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6 SEM TDC CHM M 1

2015

(May)

CHEMISTRY

(Major)

Course : 601

(Physical)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct option : 1×5=5

(a) In photosynthesis chlorophyll acts as

(i) a catalyst

(ii) photosensitizer

(iii) photoinhibitor

(iv) None of the above

(b) PVC is a

(i) chain polymer

(ii) step polymer

(iii) natural polymer

(iv) copolymer

(c) The substance that decreases the efficiency of a catalyst is called

(i) negative catalyst

(ii) catalytic poison

(iii) catalytic promoter

(iv) positive catalyst

(d) The maximum possible number of phases that can coexist in equilibrium in a two-component system is

(i) 1

(ii) 2

(iii) 3

(iv) 4

(e) The unit of molecular partition function is

(i) cm^{-1}

(ii) S^{-1}

(iii) $JK^{-1} mol^{-1}$

(iv) dimensionless

(Continued)

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

(a) State and explain Lambert-Beer law. 2

(b) What is degree of polymerization? A sample of polystyrene has an average molecular weight of 104000. What is the degree of polymerization of this sample of polystyrene? 1+1=2

(c) What do you mean by autocatalysis? Give one example. 1+1=2

(d) Explain why in case of one-component system the solid-vapour and liquid-vapour curves always have a positive slope, while the solid-liquid curve may have a positive or negative slope. 2

(e) Define canonical and grand-canonical ensembles. 2

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

(a) Derive the rate expression for the reaction

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

assuming steady-state approximation for H and Br. How would you account for the low quantum yield for this reaction? 3+½=3½

(Turn Over)

(b) Discuss the phenomenon of fluorescence and phosphorescence in terms of singlet and triplet states. What is LASER? 2½+1=3½

(c) What is photostationary state? Discuss the dimerization of anthracene. 1+2½=3½

4. Answer *either (a) or (b)* : 5

(a) (i) Equal masses of polymer molecules with $M_1 = 9000\ g\ mol^{-1}$, $M_2 = 90000\ g\ mol^{-1}$ are mixed. Calculate the number-average and weight-average molecular weights of the polymer sample. 2

(ii) Discuss how molecular weight of a polymer can be determined from viscosity measurements. 3

(b) (i) Explain different steps involved in the mechanism of chain polymerization. 2

(ii) Write short notes on : 1½×2=3

(1) Living polymers

(2) Copolymers

(Continued)

5. Answer *either (a) or (b)* : 5

(a) (i) Explain why—

(1) a catalyst cannot start a reaction;

(2) a catalyst cannot affect the position of equilibrium of a reaction. 1+1=2

(ii) Discuss the mechanism of heterogeneous catalysis on the basis of adsorption theory. 3

(b) 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

6. Answer any *two* of the following questions : 4½×2=9

(a) (i) What do you mean by condensed system? Write the phase rule equation for such systems. 1+½=1½

(ii) Determine the number of components, number of phases and number of degrees of freedom in the following equilibria : 1½×2=3

(1) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(2) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$; when $p_{NH_3} \neq p_{HCl}$

(Turn Over)

(b) What is peritectic change? Draw and explain the labelled phase diagram of Na_2SO_4–H_2O system. 1+3½=4½

(c) (i) Explain that azeotrope is a mixture; it is not a compound. 1½

(ii) Derive Clausius-Clapeyron equation. 3

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

(a) Define thermodynamic probability. Derive Boltzmann relationship between entropy and thermodynamic probability. 1+2½=3½

(b) Define partition function. Deduce the relationship between partition function and Gibbs' free energy. 1+2½=3½

(c) Derive the equation applicable for the calculation of the molar entropy of an ideal monatomic gas. 3½

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