

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

CHEMISTRY

(1st Semester)

Course No. : CHMCC-103 (C)

(Physical Chemistry—I)

Full Marks : 70Pass 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

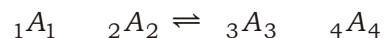
2. (a) Calculate the change in entropy when two ideal gases are mixed. 6
- (b) The absolute entropy of a substance is determined with the help of third law of thermodynamics. Explain. 4
- (c) Find $\frac{u}{v T}$ in case of van der Waals' gas using thermodynamic equation of state and comment on your result. 4

UNIT—II

3. (a) For a real gas, show that $\ln f = \int_0^p \frac{z-1}{p} dp$, 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
 $G = 13850 - 16.1 T \log T - 72.59 T$ (cal)
 calculate S at 27 °C. 3

(3)

4. (a) Consider the following reaction :



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?

($H_{\text{vap}} = 540 \text{ cal/gm}$)

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

(4)

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'.

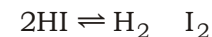
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UNIT—IV

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



were observed as

$$3.0 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

$$\text{and } 2.5 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

at 357°C and 447°C respectively. Calculate the activation energy for forward and backward reaction of

$$H = 15.5 \text{ kJ mol}^{-1}.$$

3

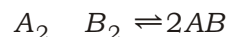
(5)

(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



are 15.5 kJ mol^{-1} and $10.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively.

Calculate the values of H^\ddagger and S^\ddagger at 1000 K.

[Given

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

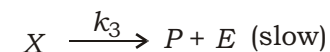
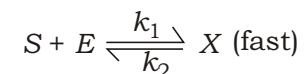
$$h = 6.623 \times 10^{-34} \text{ Js}$$

$$k_B = 1.38 \times 10^{23} \text{ JK}^{-1}] \quad 4$$

(6)

UNIT—V

9. (a) For enzyme-catalysed reaction,



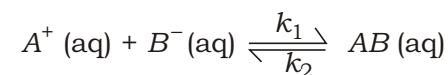
derive the rate expression for this reaction and answer the following :

(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 :



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 $8.0 \times 10^{10} \text{ s}^{-1}$ and $5.0 \times 10^6 \text{ s}^{-1}$ at 400 K, respectively. 4

(7)

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



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

$$r = \frac{k [\text{H}_2] [\text{Br}_2]^{1/2}}{1 + k' [\text{HBr}] / [\text{Br}_2]} \quad 5$$

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