2016/ODD/08/22/CHM–103/344

PG Odd Semester (CBCS) Exam., December—2016

CHEMISTRY

(1st Semester)

Course No. : CHMCC–103 (C)

(Physical Chemistry—I)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, selecting **one** from each Unit

UNIT—I

1. *(a)* What do you mean by 'exact differential'? Show that, for an ideal gas, the work function, is not an exact differential. 2+2=4

(b) State and explain zeroth law of thermodynamics. How can the concept of temperature be introduced from zeroth law of thermodynamics? 2+5=7

(c) Calculate S per litre of solution when pure N_2, H_2 and NH_3 gases are mixed to form a solution having final composition 15% N_2, 55% H_2 and 30% NH_3 (all at STP). 3

2. *(a)* Calculate the change in entropy when two ideal gases are mixed. 6

(b) The absolute entropy of a substance is determined with the help of third law of thermodynamics. Explain. 4

(c) Find $\left(\frac{u}{v}\right)_T$ in case of van der Waals' gas using thermodynamic equation of state and comment on your result. 4

UNIT—II

3. *(a)* For a real gas, show that $\ln f = \int_0^p \frac{(z-1)\,dp}{p}$, where f is the fugacity coefficient and z is the compressibility factor. 7

(b) Assuming an expression for van't Hoff isotherm, arrive at an expression for van't Hoff isochore. 4

(c) For a reaction

$G = 13\,850 - 16.1\,T\log T - 72.59\,T$ (cal)

calculate S at 27 °C. 3

4. *(a)* Consider the following reaction :

$$_1A_1 \quad _2A_2 \rightleftharpoons \ _3A_3 \quad _4A_4$$

Derive an expression for free energy change w.r.t. advancement of the reaction at constant temperature and pressure, and comment on your result in view of spontaneity of the reaction. 7

(b) Derive an expression for integrated form of van't Hoff equation and graphically explain the variation of equilibrium constant with temperature. 4

(c) What would be the boiling point of water at a place where the atmospheric pressure is 600 mm?

(H_{vap} 540 cal/gm) 3

UNIT—III

5. *(a)* Obtain an expression for the entropy production per unit time in an open system containing two phases at different temperatures. 7

(b) Derive Onsager's reciprocity relation. 7

6. *(a)* Obtain the phenomenological relation for the electrokinetic phenomena. From this, derive the relation for different electrokinetic effects and show the interrelation between these effects. 6+2+2=10

(b) Considering nonequilibrium thermodynamic system, explain the concept of 'local formulation of entropy'. 4

UNIT—IV

7. *(a)* Discuss the postulates of transition state theory and obtain the rate expression for a gaseous bimolecular reaction in terms of partition function. 3+5=8

(b) The values of rate constants for the reaction

$$2HI \rightleftharpoons H_2 \quad I_2$$

were observed as

$$3\ 0 \quad 10^{\ 5}\ \text{mol}^{\ 1}\ \text{dm}^{\ 3}\ \text{s}^{\ 1}$$

$$\text{and } 2\ 5 \quad 10^{\ 3}\ \text{mol}^{\ 1}\ \text{dm}^{\ 3}\ \text{s}^{\ 1}$$

at 357 °C and 447 °C respectively. Calculate the activation energy for forward and backward reaction of H 15 5 kJ mol ^{1}. 3

(c) Entropy decreases when reaction rates are of opposite sign while increases for reacting ions of same charge. Explain. 3

8. *(a)* Describe the effect on ionic strength on the rate constant by deriving an expression for the variation of rate constant with ionic strength. 7

(b) Discuss the effect of temperature on the rate of the reaction. 3

(c) The energy of activation and pre-exponential factor for a reaction

$$A_2 \quad B_2 \rightleftharpoons 2AB$$

are 15·5 kJ mol ^{1} and 10·9 10^{10} dm^{3} mol ^{1} s ^{1}, respectively. Calculate the values of $H^{\ddagger}$ and $S^{\ddagger}$ at 1000 K.

[Given

R 8 314 J mol ^{1} K ^{1}

h 6 623 10 ^{34} Js

k_B 1 38 10^{23} J K ^{1}] 4

UNIT—V

9. *(a)* For enzyme-catalysed reaction,

$$S + E \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X \text{ (fast)}$$

$$X \xrightarrow{k_3} P + E \text{ (slow)}$$

derive the rate expression for this reaction and answer the following :

(i) What is meant by Michaelis-Menten constant, K_m?

(ii) Draw the potential energy diagram for the enzyme-catalysed reaction.

(iii) Prove that order of reaction w.r.t. substrate changes from unity to zero at higher [*S*]. 5+2+1+2=10

(b) Calculate the relaxation time for the reaction :

$$A^{+}\,(aq) + B^{-}\,(aq) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB\,(aq)$$

for a temperature jump experiment to a final temperature 400 K. The solution was initially prepared by adding 0 02 mole of *AB* to water maintaining total volume of 1 litre. Both forward and backward reactions were first-order, k_1 and k_2 are 8 0 10^{10} s ^{1} and 5 0 10^{6} s ^{1} at 400 K, respectively. 4

10. *(a)* What are the main steps involved in a chain reaction? Discuss them with reference to the gas phase reaction

$$H_2\ (g) \quad Br_2\ (g) \rightleftharpoons 2HBr\ (g)$$ 2

(b) Show that the rate of the above reaction is given by the expression

$$r \quad \frac{k\ [H_2]\,[Br_2]^{1/2}}{1 \quad k\ [HBr]\,/\,[Br_2]}$$ 5

(c) Discuss Belousov-Zhabotinskii reaction mechanism for oscillatory reaction. 7

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