2017/ODD/08/22/CHM–103/227

PG Odd Semester (CBCS) Exam., December—2017

CHEMISTRY

(1st Semester)

Course No. : CHMCC–103

(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)* State and explain Euler's theorem and hence show that internal energy (U) is an exact differental. 2+2=4

(b) Calculate the work done in an isothermal reversible process and show that it is greater than the corresponding irreversible work. 4+4=8

(c) Assuming ideal behaviour, calculate the S_{max} for the mixture of 0·8 mole O_2 and 0·2 mole N_2, each at 1 atm and 25 °C. 2

2. *(a)* Assuming one mole ideal gas as the working substance in a Carnot cycle, arrive at a definition of entropy. 10

(b) Explain the term 'Clausius inequality' in terms of reversible and irreversible changes. 4

UNIT—II

3. *(a)* For any thermodynamic extensive property G, such that

$$G\,(P, T, n_1, n_2, \cdots, n_i\ \cdots)$$

where, P and T are pressure and temperature, respectively and n_i is the number of moles of component i, show that $\ _i\ n_i d\ _i\ \ 0$, where

$$_i \quad \frac{G}{n_i}\ _{P,T,n_{j,\,j\ \ i}}$$ 8

(b) Show that decrease in Helmholtz free energy at constant temperature and pressure is equivalent to maximum work output by the system. 3

(c) Establish the condition for spontaneous vapourization of water. Given H 9590 cal mole ^{1} and S 26 e.u. for the process. 3

4. *(a)* Does the equilibrium constant of a chemical reaction depend on the following?

(i) Standard state chosen for reactants and products

(ii) The stoichiometric representations of the reaction

Justify your answer. 4+4=8

(b) Find the conditions of equilibrium and spontaneity of a process in terms of Gibbs free energy (G) and Helmholtz free energy (A). 2+2=4

(c) For a reaction at 127 °C, G 12 kcal and H 17 5 kcal. Find out S. 2

UNIT—III

5. *(a)* Derive an expression for entropy production due to heat flow. 6

(b) What is the principle of detailed balancing of chemical reactions? How does it lead to the principle of microscopic reversibility? 2+6=8

6. *(a)* Derive Saxen's relations of electrokinetic effects. 8

(b) Obtain an expression of the entropy production in chemical reaction. 6

UNIT—IV

7. *(a)* Using thermodynamic formulation of activated complex theory, obtain the rate constant expression of unimolecular and bimolecular gas phase reaction. Discuss the significance of $^{\ddagger}S$. 7+1=8

(b) Which reaction will have the greater temperature dependence on rate constant—one with small value of E_a or one with large value of E_a? Explain. 2

(c) Discuss the role of solvents on reaction rate by considering thermal decomposition of N_2O_5 as an example. 4

8. *(a)* The Arrhenius activation energy and pre-exponential factor for the reaction

$$H\,(g) \quad Br_2\,(g) \quad HBr\,(g) \quad Br\,(g)$$

are

$$15{\cdot}5 \text{ kJ mol}^{\ 1} \text{ and}$$
$$1\ 09 \quad 10^{11} \text{ dm}^3 \text{ mol}^{\ 1} \text{ sec}^{\ 1}$$

respectively. What are the values of $^{\ddagger}H$ and $^{\ddagger}S$ at 1000 K based on standard state of 1·00 mol dm ^{3}? Assume ideal gas behaviour. 4

(b) With the help of transition state theory, compare the rate constant for the reaction $A \quad B \rightleftharpoons X^{\ddagger}$, in gaseous state and solution phase. 4

(c) What is 'secondary salt effect'? Discuss the influence of ionic strength in which a reaction is catalyzed by H produced by weak acid. 2+4=6

UNIT—V

9. (a) Discuss the acid-base catalysis and suggest an overall rate expression for acid-base catalysis. From the overall rate expression, obtain the following :

(i) Convert the equation as a function of single variable [H] and [OH].

(ii) Discuss Scrabble diagram.

(iii) What will be the value of rate constant for H catalysis and for OH catalysis? 2+2+2+2+1=9

(b) What is Lineweaver-Burke plot? The intercept and slope of the Lineweaver-Burke plot were obtained as $5\ 0\quad 10^{3}$ and $1\ 5\quad 10^{5}$, respectively. Calculate the value of K_m and maximum rate. 1+4=5

10. (a) What is a Belousov-Zhabotinsky reaction? Discuss the Belusov-Zhabotinsky reaction based on Oregonator model. 1+8=9

(b) Discuss the mechanism of H_2-O_2 reaction. 5

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