6 SEM TDC CHM M 1 (N/O)

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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

(*Turn Over*)

(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 photo-chemical 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 hetero-geneous 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

            (Continued)

(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 :　　　$2 \times 5 = 10$

  (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

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

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

(a) State and explain Beer-Lambert law. Define molar extinction coefficient.

3+½=3½

(b) Discuss the kinetics of dimerization of anthracene. 3½

(c) What do you mean by quenching of fluorescence? Describe chemiluminescence. 1½+2=3½

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

5. Answer any *one* question from the following :   5
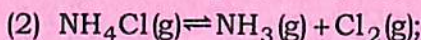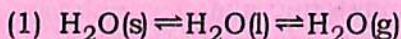
   (a)   *(i)*   Write the important steps of surface reaction.   2

          (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) $H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$

            (2) $NH_4Cl(g) \rightleftharpoons NH_3(g) + Cl_2(g)$;

$$p_{NH_3} = p_{Cl_2}$$

          (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. $1 + 2\frac{1}{2} + 1 = 4\frac{1}{2}$

(c) Define cryohydric point. Discuss the phase diagram of KI-H_2O system.

$$1+3½=4½$$

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

$$3½×2=7$$

(a) Define partition function. Write the mathematical expression for translational partition function. Calculate the translational partition function for benzene in a volume of $1\ m^3$ at $25\ °C$.

$$1+1+1½=3½$$

(b) Derive the equation for the calculation of the molar entropy of an ideal monatomic gas.

$$3½$$

(c) From partition function of an ideal monatomic gas, show that molar heat capacity at constant volume, $C_V = \frac{3}{2}R$. $3½$

(Continued)

(Old Course)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

1. Select the correct answers :   1×5=5

   (a) The true statement about photo-chemical 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

(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 ice $\rightleftharpoons$ water $\rightleftharpoons$ 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

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 ($M = 15 \cdot 5$ kg mol^{-1})

ribonuclease ($M = 13 \cdot 7$ kg mol^{-1})

myoglobin ($M = 17 \cdot 2$ 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 $H_2 + Br_2 \xrightarrow{h\nu} 2\,HBr$, assuming steady-state approximation for H and Br atoms. How would you account for the low quantum yield for this reaction? $2\frac{1}{2} + 1 = 3\frac{1}{2}$

(*Turn Over*)

(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. $1+3+1=5$

(Continued)

(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 :
$$4\frac{1}{2}\times2=9$$

(a) What is peritectic change? Draw and explain the labelled phase diagram of Na_2SO_4-H_2O 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 : $1\frac{1}{2}\times2=3$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$
$$\text{when } P_{NH_3} \neq P_{HCl}$$

(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. $1\frac{1}{2}$

(Turn Over)

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. $\quad 1+1\frac{1}{2}+1=3\frac{1}{2}$

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

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

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