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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 298K.

(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 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. 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

$$2SO_3(g) \rightleftharpoons 2SO_2(g)+O_2(g)$$ for which $K_p=3{\cdot}5 \times 10^{-23}$ *atm* at 27°C. 3

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

(f) (i) 0.5*g* of a non-volatile solute of molar mass 60*g* mol^{-1} is dissolved in 100*g* 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*. 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 : 10×3=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, 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. 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 $C_6H_{12}O_6(S)$ is $-2816\ kJ\,mol^{-1}$ 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 $-286.2\,kJ\,mol^{-1}$ 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. 2½×2=5

(ii) Show that :

$\Delta G_{mix} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$ 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 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ if ΔG^o for this reaction is $130.2\ kJmol^{-1}$. 2

(h) (i) Show that :

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

under what conditions,

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

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