

Chemistry: Paper I: Physical Chemistry.

QP Code : 19163

(2½ Hours)

Total Marks : 60

- N.B. : (1) All questions are compulsory.
(2) Figures to the right indicate full marks.
(3) Use of non-programmable calculator is allowed.

Useful Constant :

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$m_e = 1.602 \times 10^{-31} \text{ kg}$$

$$e = 1.602 \times 10^{-19} \text{ C}$$

$$k = 1.3811 \times 10^{-23} \text{ JK}^{-1}$$

$$1 \text{ J} = 6.24 \times 10^{18} \text{ eV}$$

$$1 \text{ eV} = 8.06 \times 10^3 \text{ cm}^{-1}$$

$$1 \text{ atmosphere} = 1.01325 \times 10^5 \text{ Nm}^{-2}$$

$$N = 14; \text{ H} = 1.0 \text{ O} = 16$$

1. (a) Attempt any two of the following :
- Explain the entropy changes that take place when a substance undergoes phase transitions. 4
 - Derive an expression to show the variation of enthalpy of a reaction with temperature. 4
 - Explain the determination of absolute entropies in terms of heat capacity. 4
 - What is Joule-Thomson effect? How is it studied experimentally? 4
- (b) Attempt any one of the following :
- Define inversion temperature and calculate its value for hydrogen gas. The van der Waals constants for hydrogen gas are :
 $a = 0.0245 \text{ Nm}^4 \text{ mol}^{-2}$, $b = 2.67 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ 4
 - Hydrazine is a potential rocket fuel. Determine whether it can be synthesized from the following reaction at 298K
$$\text{NH}_4\text{NO}_3(s) + 3\text{H}_2(g) \rightarrow 3\text{H}_2\text{O}(g) + \text{N}_2\text{H}_4(g)$$

The standard enthalpy change for the above reaction at 298K is -310.9 kJ. The standard entropies for $\text{NH}_4\text{NO}_3(s)$, $\text{H}_2(g)$, $\text{H}_2\text{O}(g)$ and $\text{N}_2\text{H}_4(g)$ are 150, 130, 189 and 120 $\text{JK}^{-1} \text{ mol}^{-1}$ respectively. 4
2. (a) Attempt any two of the following :
- Define fugacity. How will you determine fugacity from equation of state? 4
- Show that (p) $\Delta S_{\text{mix}} = -nR \sum x_i \ln x_i$ 4
(q) $\Delta H_{\text{mix}} = 0$
 - Derive Gibbs-Duhem-Margules equation. 4
 - Give a brief account of chemical potential of real solutions. 4

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2. (b) Attempt any one of the following :

- (i) Calculate ΔG_{mix} , ΔH_{mix} and ΔS_{mix} at 25°C and 1 atmosphere when 10 moles of He are mixed with 20 moles of Ne. 4
- (ii) At 450°C and 600 atmosphere pressure, the equilibrium constant for the reaction $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$ is 4.516×10^{-5} . Calculate the degree of conversion of $\text{N}_{2(\text{g})}$ and $\text{H}_{2(\text{g})}$ to $\text{NH}_{3(\text{g})}$, assuming that the system is a mixture of real gases. Fugacity coefficient are $\gamma_{\text{N}_{2(\text{g})}} = 1.3238$, $\gamma_{\text{H}_{2(\text{g})}} = 1.2874$, $\gamma_{\text{NH}_{3(\text{g})}} = 0.8548$.

3. (a) Attempt any two of the following :

- (i) Explain the phase diagram of two component system of solid gas involving formation of amino compounds. 4
- (ii) Draw and discuss the phase diagram of two component system in which the two components form a stable compound with incongruent melting point. 4
- (iii) Draw and explain the phase diagram for three component system of liquids with the formation of two pairs of partially miscible liquids. 4
- (iv) Discuss the application of phase rule to ternary system of double salt decomposed by water. 4

(b) Attempt any one of the following :

- (i) Derive thermodynamically an expression for the Gibbs adsorption isotherm. 4
- (ii) Derive thermodynamically the Laplace equation of pressure difference across curved surface. 4

4. (a) Attempt any two of the following :

- (i) Discuss in brief the solid oxide fuel cell. 4
- (ii) What are membranes? Give the functions of cell membrane. 4
- (iii) Discuss the Debye-Huckel limiting law applicable to electrolytic solution of appreciable concentration. 4
- (iv) Explain the relaxation effect for conductance of strong electrolytes. 4

(b) Attempt any one of the following :

- (i) Calculate the resting membrane potential for :

Ion species	Intracellular concentration in mM	Extracellular concentration in mM
K ⁺	155	4
Ca ²⁺	10 ⁻⁴	1.5

Given : $\left(\frac{2.303RT}{F} = 61 \right)$

- (ii) Calculate the mean activity coefficient of $1.0 \times 10^{-2} \text{m ZnCl}_2$ in $5 \times 10^{-3} \text{m ZnSO}_4$ Solution ($A = 0.509$ for water at 298K)

5 (a) Attempt any **four** of the following :

- (i) Draw and explain the Maxwell's thermodynamic square.
- (ii) Explain how the standard molar entropies are dependent on structure of a compound with the help of suitable example.
- (iii) What do you understand by the term thermodynamic excess function? Write the expression for excess Gibb's free energy and excess enthalpy.
- (iv) Explain the term Exo-ergonic and Endo-ergonic reactions.
- (v) Explain the applications of phase rule to ternary systems of hydrate dehydrated by second salt.
- (vi) Write mathematical expression of BET equation. How is it used to determine surface area of solid adsorbent?
- (vii) Give the advantages of fuel cells over conventional cells.
- (viii) Explain the Debye-Falkenhagen effect.

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