

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 :  $1 \times 7 = 7$

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

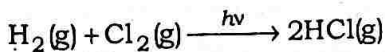
(b) When 100 numbers of photons are absorbed by a reacting system,  $10^5$  numbers of molecules of a reactant are converted into products. What is the quantum yield of the reaction?

- (c) Ice and water-phase diagram has negative slope. Explain.
- (d) Give the signs of  $\Delta H$  and  $\Delta S$  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.

- (c) The quantum efficiency for the photochemical reaction



is  $1.0 \times 10^6$  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 monomolecular layer is  $0.129 \text{ dm}^3$  per gm of the gel at 1 atm and 273 K. If each nitrogen molecule occupies  $1.62 \times 10^{-19} \text{ m}^2$  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

(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

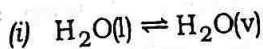
$$\Delta G_{\text{mix}} = nRT \sum x_i \ln x_i$$

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

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

(a) Write the mechanism of the  $\text{H}_2\text{—Cl}_2$  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 :



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

(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?

$$1+1\frac{1}{2}+1\frac{1}{2}+1=5$$

(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) :

$$5 \times 2 = 10$$

(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,  $7.57 \times 10^{-6}$  moles of CO is formed in 20 minutes. If the energy of radiation absorbed corresponds to  $2.41 \times 10^{-3} \text{ J s}^{-1}$ , calculate the quantum efficiency for the formation of CO.

5

(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.

( 7 )

- (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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