Module – II (Free energy in chemical Equilibria)

lect-01

CO_2 = To acquire the knowledge of free energy concept for the thermodynamics associated with chemical reactions and equilibrium.

Topic :- Introduction to use free-energy in chemical Equilibria :-

1. Energy :- " The ability or capacity of the body to do work under the given set of condition".

→ It is expressed in cals or kilocalories / Joules or kilo-joules.

2. Work :- " Work is a mode of transference of energy between the system and the surroundings.

→ If a force 'F' acting on a body moves it through a distance x, then work done is expressed as ;

$$\boxed{Work = F \times x}$$

3. Internal energy (E) :-

The total amount of energy associated with a definite amount of a substance under a given set of conditions is referred to as the internal energy of that substance

→ change in internal energy is,

$$\boxed{\Delta E = E_P - E_R}$$

where, E_P → Energy of Product

E_R → Energy of Reac

4. Enthalpy or Heat Content (H) :-

→ The heat changes at contant pressure,

→ **Def**

→ Def^n:- The sum of internal energy and Pressure-volume energy of a system under a particular conditions is known as Enthalpy of the system.

Mathematically :- $H = E + PV$.

$$\Delta H = H_{\text{final state}} - H_{\text{initial state}}.$$

5. Relationship between ΔH & ΔE :-

$$\boxed{\Delta H = \Delta E + P\Delta V}.$$

When, $\Delta H < \Delta E$, i.e, chemical reaction is exothermic.

When, $\Delta H > \Delta E$, i.e, chemical reaction is endothermic.

Continue... for one class

lect-02 :-

Topic :- Concept of Entropy, Defⁿ, Unit of Entropy :-

Defⁿ :-

Concept :-

It is a property that is used to express this extent of disorder or randomness of a system.

→ It is a state function, therefore it depends only on the initial and final states of the system.

→ Change in entropy is,

$$\Delta S = S(\text{final state}) - S(\text{initial state})$$

→ For a reversible process at equilibrium :-

$$\boxed{dS = \frac{dq_{rev}}{T}}$$

Defⁿ :- Entropy change (ΔS) is defined as the amount of heat absorbed by the system in a reversible manner divided by the absolute temperature at which the heat is absorbed.

Unit of Entropy :-

Calories per degree (cal deg^{-1})

or

Joule per Kelvin (JK^{-1})

Molar entropy :-

For 1 mole of the substance, the entropy is known as Molar entropy.

→ The greater the randomness or disorder in a system, the higher is its entropy.

Ex- $H_2O(l) \longrightarrow H_2O(g)$

less — More entropy

Ex- $CaCO_3(s) \longrightarrow CaO + CO_2(g)$

less entropy — More entropy

lect-03 :-

Topic - Evaluation of Entropy :-

Entropy Changes for an ideal gas :-

For 1 mole of an ideal gas,

$$\boxed{\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}}$$

or

$$\boxed{\Delta S = 2.303\, nC_v \log \frac{T_2}{T_1} + 2.303\, nR \log \frac{V_2}{V_1}}$$

Where, ΔS → Change of entropy
C_v → Molar heat at constant volume.
T_1 & T_2 → Initial and final temperature.
R → constant ($8.314\, JK^{-1} mol^{-1}$)
or
(1.987 cal$deg^{-1} mol^{-1}$)
V_1 & V_2 → Initial and final volume.

Numerical :-

Q.1. Calculate the entropy change when 3 moles of an ideal gas ($C_v = 7.88$ cal deg^{-1} mol^{-1}) are heated from a volume of 200L at 50°C to a volume of 300L at 150°C.

Soln:- Given data :-

$n = 3$ mole
$C_v = 7.88$ cal deg^{-1} mol^{-1}
$R = 1.987$ cal deg^{-1} mol^{-1}.
$T_1 = 273 + 50 = 323K$
$T_2 = 273 + 150 = 423K$

$V_1 = 200L$

$V_2 = 300L$.

According to the formula,

$$\Delta S = 2.303\, n C_v \log \frac{T_2}{T_1} + 2.303\, nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 3 \times 7.88 \log\left(\frac{423}{323}\right) + 2.303 \times 3 \times 1.987 \times \log\left(\frac{300}{200}\right)$$

$$= 6.377 + 2.417$$

$$\boxed{\Delta S = 8.794 \text{ cal deg}^{-1}.}$$ Ans

lect - 04

Topic :- Numerical for entropy change ie, Evaluation of Entropy for isothermal Process for entropy change.

② For 1 mole of an ideal gas :-

$$\boxed{\Delta S = n C_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}}$$

Where n = no. of moles.

C_p = Molar heat at constant Pressure.

T_1 & T_2 = Initial & final temp.

R = Constant
(8.314 $JK^{-1} mol^{-1}$)
or
1.987 cal $deg^{-1} mol^{-1}$

P_1 = Initial pressure

P_2 = Final Pressure.

Numerical :-

Q② Calculate the entropy change involved in expanding 1 mole of an ideal gas from 15 L at 2 atm pressure to 50 L at 1 atm pressure. (C_p = 7.42 cal deg^{-1} mol^{-1}).

Soln :- Given data :-

n = 1 mole

C_p = 7.42 cal deg^{-1} mol^{-1}.

$R = 1.987$ cal deg^{-1} mol^{-1}.

$P_1 = 2$ atm

$P_2 = 1$ atm

$V_1 = 15L$

$V_2 = 50L$

For an ideal gas,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\Rightarrow \frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \frac{50\times1}{15\times2} = \frac{50}{30} = \frac{5}{3}.$$

According to formula :-

$$\Delta S = nC_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

or

$$= 2.303\, n\, C_p \log\frac{T_2}{T_1} + 2.303\times R\times\log\frac{P_1}{P_2}$$

$$= 2.303\times1\times7.42\log\left(\frac{5}{3}\right) + 2.303\times 1.987\times\log\left(\frac{2}{1}\right).$$

$$= 17.08826\times0.2218 + 4.576061\times0.3010$$

$$= 3.790176068 + 1.377394361$$

$$= 5.167570429$$

$$\boxed{\Delta S = 5.168 \text{ cal deg}^{-1}}$$. Ans

lect - 05

Topic :- Evaluation of Entropy :-

For isothermal process :-

When $T_1 = T_2$

$$\rightarrow \boxed{\Delta S_T = nR \ln \frac{V_2}{V_1}}$$

or

$$\boxed{\Delta S_T = 2.303 \times n \times R \log \frac{V_2}{V_1}}$$

$$\rightarrow \boxed{\Delta S_T = nR \ln \frac{P_1}{P_2}}$$

or

$$\boxed{\Delta S_T = 2.303 \times n \times R \log \frac{P_1}{P_2}}$$

Where, $V_2 > V_1$ or $P_1 > P_2$

ΔS_T is (+ve) but in contraction, $V_2 < V_1$ or $P_1 < P_2$.

Hence ΔS_T is (−ve). so, it concluded entropy increases and contraction decreases.

Numerical :-

Q.③ Calculate the change in entropy accompanying the isothermal expansion of 5 moles of an ideal gas at 330K until its volume has increased six times

Solⁿ!- Given data :- $V_1 = 1$, $V_2 = 6$
$n = 5$ moles.
$R = 8.314\ JK^{-1} mol^{-1}$.

According to formula,

$$\Delta S_T = 2.303\ nR \log \frac{V_2}{V_1}$$

$$= 2.303 \times 5 \times 8.314\ JK^{-1} mol^{-1} \log\left(\frac{6}{1}\right)$$

$$= 2.303 \times 5 \times 8.314 \times 0.7782\ JK^{-1}.$$

$$\boxed{\Delta S_T = 74.5\ JK^{-1}}$$ Ans

Q.4.) 5 moles of an ideal gas expands isothermally and reversibly at 27°C form an initially volume of 5dm³ against a pressure that is gradually reduced. calculate change of entropy at constant temp.

Solⁿ!- Given data :- $n = 5$ mole.
$R = 8.314\ JK^{-1}$
$V_1 = 5 dm^3$
$V_2 = 50 dm^3$

According to formula :-

$$\Delta S_T = nR \ln \frac{V_2}{V_1} \quad \text{or} \quad \Delta S_T = 2.303 \times n \times R \log \frac{V_2}{V_1}$$

$$= 5 \times 2.303 \times 8.314 \times \log\left(\frac{50}{5}\right)$$

$$= 95.73571 \times 1$$

$$\boxed{\Delta S_T = 95.73571\ JK^{-1}}$$. Ans

lect-06 :-

Numerical :-

Q ⑤ 1 mole of an ideal gas at 300K expands reversibly from $3 \times 10^{-2} m^3$ to $5 \times 10^{-2} m^3$. Calculate the entropy change for the gas.

Soln :- Given data :-

$n = 1$ mole

$R = 1.987$ cal deg^{-1} mol^{-1}

$V_1 = 3 \times 10^{-2} m^3$

$V_2 = 5 \times 10^{-2} m^3$

According to formula :-

$$\Delta S_T = 2.303 \times n \times R \log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times 1 \times \cancel{1.987} \times 1.987 \log\left(\frac{5 \times 10^{-2}}{3 \times 10^{-2}}\right)$$

$$= 4.576061 \times 0.22184$$

$= 1.01515$ cal deg^{-1} ~~mol~~.

Q6. Calculate the entropy change when 1 mole of an ideal gas is heated from 20°C to 40°C at a constant pressure. The molar heat at constant pressure of the gas over this temp. range is 6.189 cal deg^{-1}.

Soln:- Given data:-

$n = 1$ mole.

$C_p = 6.189$ cal deg^{-1}.

$T_1 = 273 + 20 = 293K$.

$T_2 = 273 + 40 = 313K$.

According to formula:-

$\Delta S_p = n c_p \ln \frac{T_2}{T_1}$ or $2.303 \times n \times c_p \log \frac{T_2}{T_1}$

$= 2.303 \times 1 \times 6.189 \times \log \left(\frac{313}{293}\right)$

$= 14.253267 \times 0.02867$

$= 0.40864116489$

$\boxed{\Delta S_p = 0.4087 \text{ cal deg}^{-1}}$. Ans lect-note-⑧

Topic - Free-energy concept i.e, free-energy change with pressure for an ideal gas :-

Formulation :-

At constant temperature,

$$dG = Vdp \quad \text{------} (i)$$

If pressure changes from P_1 to P_2, the corresponding free-energy will change from G_1 to G_2

Integrating eqn (i) :

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} Vdp \quad \text{--------} (ii)$$

For an ideal gas,

$$V = \frac{nRT}{P}$$

Substituting the value of 'V' in eqn (ii)

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P} dp$$

$$\Rightarrow \Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

or

$$\boxed{\begin{aligned}\Delta G &= 2.303\, nRT \log \frac{P_2}{P_1} \\ \Delta G &= 2.303\, nRT \log \frac{V_1}{V_2}\end{aligned}} \quad \text{---(iii)}$$

Where V_1 & V_2 are the initial and final volumes respectively.

G is a state function.

Numerical :-

Q.1) ΔG for a reaction at 300K is −16Kcal; ΔH for the reaction is −10Kcal. What is the entropy of the reaction? What will be ΔG at 330K?

Soln :- Given data :- $\Delta G = -16\,\text{Kcal}$.
$\Delta H = -10\,\text{Kcal}$.
$T = 300\text{K}$.

(i)

So, According to formula of free-energy concept.

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-10\,\text{Kcal} - (-16\,\text{Kcal})}{300\text{K}}$$

$$= \frac{-10\,\text{Kcal} + 16\,\text{Kcal}}{300\text{K}} = 0.02\,\text{KcalK}^{-1}$$

$$\boxed{\Delta S = 0.02\,\text{KcalK}^{-1}} = 20\,\text{calK}^{-1}. \text{ Ans}$$

(ii) ΔG at 330K :-

$$\Delta G = \Delta H - T\Delta S$$

$$= -10\,\text{Kcal} - 330\cancel{\text{K}} \times 0.02\,\text{Kcal}\,\cancel{\text{K}^{-1}}$$

$$= -10\,\text{Kcal} - 6.6\,\text{Kcal}$$

$$\boxed{\Delta G = -16\,\text{Kcal}}. \text{ Ans}$$

Lect note -(09)

Topic - Numerical continue....

Q.2. Calculate the free energy change when 4 moles of an ideal gas expands from a pressure of 10 atm to 1 atm at 25 °C.

Soln:- Given data :-

$P_1 = 10$ atm.

$P_2 = 1$ atm.

$n = 4$ moles.

$R = 8.314 \ JK^{-1} mol^{-1}$

$T = 273 + 25 = 298K$.

According to formula,

$$\Delta G = 2.303 \, nRT \log \frac{P_2}{P_1}$$

$$= 2.303 \times 4 \times 8.314 \times 298 \log \left(\frac{1}{10}\right)$$

$$= 22823.393264 \log \left(\frac{1}{10}\right)$$

$$= 22823.393264 \times (-1)$$

$$= -22823.39 \ \cancel{mol} \times J\cancel{K^{-1}} \cancel{mol^{-1}} \times \cancel{K}$$

$$\boxed{\Delta G = -22823.39 \ J}$$ (Ans

Q③ For a reaction at 298 K, $2A + B \longrightarrow C$. $\Delta H = 100\,\text{Kcal}$ and $\Delta S = 0.50\,\text{Kcal}\,K^{-1}$. Assuming ΔH & ΔS to be constant over the temperature change, at which temperature the reaction will become spontaneous.

Soln :- Given data → $\Delta H = 100\,\text{Kcal}$

$\Delta S = 0.50\,\text{Kcal/K}$

ΔG is related to ΔH as

As we know that $\Delta G = \Delta H - T\Delta S$.

A reaction is spontaneous when, ΔG is (-ve)

i.e, $\Delta G < 0$.

Putting $\Delta G = 0$ and the values of ΔH and ΔS, we have,

$$0 = 100 - (T \times 0.50)\,.$$

$$T = \frac{100}{0.50}\,.$$

$$= 200\,K\,.$$

∴ Thus, ΔG is (-ve) at temperature above 200K. Hence, the given reaction will be spontaneous above 200K.

lect note -⑩

Topic - Gibbs-Helmholtz Equation :-

At constant pressure, the change of free-energy with temperature is,

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S} \text{ - - - - - - - (i)}$$

Consider, a system change reversibly and isothermally from state 1 to state 2.

If the free energy and entropy of the system in state 1 are G_1 & S_1.

for state 2 are G_2 and S_2.

Then the entropy change of the system is,

$$\boxed{\Delta S = S_2 - S_1} \text{ - - - - - - (ii)}$$

From eqn (i), we can write..

$$S_1 = -\left(\frac{\partial G_1}{\partial T}\right)_P$$

$$S_2 = -\left(\frac{\partial G_2}{\partial T}\right)_P$$

Substituting the value of S_1 & S_2 in eqn (ii)

$$\Delta S = \left[-\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P \right]$$

$$= -\left[\frac{\partial (G_2 - G_1)}{\partial T}\right]_P$$

$$\boxed{\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P} \quad --- \text{(iii)}$$

For an isothermal process,

$$\Delta G = \Delta H - T\Delta S$$

Substituting this ΔS in eqn (iii)

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta G = \Delta H - T\left(-\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Rightarrow \boxed{\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P}$$

This is known as J. W. Gibbs & H. von Helmholtz eqn so, according to name the eqn name is Gibbs-Helmholtz Equation.

lect - 11 :-

Topic - Gibbs-Helmholtz Equation

Numerical:-

Q.1. For the following reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The free-energy change at 25°C and 35°C are -3.98 and -3.37 Kcal. Calculate the heat of reaction at 35°C.

Soln !- Given data !-

$G_1 = -3.98$ Kcal

$G_2 = -3.37$ Kcal.

$T_1 = 273 + 25 = 298K$

$T_2 = 273 + 35 = 308K$

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Rightarrow \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{G_2 - G_1}{T_2 - T_1}$$

$$= \frac{-3.37 - (-3.98)}{308 - 298}$$

$$= \frac{0.61}{10} = 0.061.$$

$\boxed{\text{At } 35°C}$, $\Delta G = -3.37$ Kcal

$T = 308K$

$$-3.37 = \Delta H + 308(0.061)$$

$$\Delta H = -3.37 - 18.79$$

$$\boxed{\Delta H = -22.16 \text{ Kcal}}$$. Ans

Q.② For the following reaction :-

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

The value of enthalpy change and free-energy change are -68.32 & -56.69 kcal respectively at 25°C. Calculate the value of free energy change at 30°C.

Soln :- Given data :-

$\Delta G = -56.69$ Kcal

$\Delta H = -68.32$ Kcal ;

$T = 273 + 25 = 298K$.

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-56.69 + 68.32}{298} = \frac{11.63}{298}$$

$$= 0.039$$

Assuming that $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ remains constant over this range of temp., at 30°C we can write, Formula.

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\Delta G = -68.32 + 303 \times 0.039$$

$$= -68.32 + 11.81$$

$$\boxed{\Delta G = -56.51 \text{ Kcal}}$$. Ans

lect - 12 :-

Topic :- Claypeyron - Clausis Equation :-

let us consider two phases A & B of the same component in equilibrium with constant temp 'T' and pressure 'P'.

$$A \rightleftharpoons B$$

Suppose free energies per mole of the substance in the two phases A and B are G_A and G_B respectively.

→ The system is in equilibrium, there is no change in free energy.

$$\boxed{G_A = G_B} \quad ---- (i)$$

If the temp is raised to T+dT, the pressure 'P' will increase to P+dp. For this change, the molar free-energy becomes $G_A + dG_A$ & $G_B + dG_B$.

As the two phases are in equilibrium.

$$\boxed{G_A + dG_A = G_B + dG_B} \quad ---- (ii)$$

Phase change the work-done is only because of the volume change, the change in energies dG_A & dG_B

$$\boxed{dG = V.dp - S.dT} \quad --- (iii)$$

Therefore,

$$dG_A = V_A dp - S_A dT \text{ - - - - - (iv)}$$

$$dG_B = V_B dp - S_B dT \text{ - - - - - (v)}$$

V_A & V_B are the molar volumes of the phases A & B respectively. S_A & S_B are their enthalpies.

$$V_A dp - S_A dT = V_B dp - S_B dT$$

$$\Rightarrow \frac{dp}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A} \text{ - - - - - (vi)}$$

where ΔS = Molar entropy change.

$V_B - V_A$ = change in volume.

From Gibbs-Helmholtz Eqn :-

$$\Delta G = \Delta H - T\Delta S \text{ - - - - - - (vii)}$$

$$\Delta G = 0 \quad [\text{from eqn (i)}]$$

$$\Delta H - T\Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T} \text{ - - - - - - (viii)}$$

Placing this eqn (vi)

$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{V_B - V_A} = \frac{\Delta H}{T(V_B - V_A)}} \text{ - - - (ix)}$$

This is claypeyron clausis eqn.

$\frac{dP}{dT}$ → Rate of change of Pressure with temp.

T → Temp.

ΔH → Enthalpy for phase change.

lect-13 :-

Topic :- Integrated form of Claypeyron-Clausis eqn for liquid-vapour Equilibrium

Formulation :-

In liquid vapour Equilibrium.

$$V_v >> V_L$$

Hence, $V_v - V_L \approx V_v$.

The claypeyron-clausius equation takes the form,

$$\frac{dP}{dT} = \frac{\Delta H_v}{T V_v} \quad \text{--- (i)}$$

Assuming the vapours behave ideally.

$$PV_v = RT$$

$$V_v = \frac{RT}{P}$$

Inserting this value in eqn (i)

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(RT/P)}$$

Or

$$\frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

Integrating, on the assumption that ΔH_v is constant over a small temp. change.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

or

$$\boxed{\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

Where P_1 and P_2 are the vapour Pressures at T_1 & T_2 respectively.

Lect - 14

Topic - Numerical :-

Q.1 The latent heat of vaporisation of benzene at its boiling point (80°C) is 7413 cal mol^{-1}. What is the vapour pressure of C_6H_6 at 27°C.

Soln:-

Given data:- $\Delta H_v = 7413\ cal\ mol^{-1}$

$T_1 = 80°C = 80 + 273 = 353K$.

$P_1 = 1atm = 760\,mm\,Hg$.

$T_2 = 27°C = 27 + 273 = 300K$.

$P_2 = ?$

According to formula:-

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{P_2}{760\,mmHg} = \frac{7413\ cal\ mol^{-1}}{2.303 \times 1.987\ cal\ mol^{-1}K^{-1}}\left[\frac{300 - 353}{300 \times 353}\right]$$

$$= \frac{7413 \times (-53)}{2.303 \times 1.987 \times 300 \times 353}$$

$$= \frac{-392889}{484604.8599}$$

$$= -0.8107.$$

$$\log \frac{760\,mmHg}{P_2} = 0.8107.$$

or

$$\frac{760\,mmHg}{P_2} = Antilog\,(0.8107)$$

$$= 6.4670.$$

Hence, $\boxed{P_2 = \frac{760}{6.4670} = 117.52\,mmHg}$. Ans

Q2) If the atmospheric pressure is 535 mm of Hg. Find the temp. at which water will boil. Latent heat of vapourisation of water is 545.5 Cal/g at 100°C temp.

Soln:- Given data:- $P_1 = 535$ mm Hg.

$P_2 = 1\,atm = 760$ mm Hg.

$T_1 = ?$ $T_2 = 100 + 273 = 373K$.

$\Delta H_v = 545.5$ cal/g

$= 545.5 \times 18$ cal/mol

$= 9819$ cal mol^{-1}

$R = 1.987$ cal K^{-1} mol^{-1}.

According to formula:-

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{760}{535} = \frac{9819 \text{ cal mol}^{-1}}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}}\left[\frac{1}{T_1} - \frac{1}{373}\right]$$

$$\Rightarrow \left[\frac{1}{T_1} - \frac{1}{373}\right] = \frac{\cancel{0.6973916964}\ 0.1524598102}{9819}$$

$$= 0.00007102$$

$$\Rightarrow \frac{1}{T_1} - 0.002681 K^{-1} = 0.00007102 K^{-1}$$

$$\Rightarrow \frac{1}{T_1} = 0.00275202 K$$

$$\Rightarrow T_1 = \frac{1}{0.00275202 K^{-1}}$$

$$\boxed{T_1 = 363.369 K.}$$

lect-15 :-

Topic – Gibbs free energy (G) as a Criterion of equilibrium and spontaneous change :-

By defⁿ :-

(i) If ΔG is (-ve) ($\Delta G < 0$), the process is spontaneous.

→ ΔG can be (-ve), if Both the energy and entropy factors are favourable, i.e, ΔH is (-ve) & $T\Delta S$ is (+ve).

Ex - $C(s) + O_2(g) \longrightarrow CO_2(g)$

$$\boxed{\Delta H = -393.5\ KJ}$$

→ Both the energy and entropy factors have (-ve) sign but $\Delta H > T\Delta S$ i.e, the energy factor is favourable while the entropy factor is not favourable and the magnitude of ΔH is more than that of $T\Delta S$, e.g:-

$$\underset{\text{More random}}{N_2(g) + 3H_2(g)} \longrightarrow \underset{\text{less random}}{2NH_3(g)} \quad \boxed{\Delta H = -92.36\ KJ}$$

favourable.

→ Both the energy and entropy factors have +ve sign but $\Delta H < T\Delta S$ Or $T\Delta S > \Delta H$, i.e, the entropy factor is favourable while the energy factor is not favourable and magnitude of $T\Delta S$ is more than on ΔH.

$$\underset{\text{less random}}{CaCO_3(s)} \longrightarrow \underset{\text{More random}}{CaO(s) + CO_2(g)} \quad \boxed{\Delta H = 178\ KJ}$$

Not favourable

b) If (ΔG is 0), the Process is in the equilibrium state and thus there is no net change in either direction. This happens when one of the factor is favourable and the other is opposing but they are equal in magnitudes.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g).$$

$$\Delta H = -51.86 KJ.$$

→ In this reaction, the energy factor favours but the entropy factor (randomness factor) opposes up to the same extent. Thus equilibrium exists

c) If ΔG is (+ve), the process does not occur in the forward direction.

ΔG can be (+ve), if;

a) Both the energy and entropy factors oppose i.e, ΔH has (+ve) sign and $T\Delta S$ has (-ve).

b) Both the factors have +ve sign but $\Delta H > T\Delta S$.

c) Both the factors have (+ve) sign but $T\Delta S > \Delta H$.

Lect-16 :-

Topic :- Van't Hoff Isochore :-

It deals with the variation of equilibrium constant with temperature.

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\ln K_{eq} = \frac{-\Delta G^\circ}{RT}$$

$$= \frac{-(\Delta H^\circ - T\Delta S^\circ)}{RT}$$

$$= \frac{-\Delta H^\circ}{RT} + \frac{\cancel{T}\Delta S^\circ}{R\cancel{T}}$$

$$= \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$$\therefore \ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad \text{------ (i)}$$

$$\therefore \ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad \text{------ (ii)}$$

$$\therefore (\ln K_2 - K_1) = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} - \left(\frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}\right)$$

$$= \frac{-\Delta H^\circ}{RT_2} + \cancel{\frac{\Delta S^\circ}{R}} + \frac{\Delta H^\circ}{RT_1} - \cancel{\frac{\Delta S^\circ}{R}}$$

$$= \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1}$$

$$\therefore \ln(K_2 - K_1) = \left(\frac{\Delta H^\circ}{RT_1} - \frac{\Delta H^\circ}{RT_2}\right)$$

$$= \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\boxed{\ln(K_2 - K_1) = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)} \quad (\text{Or})$$

$$\boxed{\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

This is called Van't Hoff isochore.

Numerical :-

Q.1. The equilibrium constant for the reaction :- $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ is 18.5 at 925 K and 9.25 at 1000 K. Calculate standard enthalpy of the reaction. Also calculate ΔG° and ΔS° at 925 K.

Sol^n :- Given data :-

$T_1 = 925\ K$
$T_2 = 1000\ K$
$K_1 = 18.5$
$K_2 = 9.25$
$\Delta H^\circ = ?$
$R = 8.314\ KJ\ mol^{-1}$

According to formula :-

from Van't Hoff isochore :-

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{K_{1000K}}{K_{925K}} = \frac{\Delta H^\circ}{2.303 \times 8.314\ JK^{-1} mol^{-1}}\left(\frac{1000 - 925}{925 \times 1000}\right)$$

$$\Rightarrow \log \frac{9.25}{18.5} = \frac{\Delta H^\circ}{2.303 \times 8.314}\left(\frac{75}{925000}\right)$$

$$\Rightarrow \log(0.5) = \frac{\Delta H^\circ \times 75}{17711106.35}$$

$$\Rightarrow -0.3010299 = \frac{\Delta H^\circ \times 75}{17711106.35} \Rightarrow \boxed{\begin{aligned}\Delta H^\circ &= -71087.6343 \\ &= -71.08\ KJ\ mol^{-1}\end{aligned}}$$

$$\Rightarrow \Delta G^\circ = -2.303RT \log K_{eq}$$

$$= -2.303 \times 8.314\ J mol^{-1} \times 925 \log 18.5$$

$$= -17711.10635 \times 1.26717$$

$$= -22442.9826\ J mol^{-1}$$

$$\boxed{= -22.4\ KJ\ mol^{-1}}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{(-71087 - (-22442))}{925}$$

$$= -52.58918\ J mol^{-1} K^{-1}$$

$$\boxed{\Delta S^\circ = -52.6\ J mol^{-1} K^{-1}}$$

lect - 17 :-

Topic :- Numerical , Vant Hoff isothermal continue - -

Q1) Enthalpy and Entropy changes of a reaction are $40.63\ KJmol^{-1}$ & $108.8\ JK^{-1}\ mol^{-1}$ respectively. Predict the feasibility of the reaction at 27°C .

Soln:- Given data!-

$\Delta H = 40.63\ KJ\ mol^{-1}$.

$= 4063\ J\ mol^{-1}$.

$\Delta S = 108.8\ JK^{-1}\ mol^{-1}$

$T = 27 + 273 = 300K$.

$\Delta G = \Delta H - T\Delta S$

$= 4063 - 300 \times 108.8$

$= 40630 - 32640$

$$\boxed{\Delta G = +7990\ J\ mol^{-1}}$$

or

$$\boxed{\Delta G = 7.99\ KJ\ mol^{-1}}$$

So, ΔG is (+ve) , the reaction is not feasible or it is non-spontaneous .

Q②) ΔH & ΔS for the reaction ,

$$Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g) .$$

are $30.56\ KJ\ mol^{-1}$ & $66.0\ JK^{-1}\ mol^{-1}$. respectively . Calculate the temp. at which the free energy change for the reaction will be zero .

Soln:- $\Delta G = \Delta H - T\Delta S$.

At Equilibrium, $\Delta G = 0$

So, that, $0 = \Delta H - T\Delta S$

$\Rightarrow \Delta H = T\Delta S$

$\Rightarrow T = \dfrac{\Delta H}{\Delta S}$

Where, $\Delta H = 30.56\,kJ\,mol^{-1}$

$= 30560\,J\,mol^{-1}$

$\Delta S = 66\,J\,K^{-1}\,mol^{-1}$.

$$T = \frac{30560\,\cancel{J}\,\cancel{mol^{-1}}}{66\,\cancel{J}\,K^{-1}\,\cancel{mol^{-1}}}$$

$$\boxed{T = 463.030\,K}$$. Ans