2017/ODD/08/22/CH–103 (C)/075

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

CHEMISTRY

(1st Semester)

Course No. : CH–103 (C)

(Physical Chemistry—I)

Full Marks : 75
Pass Marks : 30

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

UNIT—I

1. *(a)* State and explain Euler's theorem for exactness and hence show that internal energy (U) is an exact differential. 1+2+2=5

(b) Calculate the work done in an isothermal reversible process and show that it is greater than the corresponding irreversible work. 4+3=7

(c) A gas expands against a variable external pressure given by, $P \quad \frac{10}{V}$ atm, where V is the volume of the gas at each stage of expansion. Further, in expanding from 10 to 100 litres, the gas undergoes a change in internal energy, $U \quad 100$ cal. How much heat has been absorbed? 3

2. *(a)* Calculate the change in entropy when two ideal gases are mixed. 8

(b) Show that in the vicinity of absolute zero, all processes should occur without any alteration in entropy values. 4

(c) For a reaction

$$G \quad 13{\cdot}850 \quad 16{\cdot}1T\log T \quad 72{\cdot}59T \text{ (cal)}$$

calculate S at 327 °C. 3

UNIT—II

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

$$G(P, T, n_1, n_2, ..., n_i, ...)$$

where P and T are pressure and temperature, respectively and n_i is the number of moles of component i, show that

$$\sum_i n_i d\mu_i = 0$$

where $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j, j \neq i}$ 8

(b) Show that decrease in Helmholtz free energy at constant temperature and pressure is equivalent to maximum work output by the system. 4

(c) Find the condition of equilibrium and spontaneity of a process in terms of Gibbs' free energy (G). 3

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

(i) Standard state chosen for the reactants and products

(ii) The stoichiometric representation of the reaction

Justify your answer. 4+4=8

(b) Derive an expression for the integrated form of van't Hoff equation and graphically explain the variation of equilibrium constant with temperature. 5+2=7

UNIT—III

5. *(a)* Derive an expression for entropy production due to heat flow. 7

(b) Derive Saxen's relation of electrokinetic effects. 8

6. *(a)* Derive Onsager's reciprocity relation. 7

(b) Obtain an expression for entropy production per unit time in an open system containing two phases at different temperatures. 8

UNIT—IV

7. *(a)* Derive statistically the rate equation on the basis of the theory of absolute reaction rate. 8

(b) Explain the effect of ionic strength on reaction rate. 7

8. *(a)* How does the reaction in solution differ from those in the gas phase? 5

(b) Discuss the effect of temperature on the reaction rate. How is the activation energy of a reaction calculated? 3+2=5

(c) Discuss the effect of solvent on the rate of a reaction. 5

UNIT—V

9. *(a)* What is a Belousov-Zhabotinskii reaction? Explain Belousov-Zhabotinskii reaction for an oscillatory reaction. 1+9=10

(b) Obtain an overall rate expression for the acid-base catalysis. Explain Skrabal diagram. 3+2=5

10. *(a)* Give a brief account of relaxation method for studying fast reaction. 6

(b) Discuss the mechanism of chain reaction between H_2 and Br_2 to obtain the rate equation

$$\frac{d[\mathrm{HBr}]}{dt} \quad \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{3/2}}{[\mathrm{Br_2}] \quad k \quad [\mathrm{HBr}]}$$

How does the rate equation in thermal reaction differ from photochemical reaction? 7+2=9

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