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Your Roll No................

5776

B.Sc. (Hons.) Chemistry/III Sem. B

Paper—CHHT-307

PHYSICAL CHEMISTRY–II

(Admission of 2010 and onwards)

Time : 3 Hours *Maximum Marks* : 75

(Write your Roll No. on the top immediately on receipt of this question paper.)

Use separate answer-sheets for Section A and Section B.

Answer *six* question in all, selecting at least *two* questions from each Section. Question No. 1 is compulsory.

(Use of scientific calculator is allowed)

$R = 8.314\ JK^{-1}\ mol^{-1}$; $N = 6.023 \times 10^{23}\ mol^{-1}$

1. Attempt any *five* of the following :

(*a*) Isothermal reversible work obtained in the expansion of an ideal gas is greater than that of a non-ideal gas.

(*b*) The Helmholtz free energy function is sometimes referred to as work function.

(*c*) Using entropy as a criterion for spontaneity ΔS(universe) is considered but in case of Gibbs free energy, normally ΔG(System) is considered.

(*d*) Molecular masses of benzoic acid determined from freezing point depression measurements using (*i*) its solution in water and (*ii*) its solution in benzene are not the same.

(*e*) For spontaneous mixing of gases μ_i must be smaller than μ_i^*(Pure).

(*f*) Zeroth law of thermodynamics. 3×5

Section A

2. (*a*) If pressure, volume and temperature of one mole of a gas are related as $\left(P + \frac{a}{V^2}\right)V = RT$, show that :

(*i*) P is a state function;

(*ii*) *d*P is an exact differential.

(*iii*) Enthalpy of combustion;

(*iv*) Bond energy and Bond dissociation energy.

(*b*) Using bond energy data calculate the enthalpy change for the reaction :

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Data given :

$DH°(C{=}C) = 610\ kJmol^{-1}$, $DH°(H - H) = 436\ kJmol^{-1}$,

$DH°(C{-}H) = 413\ kJmol^{-1}$, $DH°(C - C) = 348\ kJmol^{-1}$. 8,4

4. (*a*) Show that for reversible isolated process the change of entropy is zero whereas for irreversible isolated process the entropy change is greater than zero.

(*b*) Starting from the first law of thermodynamics, show that for *n* moles an ideal gas the entropy change with temperature and volume is given by

$$\Delta S = nC_V \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

(*b*) Show that the work done by an ideal gas in a reversible adiabatic expansion from an initial state $P_1V_1T_1$ to a final state $P_2V_2T_2$ is given by

$$-w = \frac{P_1V_1 - P_2V_2}{1-\gamma} = nC_{v,m}T_1\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

where $\gamma = \frac{C_p}{C_v} = C_{p,m}/C_{v,m}$ and $C_{p,m} - C_{v,m} = R$.

(*c*) An ideal gas ($C_{p,m}$ = 29.1 $JK^{-1}mol^{-1}$) is expanded reversibly and adiabatically from a volume of 1.43 dm^3, at a pressure of 303975 Pa and temperature 298 K, to a volume of 2.86 dm^3. Calculate the final temperature and pressure of the gas. 2,5,5

3. (*a*) Explain with examples the following :

(*i*) Integral heat of solution;

(*ii*) *Enthalpy* of formation of ions in solution;

(*c*) At what temperature will the entropy of one mole of an ideal gas occupying 5 dm^3 at 300 K on expanding to 500 dm^3 increase by 38.294 JK^{-1} ? $C_V = 12.6\ JK^{-1}\ mol^{-1}$. 4,4,4

5. (*a*) What is Joule-Thomson effect ? Using the thermodynamic equation of state show that the Joule-Thomson coefficient for a van der Waals gas,

$$\mu_{j.T} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right].$$

What will be the inversion temperature of this gas ?

(*b*) Derive the following relations :

$$C_p - C_v = \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$$

$$= \left[V + \left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H\right]\left(\frac{\partial P}{\partial T}\right)_V$$

6,6

Section B

6. (*a*) Prove that :

(*i*) $\left(\frac{\partial H}{\partial P}\right)_T = 0$ for an ideal gas

(*ii*) $\left(\frac{\partial E}{\partial V}\right)_P + P = C_p\left(\frac{\partial T}{\partial V}\right)_P$.

(*b*) Define chemical potential. Show that the variation of chemical potential of a component *i* with pressure is given by $d\mu_i = V_{i,m}\ dP$.

(*c*) Two ideal gases are at the same temperature but at different pressures. If n_1 moles of gas 1 and n_2 moles of gas 2 are mixed isothermally, what will be the free energy of mixing ? 4,4,4

7. (*a*) Define molal depression constant. Derive thermodynamically an expression relating the freezing point depression of a solution with its molality. How is this expression utilized for the determination of molecular weight of a non-volatile solute ?

(*b*) The k_f and k_b values of solvent B are 5.0 and 15.0 units. The boiling point of the solvent is 80.0°C and its freezing point is 4.0°C. What will be the boiling point of the solution of A(solute) in B if it freezes at 3.5 °C ? 6,6

8. (*a*) Derive thermodynamically using chemical potential concept the relation :

$$\Delta G^\circ = -RT \ln K_p.$$

(*b*) For a reaction $X_2 \rightarrow 2X$, the equilibrium constant at 1225 K is 3.28×10^{-3} and ΔH° for the reaction is 216.7 $kJmol^{-1}$. Calculate ΔG° and ΔS° for this reaction at 1225 K.

(*c*) Explain with examples the coupling of endoergonic reactions with exoergonic reactions. 4,4,4

9. (*a*) Explain the terms osmosis and osmotic pressure. Using the concept of chemical potential, derive an expression for the osmotic pressure of the solution in terms of its concentration.

(*b*) Write a short note on abnormal colligative properties of solutions and van't Hoff factor.

(*c*) Calculate the osmotic pressure of 0.1 M solution of $K_4[Fe(CN)_6]$ at 300 K, assuming the salt to be 40% ionised in this solution. 4,4,4