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3 (Sem-2/CBCS) CHE HC 2

2022

**CHEMISTRY**

(Honours)

Paper : CHE-HC-2026

**(Physical Chemistry - II)**

Full Marks : 60

Time : Three hours

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

1. Answer **any seven** of the following questions :

1×7=7

- (a) Give the SI unit of energy.
- (b) Define specific heat of a system.

Contd.

(c) The variation of enthalpy of a reaction with temperature is given by

- (i) Hess's law
- (ii) Kirchhoff's equation,
- (iii) Henry's law,
- (iv) Raoult's law

*(Choose the correct option)*

(d) A process is carried out at constant pressure and temperature. It will be spontaneous if

- (i)  $\Delta G < 0$
- (ii)  $\Delta H < 0$
- (iii)  $\Delta U < 0$
- (iv)  $\Delta S < 0$

*(Choose the correct option)*

(e) A solution is a

- (i) homogeneous mixture of only two components

(ii) homogeneous mixture of any number of components

(iii) heterogeneous mixture

(iv) anything mixed with water

*(Choose the correct option)*

(f) What is excess thermodynamic function ?

(g) Name a colligative property that is used to determine the molar mass of a protein.

(h) Equimolar solutions of glucose and sodium chloride are not isotonic. Justify.

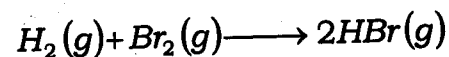
(i) Find the value of work done when 2 moles of an ideal gas is allowed to expand from 1 L to 10 L against vacuum at 298 K.

(j) Name the thermodynamic property that measures the disorderliness of a system.

2. Answer **any four** of the following questions : 2×4=8

- (a) Define intensive property. Give *one* example.
- (b) State Zeroth law of thermodynamics.
- (c) Define explosion temperature and adiabatic maximum flame temperature.
- (d) What do you mean by network ? Briefly explain.
- (e) Explain residual entropy.
- (f) Define fugacity function.
- (g) An ideal gas undergoes a single step expansion a constant external pressure  $P$  from  $(P_1, T, V_1)$  to  $(P, T, V_2)$ . What is the magnitude of work done by the system ?

(h) Find  $\Delta H$  of the reaction :



Given :

$$\Delta H_{H-H} = 435.1, \Delta H_{Br-Br} = 192.5,$$

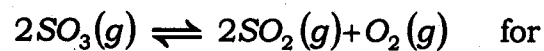
$$\Delta H_{H-Br} = 368.2 \text{ kJ/mol.}$$

3. Answer **any three** of the following questions : 5×3=15

- (a) (i) State Path function with suitable example. 2
- (ii) Show that in an isothermal expansion, the work is done at the expense of the heat absorbed. 3
- (b) Derive the Gibbs - Helmholtz equation.
- (c) (i) Write short note on the third law of thermodynamics. 3
- (ii) Explain briefly how absolute entropy of a molecule can be determined from heat capacity measurement. 2

(d) Give the criteria of spontaneity and thermodynamic equilibrium in terms of enthalpy, entropy, Helmholtz free energy and Gibbs free energy. 5

(e) (i) Calculate  $K_c$  for the reaction



which  $K_p = 3.5 \times 10^{-23} \text{ atm}$  at  $27^\circ\text{C}$ . 3

(ii) How molar mass can be determined from freezing point depression? 2

(f) (i) 0.5g of a non-volatile solute of molar mass  $60 \text{ g mol}^{-1}$  is dissolved in 100g of ethyl acetate at  $20^\circ\text{C}$ . What would be the vapour pressure of this solution at  $20^\circ\text{C}$ ? The vapour pressure of ethyl acetate at  $20^\circ\text{C}$  is 72.8 Torr. 3

(ii) Explain briefly any one method for measurement of vapour pressure lowering. 2

(g) What is osmotic pressure? Give detailed thermodynamic derivation of osmotic pressure of a solution having non-volatile solute.

(h) What are colligative properties? Explain two practical applications of colligative properties.

4. Answer **any three** of the following questions:  $10 \times 3 = 30$

(a) (i) State and explain first law of thermodynamics. Show that for isochoric process,  $q = \Delta U$ .  $3 + 2 = 5$

(ii) Derive the integrated Kirchhoff equation. 5

(b) (i) Define heat capacity of a system. Show that  $C_p - C_v = R$  for 1 mole of an ideal gas.  $1 + 3 = 4$

(ii) State and explain Raoult's law for vapour pressure of binary solution of volatile liquid. What is an ideal solution?  $5 + 1 = 6$

- (c) (i) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the reversible isothermal expansion of one mole of an ideal gas at  $27^\circ\text{C}$  from a volume of  $10 \text{ dm}^3$  to a volume of  $20 \text{ dm}^3$ . 4
- (ii) Explain that the entropy of the universe is increasing continuously. 2
- (iii) Explain briefly the vapour pressure *vs.* composition diagram of a binary liquid mixtures having positive deviation. 4
- (d) (i) Explain that the thermodynamic isothermal reversible work of expansion is the maximum work. 3
- (ii) Give the thermodynamic derivation of the relation between Gibb's free energy of a reaction and its reaction quotient. 5

- (iii) Give *two* limitations of first law of thermodynamics. 2
- (e) (i) Define enthalpy of neutralization. 1
- (ii) The enthalpy of combustion of glucose  $\text{C}_6\text{H}_{12}\text{O}_6(\text{S})$  is  $-2816 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Calculate  $\Delta H_f^\circ$  of  $\text{C}_6\text{H}_{12}\text{O}_6(\text{S})$ . The  $\Delta H_f^\circ$  values for  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-393.5$  and  $-286.2 \text{ kJ mol}^{-1}$  respectively. 3
- (iii) Give a brief account of coupling of exoergic and endoergic reactions. 3
- (iv) State and explain van't Hoff theory of dilute solution as applied to osmotic pressure. 3
- (f) (i) Discuss about the molecular and statistical interpretation of entropy.  $2\frac{1}{2} \times 2 = 5$

(ii) Show that :

$$\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2) \quad 5$$

(g) (i) Prove that :  $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$  5

(ii) Explain the variation of chemical potential with temperature. 3

(iii) Calculate the pressure of  $CO_2$  gas at 700K in the heterogeneous equilibrium reaction



$\Delta G^\circ$  for this reaction is

$$130.2 \text{ kJmol}^{-1}. \quad 2$$

(h) (i) Show that :

$$K_p = K_x (P)^{\Delta n_g} = K_c (RT)^{\Delta n_g}$$

under what conditions,

$$K_p = K_x = K_c? \quad 5+1=6$$

(ii) State and explain *Le Chatelier's* principle taking *any one* example. 4