compound?

4. Defining the number of phases, the number of components and the degree of freedom, derive the Gibbs phase rule relating them. How does the expression for the degree of freedom get altered for condensed systems for which pressure has a negligible effect? How is the number of components C calculated for systems in which some chemical reaction equilibria and some stoichiometric restrictions bind their concentrations? Hence show that for a solution of acetic acid in water, $C = 2$, even though there are four chemical species, namely H_2O, CH_3COOH, CH_3COO^- and H^+ present in the system.

5+1+2+2=10

(Continued)

Or

State the difference between solid compounds formed in binary condensed-phase systems with congruent and incongruent melting points. Draw the phase diagrams for both the cases and explain how the solid compound is formed from the melt and how the solid melts in each case. Give an example for each situation. 2+6+2=10

5. On the basis of hard sphere collision theory of reaction rates, obtain an expression for the rate constant of a bimolecular gaseous reaction. What is the physical significance of the steric factor P in the above expression? Estimate the steric factor P for the dimerisation of gas-phase methyl ($\cdot CH_3$) radicals at 300 K, given that their molecular diameter $d = 3 \cdot 1$ Å (related to the reactive collision cross-section as $\sigma = \pi d^2$) and that the experimental pre-exponential factor is $2 \cdot 4 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. 5+1+4=10

Or

For the elementary gaseous reaction $A + B \rightarrow$ products, obtain an expression for the rate constant of the reaction as per the transition state theory in terms of the entropy of activation and the enthalpy of activation. The reaction $A^- + H^+ \to P$ has a rate constant given by the empirical expression

$$k_2 = 2 \cdot 06 \times 10^{13} \exp(-8670\,K/T)\,dm^3\,mol^{-1}\,s^{-1}$$

(where T is the Kelvin temperature). Calculate the entropy, the energy and the enthalpy of activation at 300 K. 5+5=10

6. (a) Discuss the mechanism of the photochemical reaction between hydrogen and bromine and find the expressions for the reaction rate and the quantum yield for this reaction. 5

(b) Discuss the role of nitrogen oxides and chlorofluorocarbons in ozone layer depletion. 3

(c) Explain the phenomenon of fluorescence with the help of Jablonski diagram. 2

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