Total No. of Printed Pages—12

6 SEM TDC CHM M 1 (N/O)

2018

(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) Intersystem crossing refers to

(i) transition between two states of a system

(ii) radiationless transition between states of different spin multiplicities

(iii) transition between excited and ground states with same multiplicity

(iv) All of the above

(b) A sample of polyacrylonitrile has number average molecular weight of 106000. Its number average degree of polymerization is

(i) 2000

(ii) 1000

(iii) 3000

(iv) 200

(c) The number of components, phases and degrees of freedom for I_2 distributed between $CHCl_3$ and H_2O are

(i) 3, 2, 2

(ii) 3, 2, 1

(iii) 3, 1, 2

(iv) 2, 2, 1

(d) Which of the following is the wrong statement?

(i) A catalyst can start a reaction in some cases.

(ii) Enzymes are the examples of micro-heterogeneous catalysis.

(iii) Enzymes can act only in the presence of coenzymes.

(iv) A positive catalyst reduces the activation energy of a reaction.

(e) At absolute zero, the value of molecular partition function is

(i) 0

(ii) 1

(iii) greater than one

(iv) less than zero

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

(a) The photochemical dissociation of gaseous HI to form normal H_2 and I_2 requires radiation of 4040 Å. Determine the molar heat of dissociation of HI.

(b) What is glass transition temperature? How is it important?

(c) Explain the actions of catalytic promoters and catalytic poisons.

(d) "A mixture of Sn and Pb is used for soldering." Explain giving proper reason.

(e) Define canonical and grand-canonical ensembles.

3. Answer any *two* questions from the following : $3\frac{1}{2}\times2=7$

(a) Discuss 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? $3+\frac{1}{2}=3\frac{1}{2}$

(b) The decomposition of HI takes place by the following mechanisms :

$$HI + h\nu \rightarrow H + I$$
$$H + HI \rightarrow H_2 + I$$
$$I + I \rightarrow I_2$$

Deduce the expression for the rate of this reaction. What is the quantum efficiency of the reaction? $3+\frac{1}{2}=3\frac{1}{2}$

(c) What is quantum yield of a photochemical reaction? Mention any three reasons for showing low quantum yield of a reaction. $\frac{1}{2}+3=3\frac{1}{2}$

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

(a) *(i)* Define weight average and number average molecular weight of a polymer sample. 2

(ii) Write Carothers equation. In a polymerization reaction, hexamethylenediamine reacts with adipic acid in equimolar concentration to form Nylon-6,6. Calculate the molecular weight of Nylon-6,6 when the conversion is 90%. (Molecular weight of the polymer repeat unit is 226.) 1+2=3

(b) (i) Discuss the kinetics of free radical chain polymerization. 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) Discuss the effect of particle size on the catalytic activity in heterogeneous catalysis. 2

(ii) What are nanocatalysts? Discuss the efficiency of metal nanoparticles in heterogeneous catalysis. 1+2=3

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

(a) What do you mean by a phase diagram? Draw and explain the phase diagram of a simple eutectic system. 1+3½=4½

(b) Draw the phase diagram of water and lebel it. Explain it briefly giving the significance of each zone and line. 1½+3=4½

(c) Derive Clausius-Clapeyron equation. Mention its two applications. 3½+1=4½

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

(a) Show that the equilibrium distribution of particles following Boltzmann statistics is given by

$$\frac{n_i}{n} = \frac{g_i e^{-\beta\varepsilon_i}}{\Sigma g_i e^{-\beta\varepsilon_i}}$$

where $\beta = \frac{1}{kT}$. 3½

(b) Deduce Sackur-Tetrode equation for molar entropy of an ideal monatomic gas. 3½

(c) What do you mean by partition function? Discuss the physical significance of partition function. Explain the effect of temperature on partition function. 1+1½+1=3½

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Choose the correct answer : 1×5=5

(a) Photosynthesis is an example of

(i) phosphorescence

(ii) chemiluminescence

(iii) fluorescence

(iv) photosensitized reaction

(b) Which of the following is an example of step growth polymer?

(i) Polyaniline

(ii) Polyvinyl chloride

(iii) Nylon-6,6

(iv) Polystyrene

(c) The efficiency of a catalyst in catalysis depends on the

(i) molecular state

(ii) physical state

(iii) amount used

(iv) number of free valencies

(d) The number of components, the number of phases and the number of degrees of freedom at the eutectic point of a condensed system is

(i) 1, 1, 0

(ii) 2, 3, 0

(iii) 1, 1, 1

(iv) 1, 3, 0

(e) At absolute zero, the value of molecular partition function is

(i) zero

(ii) less than zero

(iii) one

(iv) greater than one

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

(a) What is bioluminescence? Give one example. 2

(b) What do you mean by degree of polymerization and extent of reaction? 1+1=2

(c) Explain the effect of temperature on enzyme catalysis. 2

(d) Explain what is meant by incongruent melting point. Give one example of a system with incongruent melting point. 1+1=2

(e) Define molar partition function. How does it differ from molecular partition function? 1+1=2

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

(a) Define quantum yield of a photochemical reaction. How do you account for the low and high quantum yields in a photochemical reaction? What is the role of chlorophyll in photosynthesis? 1+2+½=3½

(b) The decomposition of HI takes place by the following mechanisms :

$$HI + h\nu \rightarrow H + I$$

$$H + HI \xrightarrow{k_2} H_2 + I$$

$$I + I \xrightarrow{k_3} I_2$$

Show that the rate of this reaction is directly proportional to the intensity of radiation. Find the quantum yield for this reaction. 3+½=3½

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

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

(a) Discuss the kinetics of free radical addition polymerization. What is kinetic chain length? 4+1=5

(b) *(i)* Define number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weight of a polymer sample. 2

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

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

(a) *(i)* Explain why enzyme catalysts are highly specific. 1½

(ii) Derive Michaelis-Menten equation. 3½

(b) *(i)* Explain the following : 1½×2=3

(1) Effect of temperature on surface reactions

(2) Efficiency of nanoparticles as catalyst

(ii) Give one example of homogeneous catalysis and one example of heterogeneous catalysis. 1+1=2

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

(a) What is phase rule? Derive the phase rule thermodynamically. 1+3½=4½

(b) *(i)* Draw the labelled phase diagram for water system. 2

(ii) What is a triple point? The number of triple points in water and sulphur system are different although both of them are one-component systems. Explain. 1+1½=2½

(c) *(i)* Write the phase rule equation for condensed systems. 1

(ii) Discuss the phase diagram of a simple eutectic system. 3½

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

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

(b) Deduce Sackur-Tetrode equation for molar entropy of an ideal monatomic gas. 3½

(c) (i) Write the differences between grand canonical and microcanonical ensembles. 1½

(ii) Calculate translational partition function of CH_4 at 1000 K in a volume of 1 litre. 2

★★★