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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 : 1×7=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)*

(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'.

2. Answer the following question : 2×4=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 : 5×3=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 $-2878.5\ kJmol^{-1}$, $-393.5\ kJmol^{-1}$ and $-285.0\ kJmol^{-1}$ 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 $1.30 \times 10^{-3}\ molL^{-1}$. 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

$$-W_{rev} = nRT \ln \frac{P_1}{P_2}$$ 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 $\Delta S_{sys} = -\Delta S_{surr}$. 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. 2

(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

$$\Delta_r G^o = -RT ln K_x$$ 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

(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^o and ΔS^o at 700 K. 5
