2017

CHEMISTRY

(Major)

Paper : 5.2

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions in brief : $1 \times 7 = 7$

(a) Consider a heterogenous system of X phases at equilibrium containing three components. Express F for the system.

(b) State how the rate constant of a reaction between ions varies with ionic strength of the solution.

(c) 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 of B?

(d) Under what condition of pressure, would the Lindemann theory of unimolecular gaseous reaction show first-order kinetics?

(e) How many components are present in the following equilibria?

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

(f) Using the concept of chemical potential, state under what condition the three phases of water will be in equilibrium.

(g) The quantum yield for the photochemical formation of HCl is high in the absence of a matter, but low when that of matter is present. State what role matter plays in the reaction.

(Continued)

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

(a) Show how the Clausius-Clapeyron equation can be used in describing phase equilibrium.

(b) The quantum yield for the photochemical formation of HCl is high whereas HBr is very low. Why?

(c) 2 mol of substance A and 3 mol of substance B are mixed together when the total volume becomes $2 \cdot 1 \times 10^{-4}\ m^3$. If the partial molar volume of A is $2 \times 10^{-5}\ m^3\ mol^{-1}$, calculate the partial molar volume of B.

(d) A long chain fatty acid of molecular weight 256 has a density of $0 \cdot 82\ g/cm^3$. If $0 \cdot 102$ mg of the acid is required to form a closed packed monolayer film over $500\ cm^2$ of water surfaces, estimate the cross-section and length of the acid molecule.

(Turn Over)

3. Answer any *three* of the following questions : 5×3=15

(a) Write the postulates of hard-sphere collision theory. On the basis of collision theory, find an expression for the rate constant of the elementary bimolecular gaseous reaction, $A + B \rightarrow$ products. 2+3=5

(b) What is callled photostationary state of the photochemical reaction? The following mechanism has been proposed for the dimerization of anthracene :

(i) $A \xrightarrow{h\nu} A^*$

(ii) $A^* + A \xrightarrow{k_2} A_2$

(iii) $A_2 \xrightarrow{k_3} 2A$

(iv) $A^* \xrightarrow{k_4} A + h\nu$

Show that when the reaction is at photostationary state and presence of large amount of monomer, the concentration of dimer is independent of the concentration of monomer. 1+4=5

(c) Write down the Freundlich isotherm. How will you test it and determine its constants? How can it be derived from Langmuir isotherm? 1+2+2=5

(d) What do you mean by solid compound with congruent melting point? Draw the phase diagram of such a system forming two such compounds. Explain the diagram. 2+3=5

4. Answer any *two* of the following questions : 5×2=10

(a) Write the mechanism of unimolecular reaction as proposed by Lindemann. Using this mechanism, deduce an expression for the rate of unimolecular reaction. 2+3=5

(b) Calculate the activation Gibbs function, enthalpy, and entropy of the second-order hydrogenation of ethene at 327 °C. 5

Given :

$A = 1{\cdot}24 \times 10^6\ M^{-1}\ S^{-1}$

$E_a = 180\ kJ\ mol^{-1}$

(c) Define fugacity coefficient and activity coefficient. For a mixture of ideal gases at consant temperature and pressure, show that

$$\Delta_{mix} G = nRT \Sigma x_j \ln x_j$$

where the terms have their usual significances. 2+3=5

5. Answer any *two* of the following questions : 5×2=10

(a) Write the mechanism of photochemical reaction between H_2 and Br_2. Show that

$$\phi = \frac{1}{(I_{abs})^{1/2}} \cdot \frac{k_2\left(\frac{1}{k_5}\right)^{1/2}[H_2]}{1 + (k_4 [HBr] / k_3 [Br_2])}$$ 2+3=5

(b) The photochemical dissociation of gaseous HI to form hydrogen and iodine atoms, requires radiation of 404 nm or less. *(i)* Determine the molar heat of dissociation of HI. *(ii)* If radiation of 253·7 nm is used, how much energy will appear as kinetic energy of atoms? 2+3=5

(c) Define chemical potential and give its physical interpretation. Derive the expression to show the variation of chemical potential with temperature and pressure. 2+3=5

6. Answer any *two* of the following questions : 5×2=10

(a) What are the factors that influence the adsorption of gases by solid? Explain the terms adsorption isobar, adsorption isostere, and sticking probability. 2+(1×3)=5

(b) In adsorption of hydrogen over a sample of copper, monolayer formation volume per gram of copper powder was found to be $1 \cdot 36\ cm^3$ measured at STP. Calculate the specific surface area of copper. Liquid hydrogen has a density of $0 \cdot 07\ g\ cm^{-3}$. 5

(c) What is surface excess? Derive the Gibbs surface excess equation. 1+4=5

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