2014

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 why a heterogeneous catalyst is often taken in the form of finely divided powder rather than as a smooth surface.

(b) Yellow phosphorus glows in air at room temperature. State the reason behind it.

(c) State what you mean by inter-system crossing as given in Jablonski diagram.

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

(e) State why absolute alcohol cannot be prepared by fractional distillation.

(f) Let a pure substance has four phases α, β, γ and δ. State whether these four phases can exist in equilibrium at a particular temperature and pressure or not.

(g) State the main condition involving energy requirement that should be fulfilled in order to photolyze a molecule using a sensitizer.

2. Answer the following : 2×4=8

(a) In the photochemical dissociation of HI, the first step is

$$HI \xrightarrow{h\nu} H + I$$

Assuming H-atom formed to be in excited state while I-atom to be in ground state, calculate the excess energy that the excited H-atom carries as compared to the ground state H-atom. Justify your answer. Given photochemical dissociation energy and bond enthalpy of HI are 367 kJ mol^{-1} and 299 kJ mol^{-1} respectively.

(b) $CaCO_3$ (s) is heated in a closed vessel when the following reaction occurs :

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

Find the number of components.

(c) The eutectic temperature of NaCl-ice system is 252 K. Explain why temperature falls when NaCl is added to ice. What is the minimum temperature that can be attained by adding NaCl to ice?

(d) 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 2×10^{-5} m^3 mol^{-1}, calculate the partial molar volume of *B*.

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

(a) Write the basic assumptions of the collision theory of rates of reactions. Hence find out an expression for the rate constant of bimolecular gas-phase reaction.

(b) The rate constant of the second-order reaction

$$H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)$$

is $2 \cdot 34 \times 10^{-5}$ m^3 mol^{-1} s^{-1} at 400 °C. The activation energy of the reaction is 150 kJ mol^{-1}. Calculate enthalpy of activation and free energy of activation. 2+3=5

(c) For the bimolecular gas-phase reaction

$$X + Y \rightarrow A^{\ddagger} \xrightarrow{k} \text{Products}$$

find an expression relating the pre-exponential factor with entropy of activation.

(d) Discuss how the rate of uncatalysed ionic reaction is affected by the ionic strength of the solution.

(e) Write in brief about the molecular beam technique of studying molecular reaction dynamics. Name the different types of scattering of particles that may be observed in this technique. State how the scattered beams are studied. 3+1+1=5

4. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(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) In the photochemical decomposition of acetone using 313 nm radiation, $7 \cdot 57 \times 10^{-6}$ mol CO is formed in 20 minutes. If the energy of radiation absorbed corresponds to $2 \cdot 41 \times 10^{-3}$ J s^{-1}, calculate quantum efficiency for the formation of CO. 4

(c) State the reason why light emission during phosphorescence is slow. 1

Or

(d) State Stark-Einstein law of photochemical equivalence. Under what condition of radiation this law is applicable? 1+1=2

(e) When irradiated with a radiation of wavelength 253·7 nm, H_2 and O_2 react in presence of Hg vapour, but not in its absence. Explain this observation. 3

(f) In a certain photochemical reaction using 464 nm radiation, the incident light power was 15·5 W and the system absorbed 75% of the incident light. The quantum yield of the reaction was found to be 0·15. How many mol of the product was formed in the reaction in 100 s? 5

5. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Deduce Langmuir's adsorption isotherm. Show that at low pressure adsorption corresponds to first-order reaction, while at high pressure it corresponds to zero-order reaction. 3+2=5

(b) For adsorption of a substance from aqueous solution at 20 °C the Freundlich constants are $n = 2$ and $K = 0 \cdot 5$, the concentration of the solution being expressed as g L^{-1}. What mass of the substance will be adsorbed on 2 g of the solid from 1 L of the solution initially containing 2 g of the substance? 3

(c) The activation energy for the uncatalysed decomposition of NH_3 is 350 kJ mol^{-1}. But activation energy for the decomposition of NH_3 in presence of tungsten catalyst is 162 kJ mol^{-1}. Explain why this difference in activation energy occurs. 2

Or

(d) Show that for a gas obeying Langmuir equation a plot of $\ln \frac{\theta}{p}$ against θ will be linear with slope -1. (Symbols signify their usual meanings) 3

(e) Discuss the different steps of the Langmuir-Hinshelwood mechanism of gaseous reaction taking place on solid surface. 3

(f) At STP the volume of butane gas required to cover 1 kg of a sample of Ni catalyst is $1 \cdot 385 \times 10^{-6}$ m^3. If the surface area per kg of Ni catalyst is 9 m^2, find the area occupied by a butane molecule. 4

6. Answer *either (a), (b) or (c), (d),* and *(e)* :

(a) Taking the example of phenol-water system, discuss about the variation of mutual solubility of the two liquids with temperature. What is the effect of adding $0 \cdot 1$ *M* KCl on the critical solution temperature of the phenol-water system? 3+1=4

(b) Draw the phase diagram of water and explain what the different curves signify. Using Clapeyron equation, predict the slope of each curve. 3+3=6

Or

(c) Ag and Pb form an eutectic mixture with $2 \cdot 6\%$ of Ag by mass. The eutectic temperature is 576 K. The melting points of Pb and Ag are 600 K and 1243 K respectively. Draw schematic phase diagram of Pb-Ag system and mark the stable phases in various regions. Explain the changes that would occur if melt containing 60% Ag is cooled. 1+1+2=4

(d) Explain the variation of chemical potential with temperature for solid, liquid and vapour phases of a pure non-subliming substance. 3

(e) 1 mol of H_2 and 2 mol of O_2 are mixed together. Assuming that no chemical reaction occurs and the gases behave ideally, calculate entropy of mixing. 3

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