2018

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) In a system, liquid water and water vapour are in equilibrium at a pressure of 1 atm. What is the number of degree of freedom for the system?

(b) The limiting partial molar volume of $MgSO_4$ in water is $-1{\cdot}4\ cm^3\ mol^{-1}$. If 60 g anhydrous $MgSO_4$ is added to 1 litre of distilled water, then what is the expected final volume of the solution?

(c) What is the exact difference between a transition state and an activated complex?

(d) What is the main difference between a photosensitizer and a catalyst?

(e) At 600 nm, *tris*-(2,2′-bipyridyl) ruthenium (II) complex shows fluorescence with an emission lifetime of 6×10^{-7} s. On addition of a small amount of $9{\cdot}4\times10^{-4}$ mol dm^{-3} $[Fe(OH_2)_6^{3+}]$ solution, the emission lifetime of the complex decreases to $2{\cdot}17\times10^{-7}$ s. What is the role of Fe^{3+} solution in this case?

(f) Why does physisorption decrease with increase of temperature?

(g) Predict the effect of ionic strength on the rate constant of the reaction

$$[Pt(NH_3)_2Cl_2] + OH^- \rightarrow \text{Products}$$

2. Answer the following questions : $2\times4=8$

(a) "A mixture of HCl/H_2O (80% by mass of water) cannot be separated by distillation." Justify the statement.

(b) For a first-order reaction, the activation energy is 108·4 kJ mol^{-1}. What is the enthalpy of activation of the reaction at 130 °C?

(Continued)

(c) Both fluorescent and phosphorescent radiations are of shorter frequencies than the exiting light. Explain.

(d) A graph between $\log(x/m)$ and $\log P$ is a straight line at an angle of 45° with intercept on *Y*-axis equal to 0·3010. Calculate the amount of gas adsorbed per gram of the adsorbent when the pressure is 0·2 atm.

3. State the Stark-Einstein law of photochemical equivalence. What do you mean by one einstein of energy? When a sample of 4-heptanone was irradiated with 313 nm light with a power output of 50 W under conditions of total absorption for 100 s, it was found that $2{\cdot}8\times10^{-3}$ mole C_2H_4 was formed. What is the quantum yield for the formation of ethene? 1+1+3=5

Or

Draw energy profile diagrams for an exothermic and an endothermic reactions. Show that for a gaseous bimolecular reaction

$$A(g) + B(g) \rightarrow (AB)^{\dagger\dagger} \rightarrow \text{Product}$$

$E_a = \Delta H_m^{\dagger\dagger} + 2RT$, where the subscript *m* stands for molar. 1+1+3=5

(Turn Over)

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

(a) What do you mean by partial molar quantities? Explain with an example. The free energy change (ΔG) accompanying a given process is –85·77 kJ at 25 °C and –83·68 kJ at 35 °C. Calculate the change in enthalpy (ΔH) for the process at 30 °C. 2+3=5

(b) Draw and explain the phase diagram of a binary condensed phase system with the formation of an eutectic solid. Give an example of it. 4+1=5

(c) What do you mean by upper critical and lower critical solution temperatures? Give one example of each such system with appropriate phase diagram. Give an example of a system along with the phase diagram which shows both upper and lower critical temperatures. 1½+1½+2=5

(d) Derive Gibbs' phase rule. How is the number of component C calculated for systems involving ions and having some chemical reactions equilibrium among the constituents. Hence explain why KCl—NaCl—H_2O is a 4-component system whereas KCl—NaBr—H_2O is a 3-component system. 2+1½+1½=5

(Continued)

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

(a) What are the assumptions on which Langmuir isotherm is based? The following data were obtained for the adsorption of CO gas on 3·022 g of charcoal at 0 °C and 1 atm pressure. Verify that the data obey the Langmuir monolayer adsorption isotherm. Also determine the constant k and the volume corresponding to complete surface coverage : 2+3=5

P (torr)	100	200	300	400	500	600
V (cm^3)	10·2	18·6	25·5	31·4	36·9	41·6

(b) Derive BET equation for multilayer adsorption of an adsorbate on an adsorbent. 5

(c) Derive Langmuir adsorption isotherm. Show that for adsorption of a gas with dissociation ($X_2 \rightarrow 2X$) the Langmuir adsorption isotherm becomes 3+2=5

$$\theta = \frac{(kP)^{1/2}}{1+(kP)^{1/2}}$$

(d) Write the expression for BET adsorption isotherm. Diagrammatically show how increasing value of the constant C changes the shape of BET isotherm. Derive Langmuir adsorption isotherm equation from the BET equation. 1+2+2=5

(Turn Over)

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

(a) For the elementary gaseous reaction $A + B \rightarrow$ Products, obtain an expression for the rate constant of the reaction on the basis of transition state theory.

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

(c) Write an expression for the rate constant of a bimolecular gas-phase reaction on the basis of simple collision theory. What do you mean by steric requirement? Although the steric factor is normally found to be several orders of magnitude smaller than 1, for the reaction $K + Br_2 \rightarrow KBr + Br$, the experimental value of steric factor is found to be 4·8. Explain this observation. For the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$, at 628 K, the experimental and theoretical values of the pre-exponential factor are $1{\cdot}24 \times 10^6$ L mol^{-1} s^{-1} and $7{\cdot}33 \times 10^{11}$ L mol^{-1} s^{-1} respectively. What is the value of steric factor for this reaction? 1+1+2+1

(Continued)

(d) What do you mean by kinetic salt effect? Derive Brönsted-Bjerrum equation. Predict with reasons the effect of increase in ionic strength of the following reactions : 1+1+1½+1½=5

(i) $H_2O_2 + H^+ + Br^- \rightarrow P$

(ii) $C_{12}H_{22}O_{11} + OH^- \rightarrow P$

7. Answer any *two* from the following : 5×2=10

(a) With the help of a Jablonski diagram, explain all the photophysical processes that an electronically excited molecule may undergo. Give two major differences between fluorescence and phosphorescence. 3+2=5

(b) The kinetics of decomposition of HI is given by the following mechanism :

(i) $HI + h\nu \xrightarrow{k_1} H + I$

(ii) $H + HI \xrightarrow{k_2} H_2 + I$

(iii) $I + I \xrightarrow{k_3} I_2$

Show that the value of quantum yield for the reaction is 2. As the reaction proceeds and iodine accumulates, the following thermal reaction occurs :

$$H + I_2 \xrightarrow{k_4} HI + I$$

(Turn Over)

Because of the occurrence of this thermal reaction, the quantum yield of the reaction decreases from its original value. Explain this observation. $2\frac{1}{2}+2\frac{1}{2}$

(c) What do you mean by quenching of fluorescence? Derive Stern-Volmer equation. What is Stern-Volmer plot? Give an example of a quenching phenomena observed in plants. $1+3+1$

(d) 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. $2+3$

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