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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) 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

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- (iii) Temperature has very little effect on the rate of photochemical reaction
- (iv) The intensity of light has a marked effect on the rate of a photochemical reaction
- (b) Which of the following polymers is formed by step reaction polymerization?
- (i) PVC
 - (ii) Polyethylene
 - (iii) Nylon-6,6
 - (iv) Polyaniline
- (c) Chemisorption plays an important role in
- (i) heterogeneous catalysis
 - (ii) homogeneous catalysis
 - (iii) both homogeneous and heterogeneous catalyses
 - (iv) None of the above
- (d) The maximum number of phases that can be in equilibrium for a two-component system at constant temperature and pressure is
- | | |
|---------|--------|
| (i) 1 | (ii) 2 |
| (iii) 3 | (iv) 4 |

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(3)

- (e) 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)

2. Answer the following questions : 2×5=10

- (a) What are the primary and secondary processes in a photochemical reaction? 2
- (b) Define degree of polymerization. The molecular weight of a sample of polyvinylchloride is 625000. Calculate the degree of polymerization. 1+1=2
- (c) What is autocatalysis? Give one example. 1+1=2
- (d) Explain why fusion curve in water system has a negative slope whereas the sublimation curve has a positive slope. 2

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- (e) Define thermodynamic probability.
What is the relation between thermodynamic probability and entropy? $1+1=2$

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

- (a) State and explain Beer-Lambert law.
Define molar extinction coefficient. $3+\frac{1}{2}=3\frac{1}{2}$
- (b) Discuss the kinetics of dimerization of anthracene. $3\frac{1}{2}$
- (c) What do you mean by quenching of fluorescence? Describe chemiluminescence. $1\frac{1}{2}+2=3\frac{1}{2}$

4. Answer any one question from the following : 5

- (a) State the differences between addition polymerization 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) What is copolymerization? Define reactivity ratio of monomers. Mention different types of copolymer formed in terms of reactivity ratio. $1+1+2=4$
- (ii) What is Ziegler-Natta catalyst? 1

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5. Answer any one question from the following : 5

- (a) (i) Write the important steps of surface reaction. 2
- (ii) What are enzyme catalyses? Discuss the effect of temperature on enzyme catalysis. $1+2=3$
- (b) What is acid-base catalysis? Explain the theories of acid-base catalysis with suitable example. $1+4=5$

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

- (a) (i) Find the number of phases and number of components for the following equilibria : $1\times 2=2$
- (1) $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$
- (2) $\text{NH}_4\text{Cl(g)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{Cl}_2\text{(g)}$
 $P_{\text{NH}_3} = P_{\text{Cl}_2}$
- (ii) What is triple point? Explain why more than one triple points are observed in the phase diagram of sulphur. $1+1\frac{1}{2}=2\frac{1}{2}$
- (b) What do you mean by congruent melting point? Draw and explain the phase diagram of a two-component system with the formation of a congruently melting compound. Comment on the stability of such compounds. $1+2\frac{1}{2}+1=4\frac{1}{2}$

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- (c) Define cryohydric point. Discuss the phase diagram of KI-H₂O system.

$$1+3\frac{1}{2}=4\frac{1}{2}$$

7. Answer any two questions from the following :

$$3\frac{1}{2}\times 2=7$$

- (a) Define partition function. Write the mathematical expression for translational partition function. Calculate the translational partition function for benzene in a volume of 1 m³ at 25 °C.
 $1+1+1\frac{1}{2}=3\frac{1}{2}$
- (b) Derive the equation for the calculation of the molar entropy of an ideal monatomic gas. $3\frac{1}{2}$
- (c) From partition function of an ideal monatomic gas, show that molar heat capacity at constant volume, $C_V = \frac{3}{2}R$. $3\frac{1}{2}$

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(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Select the correct answers : $1\times 5=5$

- (a) The true statement about photochemical reaction is

- (i) the presence of light is the primary requirement for reactions to take place
- (ii) temperature has a very little effect on the rate of photochemical reaction
- (iii) ΔG for photochemical spontaneous reactions may be positive or negative
- (iv) All of the above

- (b) A sample of polystyrene has an average molecular weight of 208000. The degree of polymerization of this sample is

- (i) 2000
- (ii) > 2000
- (iii) < 2000
- (iv) None of the above

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- (c) Shape-selective catalysis is a reaction catalyzed by
- (i) zeolites
 - (ii) enzymes
 - (iii) platinum
 - (iv) acids or bases
- (d) The point in the pressure-temperature curve of water system where the equilibrium $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{vapour}$ exists is called the
- (i) critical point
 - (ii) triple point
 - (iii) transition point
 - (iv) eutectic point
- (e) With the increase in temperature, partition function
- (i) increases
 - (ii) decreases
 - (iii) first decreases and then increases
 - (iv) neither increases nor decreases

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

- (a) What do you mean by photo-sensitization? Explain with examples.
- (b) A protein sample consists of an equimolar mixture of
- haemoglobin ($M = 15.5 \text{ kg mol}^{-1}$)
 - ribonuclease ($M = 13.7 \text{ kg mol}^{-1}$)
 - myoglobin ($M = 17.2 \text{ kg mol}^{-1}$)

Calculate the number-average and mass-average molecular masses.

- (c) Explain the action of catalytic promoters and catalytic poisons.
- (d) A eutectic mixture has a definite composition and a sharp melting point, yet it is not a compound. Give reason.
- (e) Define canonical and grand canonical ensembles.

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

- (a) Derive the rate expression for the reaction $\text{H}_2 + \text{Br}_2 \xrightarrow{h\nu} 2 \text{HBr}$, assuming steady-state approximation for H and Br atoms. How would you account for the low quantum yield for this reaction? $2 \frac{1}{2} + 1 = 3 \frac{1}{2}$

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- (b) State and explain Lambert-Beer law. Discuss its applications in analytical chemistry. $2\frac{1}{2}+1=3\frac{1}{2}$
- (c) Discuss about the primary and secondary processes in a photochemical reaction. $1\frac{1}{2}+2=3\frac{1}{2}$

4. Answer any one of the following questions : 5

- (a) (i) Explain the term 'intrinsic viscosity'. How is it related to the molecular weight of a polymer? Discuss how the molecular weight of a polymer can be determined by viscosity measurement. $1+1+2=4$
- (ii) Write briefly about living polymers. 1
- (b) (i) Describe the mechanism of polymerization of styrene initiated by benzoyl peroxide at 60 °C. 3
- (ii) Mention the technological importance of copolymers. 2

5. Answer any one of the following questions : 5

- (a) What is enzyme catalysis? Discuss the effects of concentration, temperature and pH on the rate of enzyme catalysis. Explain why enzyme catalysts are highly specific. $1+3+1=5$

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- (b) (i) Differentiate between homogeneous catalysis and heterogeneous catalysis. Discuss the mechanism of heterogeneous catalysis on the basis of adsorption theory. $1+2=3$
- (ii) Explain the term 'autocatalysis' with one example. 2

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

- (a) What is peritectic change? Draw and explain 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) Determine the number of components, number of phases and degrees of freedom in the following equilibria : $1\frac{1}{2}\times 2=3$
- $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$
when $P_{\text{NH}_3} \neq P_{\text{HCl}}$
- (ii) Distinguish between the triple point and freezing point of a pure substance. $1\frac{1}{2}$
- (c) (i) Derive Clausius-Clapeyron equation. 3
- (ii) The possibility of a four-phase equilibria in the sulphur system is ruled out. Explain why. $1\frac{1}{2}$

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7. Answer any *two* of the following questions :

$3\frac{1}{2} \times 2 = 7$

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

(b) Deduce the relationship between partition function and Gibbs' free energy. $3\frac{1}{2}$

(c) Derive an expression for translational partition function for an ideal monatomic gas using particle in a box model. $3\frac{1}{2}$
