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B.Sc. (Hons) (Semester – 2nd)
PHYSICAL CHEMISTRY-II
Subject Code: BCHMS1-202
Paper ID: [19131610]

Time: 03 Hours **Maximum Marks: 60**

Instruction for candidates:

1. Section A is compulsory. It consists of 10 parts of two marks each.
2. Section B consist of 5 questions of 5 marks each. The student has to attempt any 4 questions out of it.
3. Section C consist of 3 questions of 10 marks each. The student has to attempt any 2 questions.

Section – A **(2 marks each)**

Q1. Attempt the following:

a. When does an extensive property become intensive properties?

b. A gas absorbs 150 J of heat and expands against the external pressure of 1.10 atm from a volume of 1.0 to 4.0 L. Calculate the change in internal energy? (1 L atm = 101.3J)

c. Why hydrogen and helium show heating in Joule-Thompson effect?

d. Prove that Cp for an ideal gas is constant and nearly equal to 5 cal degree^{-1} mol^{-1}

e. The bond dissociation energy of gaseous H_2, Cl_2 and HCl are 430 kJ mol^{-1}, 242kJ mol^{-1} and 427 kJ mol^{-1} respectively. Calculate the enthalpy of formation for HCl gas.

f. Show that $-(\Delta A)_T = W_{max}$.

g. Give importance of measuring standard free energy change.

h. Derive the relationship of equilibrium constant in terms of mole fraction (K_x) with K_p and K_c. Explain why K_x is generally not used for gaseous reaction

i. How is lowering of vapour pressure related to osmotic pressure? Derive the relationship.

j. Why is the boiling point of 0.1M $BaCl_2$ solution greater than 0.1 M sugar solution?

Section – B **(5 marks each)**

Q2. a. Derive an expression for the work done in the isothermal reversible expansion of a real gas **2**

b. The heat of reaction for the formation of ammonia by Haber's process at 300 K was found to be -91.95 kJ. What will be heat of reaction for the formation at 323 K. The molar heat capacities at 300 K for N_2 , H_2 and NH_3 are 28.45, 28.33 and 37.07 $Jmol^{-1}$ K^{-1} respectively **3**

Q3. a. What is meant by Maxwell relationship? Derive any two **3**

(i) $(\partial U/\partial S)_p = T - P(\partial T/\partial P)_s$, (ii) $(\partial T/\partial P)s = (\partial V/\partial S)p$

(iii) $(\partial T/\partial V)s = - (\partial P/\partial S)v$

b. How can you test validity of third Law of thermodynamics? **2**

Q4. a. Derive van't Hoff reaction equation (reaction isochore) giving the effect of temperature on equilibrium constant. **3**

b. Give coupling of exoergic and endoergic reactions.. **2**

Q5. a. Define Henry's law in terms of mole fraction of solute dissolved in the solution. How Raoult's law follow from it? **3**

b. The normal boiling point of water is 100 ^oC. Its vapour pressure at 80 ^oC is 0.4672 atmospheres. Calculate the molar heat of vaporization of water **2**

Q6. a. Give comparison of reversible isothermal expansion and reversible adiabatic expansion, **3**

b. The equilibrium constant of a reaction becomes double of its value when the temperature is raised from 25 ^oC to 35 ^oC. Calculate ΔH^o for the reaction. **2**

Section – C **(10 marks each)**

Q7. a. What is Joule-Thompson effect? Prove that it is an isoenthalpic process. Define Joule Thompson coefficient and inversion temperature. What is the significance of inversion temperature in adiabatic expansion of real gas. **3**

b. Distinguish between (i) isothermal and adiabatic process and (ii) isobaric and isochoric reactions. **2**

c. Prove thermodynamically that for any substance **3**

d. $C_p - C_v = [P + (\partial U/\partial V)_T] (\partial V/\partial T)_p$

e. Calculate the enthalpy of vaporization per mole for ethanol. Given that the entropy of vaporization of ethanol is 109.8 JK^{-1} mol^{-1} and boiling point of ethanol is 78.5^oC. **2**

Q8. a. Discuss the concept of residual entropy? How does it originate and how it is calculated? Calculate residual entropy of CO? **3**

b. Derive Kirchoff's equation **2**

c. Derive Clausius-Clapeyron equation for liquid-vapor equilibrium. Show how the equation ca be expressed in integrated form. What are its important applications? **3**

d. What is Nernst heat theorem How does it lead to third law of thermodynamics. How does this law help in determination of absolute entropies of a substance at the require temperature **2**

Q9. a. A solution of 8.55 g of cane sugar (mol. wt. 342) in 100g of water freezes at $-0.472^{o}C$ and a solution of 7.24 g of an unknown substance in 100g of water freezes at -0,93 ^{o}C . Determine the molecular weight of the unknown substance. **3**

b. Derive Duhem Margules equation and outline its application to non-ideal solution's **3**

c. Derive thermodynamically the law of chemical equilibrium **2**

d. The equilibrium constant K_p for a reaction at 600 K and 620 K are $1x\ 10^{-12}$ and $5\ x\ 10^{-12}$ respectively. Considering ΔH to be constant in the above temperature range, Calculate ΔH and ΔS for the reaction ($R= 8.314\ JK^{-1}\ mol^{-1}$) **2**