(c) Compute $\Delta_r G$ for the process: H_2O (l, 2 atm, 373 K) → H_2O (g, 2 atm, 373 K). (5,5,5)

8. (a) Derive the relation $\Delta S = C_p \ln\frac{T_f}{T_i} - V\alpha(P_f - P_i)$ starting from $dH = TdS + VdP$.

(b) Absolute entropy of liquid water at 298K has to be calculated. Write all the steps involved. Also write the final expression for calculation of entropy.

(c) Calculate the entropy of separating the components in 100 g of air. The composition is 21% volume O_2, 78% volume N_2 & 1% volume Ar (Atomic Weight of Ar is 40). (5,5,5)

[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 1234

Unique Paper Code : 2172011203

Name of the Paper : CHEMICAL THERMODYNAMICS AND ITS APPLICATIONS

Name of the Course : **B.Sc. (H) Chemistry**

Semester : II

Duration : 3 Hours

Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. **Q.1** is compulsory.
4. Use of scientific calculators is allowed.

1. Attempt any **five** :

(a) Why is the value of heat capacity at constant pressure greater than the value at constant volume?

(b) Reversible processes cannot be carried out in reality. Explain.

(c) Partial molar volume of a component in a solution depends on the nature as well as the amount of the other components. Explain qualitatively.

(d) Steam at 1 bar is converted to liquid water spontaneously at temperatures below 100°C although this results in decrease in its entropy. Explain.

(e) If Joule Thompson Coefficient is positive for a gas it indicates that attractive forces dominate between molecules of the gas. Is this statement true? Explain giving reason

(f) Why is the partial molar Gibbs free energy called as Chemical potential?

(g) Which of the following processes are spontaneous and why?

(c) State Hess's law of constant heat summation. Calculate the enthalpy of formation of tungsten carbide (WC) from the following data :

$W(s) + 3/2\ O_2(g) \rightarrow WO_3(s)\ \Delta_r H^\circ_{298} = -837.47$ kJ mol^{-1} $WC(s) + 5/2\ O_2(g) \rightarrow WO_3(s) + CO_2(g)\ \Delta_r H^\circ_{298} = -1195.79$ kJ mol^{-1} $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)\ \Delta_r H^\circ_{298} = -393.51$ kJ mol^{-1}.

(5,5,5)

7. (a) Derive the relation $\left\{\dfrac{\partial\left(\dfrac{\Delta_r A}{T}\right)}{\partial T}\right\}_p = -\dfrac{\Delta_r U}{T^2}$.

(b) Define enthalpy of neutralization. Why is its value always negative? The value of enthalpy of neutralization of strong acid and strong base is same for all acids and bases. Explain. Will there be a change in the value of enthalpy of neutralization if the acid or the base is a weak electrolyte? Give reason for your answer.

5. (a) Derive the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

starting from dU = dq + dw

(b) What is residual entropy? Explain giving two examples.

(c) 5 g ice at 273 K is added to 30 g water at 323 K in a thermally insulated container. All the ice melts when equilibrium is achieved. What is the final temperature? What is the total entropy change? Given $\Delta_{fus}H = 334.72 Jg^{-1}$, $C_P(1,H_2O) = 4.184\ JK^{-1}g^{-1}$.

(5,5,5)

6. (a) Describe Joule's experiment and the result obtained from it. What are its shortcomings?

(b) What is inversion temperature? Starting from the definition of μ_{JT} show that $T_i = 1/\alpha_i$ where α_i is the isobaric expansivity of the gas at the temperature T_i.

(i) Reversible isothermal expansion of ideal gas.

(ii) Vaporization of superheated water above 100°C.

(iii) Melting of ice at freezing point.

(5×3=15)

2. (a) If the equation of state of a gas is

$$\left(P + \frac{a}{V^2}\right)V = RT\text{ ; Show that P is a state function.}$$

Also prove that $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T + 1 = 0$.

(b) Show that isothermal reversible work of expansion of an ideal gas is greater than that of a van der Waals gas under similar conditions?.

(c) The value of $C_{p,m}$ for a sample of a perfect gas was found to vary with temperature as $C_{p,m}/JK^{-1}\,mol^{-1} = 20.17 + 0.3665(T/K)$. Calculate q, w, ΔU, and ΔH for one mole of the gas when the temperature is raised from 25°C to 200°C at constant pressure. (5,5,5)

3. (a) Using indicator diagram show that more work is done by the system during? expansion of an ideal gas in a reversible process than in an irreversible process.

(b) Show that chemical potential of a component in a mixture can be written in terms of enthalpy. Is this a partial molar quantity? Give reason.

(c) One mole of an ideal gas with $C_V = 3/2\,R$ undergoes adiabatic reversible expansion from 22.4 liters to 44.8 liters. If initial temperature is 27°C, calculate the final temperature and the work done in the process. (5,5,5)

4. (a) Derive the relation $C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)_V^2\left(\frac{\partial V}{\partial P}\right)_T$ starting from H = U + PV.

(b) Show that dw is not an exact differential and hence w is not a state function.

(c) What is the difference between bond dissociation enthalpy and bond energy?

The value of $\Delta_r H^\circ$ (298K) for the reaction $N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g)$ is found to be 108.76 kJ mol^{-1}. Calculate the bond enthalpy of N = N bond assuming that the structure of N_2H_2 is HN = NH. Given the following bond enthalpies : $\varepsilon_{N-N} = 163.18$ kJ mol^{-1}, $\varepsilon_{N-H} = 390.79$ kJ mol^{-1} and $\varepsilon_{H-H} = 435.89$ kJ mol^{-1}. (5,5,5)