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3 (Sem-2/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

Paper: CHE-HC-2026

(Physical Chemistry – Π)

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.

- (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.
 - 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 ΔH of the reaction:

$$H_2(g)+Br_2(g)\longrightarrow 2HBr(g)$$

Given:

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

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

- 3. Answer **any three** of the following questions: 5×3=15
 - (a) (i) State Path function with suitable example.
 - (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.
 - (ii) Explain briefly how absolute entropy of a molecule can be determined from heat capacity measurement.

- (d) Give the criteria of spontaneity and thermodynamic equilibrium in terms of enthalpy, entropy, Helmholtz free energy and Gibbs free energy.
- (e) (i) Calculate K_c for the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ for which $K_p = 3.5 \times 10^{-23}$ atm at $27^{\circ}C$.
 - (ii) How molar mass can be determined from freezing point depression?

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- (f) (i) 0.5g of a non-volatile solute of molar mass 60g mol⁻¹ is dissolved in 100g of ethyl acetate at 20°C. What would be the vapour pressure of this solution at 20°C? The vapour pressure of ethyl acetate at 20°C is 72.8 Torr.
 - (ii) Explain briefly any one method for measurement of vapour pressure lowering.

- (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:
 - (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.
 - (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, ΔU and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 27°C from a volume of $10 \ dm^3$ to a volume of $20 \ dm^3$.
 - (ii) Explain that the entropy of the universe is increasing continuously.
 - (iii) Explain briefly the vapour pressure vs. composition diagram of a binary liquid mixtures having positive deviation.
- (d) (i) Explain that the thermodynamic isothermal reversible work of expansion is the maximum work.

(ii) Give the thermodynamic derivation of the relation between Gibb's free energy of a reaction and its reaction quotient.

- (iii) Give two limitations of first law of thermodynamics. 2
- (e) (i) Define enthalpy of neutralization.
 - (ii) The enthalpy of combustion of glucose $C_6H_{12}O_6(S)$ is -2816 $kJmol^{-1}$ at 25°C. Calculate ΔH_f^o of $C_6H_{12}O_6(S)$. The ΔH_f^o values for $CO_2(g)$ and $H_2O(l)$ are -393.5 and -286.2 $kJmol^{-1}$ respectively.
 - (iii) Give a brief account of coupling of exoergic and endoergic reactions.
 - (iv) State and explain van't Hoff theory of dilute solution as applied to osmotic pressure.
 - (f) (i) Discuss about the molecular and statistical interpretation of entropy. 2½×2=5

- (ii) Show that : $\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$
- (g) (i) Prove that : $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$
 - (ii) Explain the variation of chemical potential with temperature.
 - (iii) Calculate the pressure of CO_2 gas at 700K in the heterogeneous equilibrium reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ if ΔG° for this reaction is $130.2 \ kJmol^{-1}$.
- (h) (i) Show that: $K_p = K_x(P)^{\Delta n_g} = K_c(RT)^{\Delta n_g}$ under what conditions, $K_p = K_x = K_c?$ 5+1=6

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