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3 (Sem-2/CBCS) CHE HC 2

2023

CHEMISTRY

(Honours Core)

Paper : CHE-HC-2026

(Physical Chemistry-II)

Full Marks : 60

Time : Three hours

***The figures in the margin indicate
full marks for the questions.***

(Symbols used signify their usual meaning)

1. Answer the following questions : $1 \times 7 = 7$

(a) Give one example each of the following :

(i) An extensive variable

(ii) A state function

(b) In isothermal change involving an ideal gas, $\Delta U = 0$. (State True **or** False)

Contd.

(c) Which of the following enthalpies is always negative ?

(i) Enthalpy of solution

(ii) Enthalpy of formation

(iii) Enthalpy of bond dissociation

(iv) Enthalpy of combustion

(Choose the correct option)

(d) In a reversible process $\Delta S_{sys} + \Delta S_{surr}$ is

(i) > 0

(ii) < 0

(iii) ≥ 0

(iv) $= 0$

(Choose the correct option)

(e) Give *one* example of partial molar quantity.

✓ (f) What is meant by chemical equilibrium ?

✓ (g) Define the term 'colligative property'.

Answer the following question : $2 \times 4 = 8$

✓ (a) Heat and work are *two* forms of energies. Distinguish between heat and work.

✓ (b) State and explain the equipartition of energy principle.

✓ (c) State the second law of thermodynamics. Give the SI unit of entropy.

(d) Give *one* example each of homogeneous and heterogeneous equilibrium reactions.

3. ✓ Answer **any three** question of the following : $5 \times 3 = 15$

✓ (a) What do you understand by the terms (i) internal energy, and (ii) enthalpy of a system. Give SI units of internal energy and enthalpy. Show that enthalpy change is equal to the heat absorbed when a reaction is carried out at constant pressure. $(1+1)+1+2=5$

(b) Define standard enthalpy of reaction. Calculate the standard enthalpy of formation of *n*-butane. Given that standard enthalpies of combustion of *n*-butane, $C_{(graphite)}$ and $H_2(g)$ are $-2878.5 \text{ kJmol}^{-1}$, $-393.5 \text{ kJmol}^{-1}$ and $-285.0 \text{ kJmol}^{-1}$ respectively. 1+4=5

(c) Define equilibrium constant of a chemical reaction. Give the characteristics of equilibrium constant. Calculate the equilibrium constant of a reaction at 300 K if standard Gibbs' free energy change at this temperature is 29.29 kJmol^{-1} . 1+2+2=5

(d) State Henry's law. Give the limitations of Henry's law. The solubility of pure oxygen in water at 25°C and 1.00 atm pressure is $1.30 \times 10^{-3} \text{ molL}^{-1}$. Calculate concentration of oxygen gas at 25°C and partial pressure of 0.20 atm. 1+2+2=5

(e) (i) Define Gibbs' free energy. Give the condition for spontaneity from Gibbs' free energy. 2

(ii) "Decrease in free energy is favoured by decrease in enthalpy and increase in entropy." Explain. 3

4. Answer **any three** questions of the following : 10×3=30

(a) (i) For isothermal reversible expansion of n moles of an ideal gas show that

$$-W_{rev} = nRT \ln \frac{P_1}{P_2} \quad 4$$

(ii) 2.8 grams of nitrogen gas at 300 K expands isothermally from 3 atm to 1 atm pressure. Assuming nitrogen gas to behave ideally, calculate work done W , if the expansion is reversible. Also calculate the work done if the expansion is carried out in a single step against 1 atm pressure.

4+2=6

(b) (i) For isothermal reversible process of a system show that

$$\Delta S_{sys} = -\Delta S_{surr}. \quad 4$$

- ✓ (ii) For an ideal gas undergoing adiabatic reversible process, show that

$$pV^\gamma = \text{constant, where } \gamma = \frac{C_{p.m}}{C_{V.m}}.$$

4

- ✓ (iii) Explain why the magnitude of the reversible work involved due to expansion of an ideal gas from volume V_1 to V_2 is greater in isothermal process than in adiabatic process .

2

- (c) (i) Show that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[p + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

4

- (ii) Derive the thermodynamic equation of state

$$T \left(\frac{\partial p}{\partial T}\right)_V = p + \left(\frac{\partial U}{\partial V}\right)_T$$

4

- (iii) Define chemical potential. State whether it is extensive or intensive property.

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(d) (i) Derive the Gibbs-Duhem equation involving chemical potential. Give its physical interpretation. 4+2=6

(ii) For a reaction of constituents in an ideal solution in equilibrium with its vapour, show that

$$\Delta_r G^\circ = -RT \ln K_x \quad 4$$

(e) (i) Define elevation of boiling point. 2

(ii) Using chemical potential, thermodynamically derive the relation between elevation of boiling point and amount of solute present in a dilute solution. 5

(iii) When 2.8 g of an organic substance is dissolved in 24.2 g of chloroform, the boiling point of the solvent is raised by 0.29 K. Calculate the molecular weight of the organic solute. Given K_b for 1000 g of chloroform is 8.322. 3

(f) (i) Derive an expression to show the quantitative variation of equilibrium constant of an equilibrium reaction with temperature. 5

Contd.

(ii) When NH_4Cl is heated in a closed container, the vapour pressure at 700 K is 6.0 atm. At 732 K the vapour pressure raises to 11.0 atm. Calculate the equilibrium constants for the dissociation of NH_4Cl at these temperatures. Also calculate ΔH° and ΔS° at 700 K.

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