2020

(Held in 2021)

CHEMISTRY

(Major)

Paper : 5.2

(Physical Chemistry)

Full Marks : 42

Time : 2 hours

The figures in the margin indicate full marks for the questions

(*Symbols used signify their usual meanings*)

GROUP—A

(*Marks* : 21)

Answer **all** questions

1. Answer the following as directed : 1×2=2

(a) Activated complex theory reduces to the hard-sphere collision theory when the structure of the molecules is _____.

(Fill in the blank with appropriate word)

(b) Give the relation between fugacity and activity of any component of a gas mixture.

2. Answer the following : 2×2=4

(a) State Stark-Einstein law of photo-chemical equivalence. Define one Einstein.

(b) Distinguish between physisorption and chemisorption.

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

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

(b) *(i)* Fluorescence is a fast process while phosphorescence is slow. Explain. 2

(ii) Give reasons for obtaining low and high quantum yields. 3

(c) Derive the Gibbs' phase rule. Calculate the number of phases, components and degrees of freedom for the following systems : 2+3=5

(i) $CaCO_3(s) \rightleftharpoons CaO(s) \quad CO_2(g)$
(in a closed container)

(ii) Water at its triple point

(d) Write the assumptions involved in the derivation of the Langmuir adsorption isotherm. Explain how you will determine the value of and in the Langmuir adsorption isotherm $\frac{p}{x/m}$ p. Show that Freundlich isotherm is a special case of Langmuir isotherm. 2+2+1=5

(e) For two-phase equilibrium of a one-component system, derive the Clausius-Clapeyron equation. Clausius-Clapeyron equation shows that the solid-liquid equilibrium line on a P vs. T phase diagram will have a much steeper slope than the solid-vapour or liquid-vapour lines. Why? 4+1=5

GROUP—B

(*Marks* : 21)

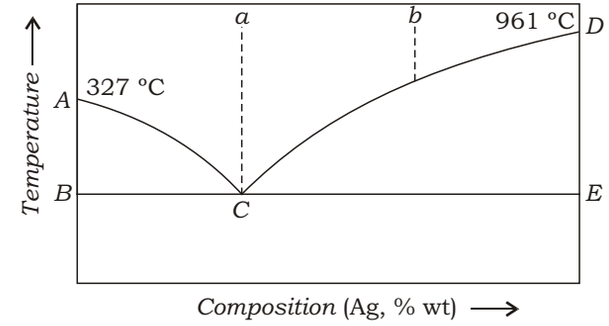
Answer *any* **three** questions

4. *(a)* The simple collision theory provides no means of calculating molar threshold energy, E_{thr}, but gives only the pre-exponential factor, A. On the basis of simple collision theory for the elementary bimolecular reaction B C products, show that A is independent of E_{thr}. 5

(b) The bimolecular elementary reaction CO O_2 CO_2 O has an observed activation energy of 51·0 kcal/mol for the temperature range 2400 K to 3000 K. If the hard-sphere diameters of O_2 and CO be 3·6 Å and 3·7 Å respectively, calculate the hard-sphere collision theory A factor. 2

5. Draw Jablonski diagram showing the radiative and non-radiative transitions, internal conversion and intersystem crossing, fluorescence and phosphorescence. Mention the type of multiplicity for fluorescence and phosphorescence. What should be the type of excited state for a photochemical reaction to occur and why? 3+2+2=7

6. A skeleton version of the temperature-composition phase diagram of lead-silver system at constant pressure is shown below :



From this diagram, answer the following :

(a) What do the curves *AC* and *DC* indicate? 2

(b) What is the temperature at line *BE* and what is the temperature called? 2

(c) Describe solid phases separate out when two melts containing Pb and Ag at *a* and *b* are cooled along the dashed line. 2

(d) Write the phases present at the point *C* in the diagram. 1

7. *(a)* What conclusion can be drawn about adsorption on the surface from each of the following? 2+2=4

(i) Rate of decomposition of HI in Pt is proportional to the concentration of HI.

(ii) On gold surface, the rate of decomposition of HI is independent of the pressure of HI.

(b) The surface tension of dilute solutions of a solute is expressed as $_0 \; ac$, where $_0$ is the surface tension of the pure solvent, *a* is a constant and *c* is the solute concentration. Show that surface excess, $_2 \; (\; _0 \;) / RT$. 3

8. *(a)* A radiation of 253 nm incident on HI results in the decomposition of $1{\cdot}85 \times 10^{\;2}$ mole per 1000 cals of radiant energy. Calculate the quantum efficiency. 4

(b) In an adsorption experiment, *m* gram of the adsorbent of molar mass *M* dissolves in *v* mL of solution to give a *c* molar solution. The solute is allowed to adsorbed in a solid surface. After the adsorption equilibrium is attained at the given temperature, the concentration of the solution is found to be *d* molar. If *x* gram is the amount adsorbed in the process, how will you calculate $\frac{x}{m}$ from the experimental data? (Assume the volume of the solution remains constant during the process.) 3

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