2019

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 : 1×7=7

(a) Give the degrees of freedom of a solution of acetic acid in water.

(b) When 100 numbers of photons are absorbed by a reacting system, 10^5 numbers of molecules of a reactant are converted into products. What is the quantum yield of the reaction?

(c) Ice and water-phase diagram has negative slope. Explain.

(d) Give the signs of ΔH and ΔS in an adsorption process.

(e) In many reactions, the entropy change of activation is negative. Explain the reason.

(f) Draw the graph representing the variation of chemical potentials of ice and water with temperature.

(g) State the Stark-Einstein law of photochemical equivalence.

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

(a) Using the Clausius-Clapeyron equation, explain the nature of variation of vapour pressures with temperature.

(b) Write down the Eyring equation and give the meanings of the terms involved in the equation.

(*Continued*)

(c) The quantum efficiency for the photochemical reaction

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

is $1{\cdot}0\times10^6$ with a wavelength of 480 nm. Calculate the number of moles of HCl formed per joule of radiant energy absorbed.

(d) The volume of nitrogen gas required to cover a sample of silica gel with mono-molecular layer is $0{\cdot}129\ dm^3$ per gm of the gel at 1 atm and 273 K. If each nitrogen molecule occupies $1{\cdot}62\times10^{-19}\ m^2$ area, calculate the surface area of the gel.

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

(a) Discuss the effect of ionic strength on the rate constant of an uncatalyzed ionic reaction. 5

(b) Write the postulates of hard-sphere collision theory. Using this theory, deduce the expression of rate constant for a bimolecular gas-phase reaction. 2+3=5

(*Turn Over*)

(c) Derive an expression for Langmuir unimolecular adsorption isotherm. Under what conditions does it reduce to Freundlich adsorption isotherm? 3+2=5

(d) Define fugacity. For a mixture of ideal gases at constant temperature and pressure, show that

$$\Delta G_{mix} = nRT\Sigma x_i \ln x_i$$

where the terms have their usual meanings. 1+4=5

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

(a) Write the mechanism of the H_2—Cl_2 photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation. 2+3=5

(b) Draw the phase diagram representing schematically each of the following :

(i) $H_2O(l) \rightleftharpoons H_2O(v)$

(ii) A temperature-composition phase diagram for binary system having a eutectic mixture

(Continued)

(iii) A temperature-composition phase diagram for a binary system having a congruent melting point

Why a eutectic mixture cannot be separated by using simple distillation? 1+1½+1½+1=5

(c) Write the Lindemann's mechanism of unimolecular reaction. Using this mechanism, deduce an expression for the rate of the unimolecular reaction. 2+3=5

5. Answer *either (a)* and *(b) or (c)* and *(d)* : 5×2=10

(a) Define chemical potential and give its physical interpretation. How does chemical potential change with the change of compositions of a system? 2+3=5

(b) In the photochemical decomposition of acetone using 313 nm radiation, $7{\cdot}57\times10^{-6}$ moles of CO is formed in 20 minutes. If the energy of radiation absorbed corresponds to $2{\cdot}41\times10^{-3}\,J\,s^{-1}$, calculate the quantum efficiency for the formation of CO. 5

(Turn Over)

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

(d) Derive the BET equation. 5

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

(a) Discuss the mechanism of hydrogenation of ethene using Ni catalyst. Also discuss the effect of surface area on the rate of the above reaction. 3+2=5

(b) Using ACT, derive the thermodynamic formulation of rate constant for a bimolecular gas-phase reaction. 5

(c) What is potential energy surface? With the help of the potential energy surface, how can you explain the different paths of a chemical reaction? Explain with an example. 1+4=5

(d) (i) Using hard-sphere collision theory expression of rate constant of a bimolecular gas-phase reaction, deduce the Arrhenius factor.

(ii) The hard-sphere diameters of O_2 and CO molecules are found to be 3·6 Å and 3·7 Å. Calculate the hard-sphere collision theory frequency factor for the bimolecular gas phase reaction between O_2 and CO at 2700 K. 3+2=5

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