

Total No. of Printed Pages—12

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(May)

CHEMISTRY

(Major)

Course : 601

(Physical Chemistry)

*The figures in the margin indicate full marks
for the questions*

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Choose the correct answer : 1×5=5

(a) Many reactions are accompanied by the emission of visible radiation. This phenomenon is known as

- (i) chemiluminescence
- (ii) phosphorescence
- (iii) fluorescence
- (iv) quenching of fluorescence

- (b) In step polymerization, the molecular weight of the polymer formed is
- (i) equal to the total molecular weight of the monomers reacted
 - (ii) less than the total molecular weight of the monomers reacted
 - (iii) more than the total molecular weight of the monomers reacted
 - (iv) None of the above
- (c) Which of the following is not a criterion of catalysis?
- (i) A catalyst remains unchanged at the end of the reaction in its mass
 - (ii) A small amount of catalyst is sufficient to bring about a considerable extent of reaction
 - (iii) A catalyst cannot change the position of equilibrium of a reaction
 - (iv) The rate of catalysis does not depend on the temperature
- (d) The number of components, number of phases and number of degrees of freedom at the triple point of water are
- (i) 1, 1, 0
 - (ii) 1, 2, 0
 - (iii) 1, 1, 1
 - (iv) 1, 3, 0

(e) A collection of a large number of independent assemblies, having the same temperature T , volume V and chemical potential μ is called

(i) microcanonical ensemble

(ii) grand canonical ensemble

(iii) canonical ensemble

(iv) None of the above

2. Answer the following questions : $2 \times 5 = 10$

(a) What is bioluminescence? Give one example. $1+1=2$

(b) Define homopolymers and copolymers with examples. $1+1=2$

(c) Explain why enzyme catalysts are highly specific in nature. 2

(d) What is condensed system? Write the phase rule equation for such system. $1+1=2$

(e) Write the basic differences between Boltzmann and Bose-Einstein statistics. 2

3. Answer any *two* questions from the following : $3\frac{1}{2} \times 2 = 7$

(a) State and explain Einstein's law of photochemical equivalence. What is quantum yield of a photochemical reaction? $2\frac{1}{2} + 1 = 3\frac{1}{2}$

(b) Define the phenomenon of fluorescence. Write two characteristics of it. Explain that the delayed fluorescence is called phosphorescence. $1 + 1 + \frac{1}{2} = 3\frac{1}{2}$

(c) (i) What are photosensitized reactions? Give one example of it. $1 + 1 = 2$

(ii) Write a short note on photoelectric cell. $1\frac{1}{2}$

4. Answer any *one* question from the following : 5

(a) (i) Define degree of polymerization and extent of reaction. Write Carothers' equation. $2 + 1 = 3$

(ii) A polymer sample composed of molecules of three sizes. Out of these 10 moles of first size have molecular weight 10000, 80 moles of second size have molecular weight 50000 and 10 moles of the third size have molecular weight 100000. Calculate the number average and weight average molecular weight of the sample. $1 + 1 = 2$

(b) (i) Write a short note on Ziegler-Natta catalyst. 2

(ii) Discuss the method of determination of molecular weight of polymer sample from viscosity measurement. 3

5. Answer any *one* question from the following : 5

(a) (i) Explain how addition of a catalyst changes the rate of a reaction. What is catalytic poison? Give one example. $1\frac{1}{2}+1+\frac{1}{2}=3$

(ii) Explain the effect of temperature on surface reactions. 2

(b) (i) Derive Michaelis-Menten equation for enzyme catalysis. 4

(ii) Why is finely divided nickel used as catalyst in heterogeneous catalysis? 1

6. Answer any *two* questions from the following : $4\frac{1}{2}\times 2=9$

(a) What do you mean by peritectic change? Discuss the labelled phase diagram of $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system. $1+3\frac{1}{2}=4\frac{1}{2}$

(b) (i) For a system A (at. mass 209, m.p. 308 °C) and a system B (at. mass 24, m.p. 652 °C), a compound is formed corresponding to 19% by mass of B. The compound melts at 710 °C yielding a liquid having the same composition. There are two eutectics (1) at 271 °C and 9% by mass of B and (2) at 550 °C and 50% by mass of B. Draw the tentative labelled phase diagram for the system and deduce the formula of the compound. $2\frac{1}{2}+1=3\frac{1}{2}$

(ii) Explain why eutectic mixture is not a true compound. 1

(c) (i) Write Clapeyron equation. Explain why fusion curve gives a negative slope but vapour pressure curve gives a positive slope in the phase diagram of water system. $1+1\frac{1}{2}=2\frac{1}{2}$

(ii) What is a triple point? Explain why sulphur system has more than one triple point. $1+1=2$

7. Answer any one question from the following : 7

(a) (i) State and explain Stirling approximation. 3

(ii) Derive an expression for translational partition function using particle in a box model for ideal monatomic gas. 4

- (b) (i) Define thermodynamic probability. What do you mean by microstates? Derive a relationship between entropy and thermodynamic probability. 1+1+3=5
- (ii) Calculate translational partition function of an ideal gas contained in a volume of 30 litres at 500 K. The molecular mass of the gas is 100 g. 2

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Choose the correct answer : 1×5=5

(a) Which one of the following is not true for a photochemical reaction?

(i) Photochemical reaction involves absorption of light

(ii) The free energy change (ΔG) of a photochemical reaction must be negative

(iii) Temperature has very little effect on the rate of a photochemical reaction

(iv) The intensity of light has a marked effect on the rate of a photochemical reaction

(b) A microcanonical ensemble consists of isolated systems each having

- (i) same value of volume (V), total number of molecules (N) and energy (E)
- (ii) same value of volume (V), total number of molecules (N) and chemical potential (μ)
- (iii) same value of volume (V), temperature (T) and chemical potential (μ)
- (iv) same value of volume (V), temperature (T) and energy (E)

(c) In chain polymers, molecular weight of polymer

- (i) equals the total molecular weight of monomer units
- (ii) is less than the total molecular weight of monomer units
- (iii) is greater than the total molecular weight of monomer units
- (iv) does not depend on the molecular weight of monomer units

(d) A catalyst increases the rate of a chemical reaction by

- (i) increasing the activation energy
- (ii) decreasing the activation energy
- (iii) reacting with the reactant
- (iv) reacting with the product

(e) The numbers of phases, components and degrees of freedom corresponding to the triple point of sulphur system are

(i) (3, 2, 1)

(ii) (3, 1, 0)

(iii) (4, 2, 0)

(iv) (2, 2, 2)

2. Answer the following questions : $2 \times 5 = 10$

(a) What is meant by photosensitization? Give example.

(b) Distinguish between homopolymers and copolymers.

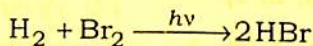
(c) Explain the action of catalytic promoters and catalytic poison.

(d) Define thermodynamic probability. Give the relationship between thermodynamic probability and entropy.

(e) Explain why fusion curve in water system has a negative slope whereas the sublimation curve has a positive slope.

3. Answer any two questions from the following : 3½×2=7

- (a) Discuss the rate expression for the reaction



assuming steady-state approximation for H and Br. How would you account for the low quantum yield for this reaction?

3+½=3½

- (b) Thermodynamically non-spontaneous reaction may also take place spontaneously in presence of light. Explain.

3½

- (c) What are primary and secondary processes in a photochemical reaction? Describe fluorescence.

2+1½=3½

4. Answer any one question from the following : 5

- (a) State the differences between addition and step reaction polymerization. Discuss various steps involved in the polymerization mechanism of styrene initiated by benzoyl peroxide at 60 °C.

2+3=5

- (b) (i) Define reactivity ratio of monomers. Mention different types of copolymer formed in terms of reactivity ratio.

1+2=3

- (ii) Briefly discuss about living polymers.

2

5. Answer any *one* question from the following : 5

(a) What is acid-base catalysis? Explain the theories of acid-base catalysis with suitable examples. $1+4=5$

(b) (i) Write the important steps of surface reaction. 2

(ii) What is enzyme catalysis? Discuss the effect of temperature on enzyme catalysis. $1+2=3$

6. Answer any *two* questions from the following : $4\frac{1}{2}\times 2=9$

(a) What do you mean by a phase diagram? Draw and explain the phase diagram of a simple eutectic system. $1+3\frac{1}{2}=4\frac{1}{2}$

(b) Draw the phase diagram of sulphur system and label it. Explain it briefly giving the significance of each zone and line. $1\frac{1}{2}+3=4\frac{1}{2}$

(c) Derive Clausius-Clapeyron equation. Mention its one application. $3\frac{1}{2}+1=4\frac{1}{2}$

7. Answer any *two* questions from the following : $3\frac{1}{2}\times 2=7$

(a) What do you mean by partition function? Discuss the physical significance of partition function. Explain the effect of temperature on partition function. $1+1\frac{1}{2}+1=3\frac{1}{2}$

- (b) Derive an expression for translational partition function for an ideal monatomic gas using particle in a box model. 3½
- (c) Deduce the relationship between partition function and Gibbs' free energy. 3½
