Concepts of Entropy :

Entropy is a quantity that tells whether a chemical reaction or a physical change can occur spontaneously in an isolated system or not. It is a measure of disorder or randomness of a system. when a system goes from a more orderly to less orderly state, randomness so also entropy increases and vice versa. Since in nature processes are generally spontaneous (or irreversible), entropy of universe is continuously increasing. when a spontaneous reaction comes to equilibrium entropy is maximum that is the nature is trying to attain the state of maximum entropy. Sign of entropy change in a reaction is positive when a solid melts, liquid vapourises or solid sublimes, the no. of molecules on the product side is more than on the reactant side.

Entropy is a state function that is the magnitude of ΔS depends only on the entropies of the system in its initial and final states. The SI unit of entropy is Joules per degree Kelvin. (JK^{-1}). $\Delta S = S_{final} - S_{initial}$ or $S_{products} - S_{reactants}$

Entropy Change, ΔS is directly proportional to the quantity of heat added to the system. For a reversible path $\Delta S \propto q_{rev}$. The magnitude of ΔS is inversly proportinal to the temperature at which heat is added to the system. It is because at low temp., a given quantity of heat makes a large change in the relative degree of order. Near absolute zero, the addition of even a small quantity of heat causes a very substantial change (ΔS is large). If the same quantity of heat is added to the system at a high temp., the system goes from an already highly random state to one just slightly more random. Hence $\Delta S \propto \frac{1}{T}$. Combinely $\boxed{\Delta S = \frac{q_{rev}}{T}}$

For reversible Carnot cycle working between temps. T_1 & T_2 $(T_2 > T_1)$ we can write $\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$

$$\Rightarrow \frac{q_2}{q_2} - \frac{q_1}{q_2} = \frac{T_2}{T_2} - \frac{T_1}{T_2}$$

$$\Rightarrow 1 - q_1/q_2 = 1 - T_1/T_2 \Rightarrow \frac{q_1}{q_2} = \frac{T_1}{T_2} \Rightarrow \frac{q_1}{T_1} = \frac{q_2}{T_2}$$

Giving +ve sign to heat absorbed (q_2) and -ve sign to heat evolved (q_1) by the system,

$$+ q_2/T_2 = -q_1/T_1 \Rightarrow \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0.$$

Hence we may conclude that when the isothermal and the adiabatic processes in a Carnot's cycle are carried out slowly (or reversibly) then the summation of q/T is equal to zero.

If any process is carried out reversibly so that dq is the amount of heat absorbed by the system from the surrounding at temp. T, then entropy change ds is,

$$ds = \frac{dq}{T}$$

In an adiabatic reversible process, $dq = 0$. Hence $ds = dq/T = 0$. Hence S = constant. Hence it can be defined as the thermal property of the substance which remain constant during an adiabatic cyclic change. Its unit is JK^{-1}. Actual entropy is difficult to define. Hence change in entropy is considered. The entropy of a system and its surroundings together increases in a thermodynamically irreversible (spontaneous) process but remains constant in a thermodynamically reversible process i.e $\Delta S_{sys} + \Delta S_{surr} = 0$ for reversible & $\Delta S_{sys} + \Delta S_{surr} > 0$ for irreversible process.

* Prove that ds is an exact differential, single valued and continuous, finite state function.

Ans. Let us consider a reversible cyclic process from state 1 to 2 & back from 2 to 1 through path a & b respectively. Hence

$$\frac{dq}{T} = \int_1^2 \frac{dq\,(a)}{T} + \int_2^1 \frac{dq\,(b)}{T} = 0.$$

$$\Rightarrow \int_1^2 \frac{dq\,(a)}{T} = -\int_2^1 \frac{dq\,(b)}{T}$$

$$\Rightarrow \int_1^2 \frac{dq\,(a)}{T} = \int_1^2 \frac{dq\,(b)}{T} \Rightarrow \int_1^2 ds\,(a) = \int_1^2 ds\,(b)$$

The above equation shows that change in entropy from state 1 to 2 is same

Entropy & unavailable energy:

Processes in nature are spontaneous or irreversible in which the entropy of universe is continuously increasing i.e. unavailable energy goes on increasing and workable energy is decreasing continuously. A spontaneous process comes to halt at equilibrium. Hence entropy is maximum.

When $\Delta S = 0$, ~~system~~ Reaction is in equili. when $\Delta S < 0 \Rightarrow$ Reaction is non-spontaneous.
when $\Delta S > 0$, reacⁿ is spontaneous.

Entropy in physical & chemical changes

(i) Physical change & phase transition:

The change of one state (S, L, G) to another is called phase transition. It occurs at definite temperatures (MP. BP). Phase transitions are accompanied by absorption or evolution of heat. In general $\Delta S = q/T$ where q is heat absorbed or evolved.

(a) Entropy of fusion: when a solid melts, the change in entropy is

$$\Delta S_{fusion} = S_{liq.} + S_{solid} = \frac{\Delta H_{fusion}}{T_{fusion}}$$

Where ΔH_{fusion} = The enthalpy of fusion

T_{fusion} = Absolute temp. at which solid melts

S_{liq} & S_{solid} = Entropy of liq. & solid respectively.

ΔS_{fusion} is always positive since $S_{liq.} > S_{solid}$.

But the ~~ve~~ for the reverse process ΔS is negative (from liq. to solid).

(b) Entropy of vapourisation: when liquid is changed to vapour at its boiling point.

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

ΔS_v is positive as $S_g > S_L$ but for the reverse process ΔS is negative.

(c) Entropy of Sublimation: when solid changes to its vapour state.

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T} \qquad \Delta S_{sub} \text{ is positive.}$$

Problems ① Q when one mole of solid with mol. wt. 46 changed into liquid, an entropy change of 26.4 JK^{-1} takes place, calculate the melting point of the solid if its enthalpy of fusion is 0.1 kJg^{-1}.

Ans $\Delta S = 26.4\ JK^{-1} mol^{-1}$, $\Delta H_f = 0.1\ kJg^{-1} = 0.1 \times 1000 \times 46\ J\ mol^{-1}$

$$\Delta S_f = \frac{\Delta H_f}{T} \Rightarrow T = \frac{\Delta H_f}{\Delta S_f}$$

② Q: Calculate the entropy change for the following reaction:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \text{ at } 298K$$

Given: $S^\circ_{H_2} = 131\ JK^{-1} mol^{-1}$, $S^\circ_{Cl_2} = 233\ JK^{-1} mol^{-1}$ $S^\circ_{HCl} = 187\ JK^{-1} mol^{-1}$

Ans: $\Delta S^\circ = S^\circ_P - S^\circ_R = (2 \times 187) - [131 + 233]$

③ Q: What is the entropy change for the conversion of one mole of ice to water at 273K and one atm. pressure.

Ans $\Delta S = \frac{\Delta H_f}{T} = 6025\ J\ mol^{-1} / 273\ K$.

Chemical change: (Entropy change for an ideal gas)

Let us consider reversible expansion of an ideal gas in a container fitted with a frictionless, weightless, movable piston at constant P and the volume changes from V_1 to V_2. Since the process is reversible 'p' of the gas is approximately equal to external pressure against which the gas is expanding.

Hence work done $= p \cdot dv$

If the work done is due to expansion of the gas ($V_2 > V_1$)

Work $dw = -p\,dv$.

from 1st law of thermodynamics $dU = dq + dw$

$$\Rightarrow du = dq - p\,dv.$$

$$\Rightarrow dq = du + p\,dv.$$

Dividing the above equation by T, we get

$$\frac{dq}{T} = \frac{du}{T} + \frac{p\,dv}{T} \Rightarrow ds = \frac{du}{T} + p\frac{dv}{T} \quad \cdots eq\,(i)$$

But $U = f(T, V)$

Hence $du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv$

Putting the value of dU in eq^n (i), we get

$$ds = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv\right] + p\frac{dv}{T}.$$

According to Joule's law $\left(\frac{\partial U}{\partial V}\right)_T = 0$. $\left(\begin{array}{l} U = f(T) \\ \text{at const } T,\ U = \text{const} \\ \text{so } \frac{\partial U}{\partial V} = 0 \end{array}\right)$

Hence $ds = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_V dT\right] + p\frac{dv}{T}$

or. $ds = \frac{C_V}{T}\cdot dT + p\frac{dv}{T}$ $\left[\because \left(\frac{\partial U}{\partial T}\right)_V = C_V\right]$

Or. $ds = C_V\frac{dT}{T} + \frac{R}{V}dv$ $\left(\because PV = RT \text{ for 1 mole} \Rightarrow \frac{P}{T} = R/V\right)$.

or. $$\int_{S_1}^{S_2} ds = C_V\int_{T_1}^{T_2}\frac{dT}{T} + R\int_{V_1}^{V_2}\frac{dv}{V}$$

$\Rightarrow$ $\boxed{\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}}$ for 1mole ---(ii)

& $\boxed{\Delta S = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}}$ for n mole ✱ (see page 7)

for an ideal gas $P_1V_1 = P_2V_2 \Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$

Hence $\boxed{\Delta S = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}}$

or. $\boxed{\Delta S = nC_V\ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}}$ ......(iii)

(i) At constant temperature, (Isothermal Process) $(\Delta S)_T = nR \ln \frac{V_2}{V_1}$

$= nR \ln \frac{P_1}{P_2}$

$= 2.303\, nR \log \frac{V_2}{V_1}$ .... (iv)

(ii) At constant pressure, (Isobaric Process) $(\Delta S)_p = nC_p \ln T_2/T_1 = 2.303\, nC_p \log T_2/T_1$ ...(v)

(iii) At constant volume, (Isochoric Process) $(\Delta S)_v = nC_v \ln \frac{T_2}{T_1}$

$= 2.303\, nC_v \log \frac{T_2}{T_1}$ ..... (vi)

Entropy of a mixture of ideal gas:

For one mole of ideal gas the change in entropy is:

$$ds = C_v \frac{dT}{T} + R\frac{dv}{V}$$

Integrating the above equation, we get

$S = C_v \ln T + R \ln V + S_0$ where S_0 is integration const.

For 1 mole of ideal gas $PV = RT \Rightarrow V = \frac{RT}{P}$.

Hence $S = C_v \ln T + R \ln \frac{RT}{P} + S_0$ $(\because V = RT/P)$

$\Rightarrow S = C_v \ln T + R \ln R + R \ln T - R \ln P + S_0$.

$\Rightarrow S = (C_v + R)\ln T + (R \ln R + S_0) - R \ln p$.

$\Rightarrow \boxed{S = C_p \ln T - R \ln P + S_0'}$ $(\because C_p - C_v = R$ or $C_p = C_v + R$, $R \ln R + S_0 = S_0')$.

Let us consider a gaseous mixture containing $n_1, n_2, \cdots$ moles of various gases with partial pressures $P_1, P_2 \cdots$ respectively.

Hence $S = n_1(C_p \ln T - R \ln P_1 + S_0') + n_2(C_p \ln T - R \ln P_2 + S_0') + \cdots$

$= \Sigma n (C_p \ln T - R \ln P + S_0')$

But partial pressure p = mole fraction $(x) \times$ total pressure P.

Hence $S = \Sigma n (C_p \ln T - R \ln Px + S_0')$.

$\Rightarrow \boxed{S = \Sigma n (C_p \ln T - R \ln P - R \ln x + S_0')}$

Entropy change during mixing of ideal gases:

Let us consider the mixing of two or more gases in an irreversible process accompanied by increase in entropy.

Let $n_1, n_2, \cdots$ are the no. of moles of ideal gas 1 & 2
$V_1, V_2, \cdots$ are the volumes of individual gas.

At constant temp., $\Delta S_{mixing} = S_{final} - S_{initial}$.

$= [n_1 R \ln (V_1 + V_2 + \cdots) - n_1 R \ln V_1] + n_2 R \ln (V_1 + V_2 + \cdots) - n_2 R \ln V_2] + \cdots$

$$\Delta S_{mixing} = -n_1 R \ln \frac{V_1}{(V_1+V_2+\cdots)} - n_2 R \ln \frac{V_2}{(V_1+V_2+\cdots)}$$

But $\frac{V_1}{(V_1+V_2+\cdots)} = \frac{n_1}{n_i} = x_1$ and $\frac{V_2}{(V_1+V_2+\cdots)} = \frac{n_2}{n_i} = x_2$

(since $V \propto n$ as $PV = nRT$
$\Rightarrow V = nRT/p$
At const. P&T
$V = n \times \text{const.}$
$\Rightarrow V \propto n$)

where n_i = total number of moles in the gas

x = mole fraction of individual gas.

Hence $\Delta S_{mixing} = -Rn_1 \ln x_1 - n_2 R \ln x_2 - \cdots$

$$= -R(n_1 \ln x_1 + n_2 \ln x_2 + \cdots)$$

$$\Rightarrow \boxed{\begin{aligned}\Delta S_{mixing} &= -R\sum n_i \ln x_i \\ &= -R\sum x_i \ln x_i\end{aligned}} \quad (\because n_i \propto x_i)$$

Problem:

Calculate the change in entropy suffered by two moles of an ideal gas when it expands from a volume of 100 litres at 323 K to a volume of 150 lits at 423 K. ($C_v = 32.97\ JK^{-1} mole^{-1}$, and $R = 8.314\ JK^{-1} mole^{-1}$).

Ans. We know that $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

Given $T_1 = 323K$, $T_2 = 423K$, $V_1 = 100$ lit, $V_2 = 150$ lit

$n = 2$, $C_v = 32.97\ JK^{-1} mole^{-1}$, $R = 8.314\ JK^{-1} mole^{-1}$

Putting the given data in the above equation:

$$\Delta S = \left(2 \times 2.303 \times 32.97 \log \frac{423}{323}\right) + \left(2 \times 2.303 \times 8.314 \log \frac{150}{100}\right)$$

$$= 24.52\ JK^{-1} \text{ (Ans)}$$

Problem: One mole of He expands reversibly from a temp. of 298K and pressure of 1 atm to a ~~temp. of 298K and a press-~~ ~~ure of 1atm to a~~ temp. of 273 K and pressure of 0.6579 atm. Assuming $C_v = \frac{3}{2}R$, calculate the entropy change of the process.

Ans We know that:

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

$$= 2.303\, nC_p \log \frac{T_2}{T_1} + 2.303\, nR \log \frac{P_1}{P_2}$$

Here $C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R = 2.5 \times 8.314\ JK^{-1} mol^{-1}$

$n = 1$, $T_1 = 298K$, $T_2 = 273K$, $P_1 = 1$ atm, $P_2 = 0.6579$ atm

Hence $\Delta S = \left(1 \times 2.5 \times 8.314 \times 2.303 \log \frac{273}{298}\right) + \left(1 \times 8.314 \times 2.303 \log \frac{1}{0.6579}\right) = 1.66\ JK^{-1}$.

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

* From combined gas equation $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \frac{V_2}{V_1} = \frac{P_1T_2}{T_1P_2}$$

Putting the value of V_2/V_1 in the above equation,

$$\Delta S = nC_v \ln T_2/T_1 + nR \ln V_2/V_1$$

$$= nC_v \ln T_2/T_1 + nR \ln \frac{P_1T_2}{T_1P_2} \qquad (\because C_p - C_v = R)$$

$$= n(C_p - R) \ln T_2/T_1 + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$$

$$= nC_p \ln \frac{T_2}{T_1} - \cancel{nR \ln \frac{T_2}{T_1}} + nR \ln \frac{P_1}{P_2} + \cancel{nR \ln \frac{T_2}{T_1}}$$

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

Free Energy (G).

It is a state function. Mathematically,

$$\boxed{G = H - TS} \quad \text{.... (i)}$$

It is a measure of energy available for doing useful work.

Change in free energy between two states of a system:

$$\Delta G = G_2 - G_1 = (H_2 - H_1) - (S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{.... (ii)}$$

But $\Delta H = \Delta U + P\Delta V$ (at const. P). Hence $\Delta G = \Delta U + P\Delta V - T\Delta S$ --(iii) at const P & T.

To know the maximum work obtainable from a system during the given change, Helmholtz introduced a state function 'A' called the work function or Helmholtz function & mathematically $A = U - TS$ ---(iv). We can write for a change from state 1 to 2 at const. temp.

$$\Delta A = \Delta U - T\Delta S \quad \text{.... (v)}$$

$$\Rightarrow \Delta A = \Delta U - q \quad \left(\because \Delta S = \frac{q}{T}\right) \quad \text{... (vi)}$$

According to 1st law of thermodynamics $dU = q + w$

when work is done by the system w is negative.

Hence $dU = q - w \Rightarrow -w = dU - q$ ---- (vii)

Comparing equation (vi) and (vii) we get $\Delta A = -w$

or $\boxed{-\Delta A = w}$ ... (viii)

Hence we may conclude that decrease in function A give the maximum work obtainable from the system during the given change.

Comparing equation (iii) and (v) we get

$$\Delta G = \Delta A + pdv \quad (\text{at const. } p \,\&\, T)$$

$$\Rightarrow \quad \Delta G = -w + pdv \quad (\because \Delta A = -w)$$

$$\Rightarrow \quad -\Delta G = w - pdv \quad \ldots\ldots\ldots (ix)$$

Hence decrease in free energy = Max. work obtainable − work done by expansion against const. external p

So $\boxed{\text{Net or Useful work} = -\Delta G = w - p\cdot dv}$ at const T & p.

FREE ENERGY

We know that $\Delta S > 0$ (positive) for a spontaneous or feasible process & $\Delta S = 0$ when a system is in equilibrium. The feasibility of a process can be decided if we know the entropy of the system as well as surrounding which is not always convenient. The entropy change is more conveniently determined with two more state functions such as work function (A) and free energy function (G).

(a) Helmhotz free energy of work function (A):

Mathematically $A = U - TS$ where U = internal energy
T = absolute temperature
S = entropy of the system.

Hence change in work function $\Delta A = \Delta U - T\Delta S$ ....(i)

But when the change is brought reversibly, $\Delta S = \frac{q_{rev}}{T}$ ...(ii)

According to ~~2nd~~ 1st law of thermodynamics for an isothermal reversible process $\Delta U = q_{rev} - W_{max}$ .....(iii)

Putting the value of ΔS & ΔU in eq^n (i), we get

$$\Delta A = (\cancel{q_{rev}} - W_{max}) - \cancel{T}\frac{q_{rev}}{\cancel{T}} = -W_{max}$$

$\Rightarrow \boxed{-\Delta A = W_{max}}$ $\Rightarrow$ At constant temp., for a process decrease in work function $(-\Delta A)$ gives maximum work done by the system. Hence it is call work function.

(b) Free energy function (G):

Mathematically $G = H - TS$, where H = enthalpy of System.
T = Abs. temp of system
S = entropy of system

Since H & S are state function, G is also a state function. Hence change in free energy $\Delta G = \Delta H - T\Delta S$ ..... (i)

But $\Delta S = \frac{q_{rev}}{T}$ & $\Delta H = \Delta U + P\Delta V$ (at const. P).

Putting the values of ΔS & ΔH in eq^n (i) we get,

$$\Delta G = \Delta U + P\Delta V - \cancel{T}\frac{q_{rev}}{\cancel{T}} = \Delta U + P\Delta V - q_{rev}$$

$$\Rightarrow \Delta G = (\Delta U - q_{rev}) + P\Delta V = -W_{max} + P\Delta V \quad (\because \Delta U - q_{rev} = -W_{max})$$

$\Rightarrow \boxed{-\Delta G = W_{max} - P\Delta V}$ $P\Delta V \rightarrow$ Pressure-Volume work due to the expansion against the external P.

Hence we may conclude that decrease in free energy accompanying a process taking place at constan T & P is equal to maximum work obtainable from the system other than the work of expansion.

Variation of free energy with Temp. & pressure:

We know that $G = H - TS$ ...(i) & $H = U + PV$ ...(ii)

Hence $G = U + PV - TS$ .....(iii)

Differentiating the above equation we get,

$$dG = dU + PdV + VdP - TdS - SdT \quad \text{....(iv)}$$

Again $dS = \frac{q_{rev}}{T} = \frac{dU + PdV}{T} \Rightarrow TdS = dU + PdV$.

Putting the value of TdS in equation (iv) we get

$$dG = \cancel{dU} + P\cancel{dV} + VdP - \cancel{dU} - P\cancel{dV} - SdT = VdP - SdT$$

$$\boxed{dG = VdP - SdT} \quad \text{...(v)}$$

The above equation gives that the change in free energy with the change in Temp. & Pressure in a reversible process.

Case I At const. temp. $dT = 0$

Hence $dG = VdP$ or. $\boxed{\left(\frac{dG}{dP}\right)_T = V}$ ....(vi)

or. $$\int_{G_1}^{G_2} dG = V\int_{P_1}^{P_2} dP$$

For n mole of ideal gas, $PV = nRT \Rightarrow V = \frac{nRT}{P}$

Putting the value of V in the above equation we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P}\, dP \Rightarrow \Delta G = nRT\int_{P_1}^{P_2} \frac{dP}{P}$$

or, $$\boxed{(\Delta G)_T = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}} \quad \text{---(vii)}$$

Case II: At const. P, $dP = 0$.

Hence $dG = -SdT \Rightarrow \boxed{\left(\frac{dG}{dT}\right)_P = -S}$ ....(viii)

Problem: Calculate the free energy which occurs when 2 moles of an ideal gas expands reversibly and isothermally at 300K from initial state of 4 lits to 40 lits.

Ans. Given $n = 2$, $T = 300K$, $V_1 = 4$ lit., $V_2 = 40$ lits., $R = 1.987$ cal K^{-1} mol^{-1}

$$(\Delta G)_T = nRT \ln \frac{V_1}{V_2} = -2745.6 \text{ cal}.$$

Variation of work function with temp. & volume:

We know that $A = U - TS$

differentiating the above equation we get $dA = dU - Tds - SdT$ ....(i)

Again $ds = \frac{q_{rev}}{T} = \frac{dU + Pdv}{T} \Rightarrow Tds = dU + Pdv$ ....(ii)

From equation (i) & (ii) we get $dA = d\cancel{U} - d\cancel{U} - Pdv - sdT$

or. $dA = -Pdv - SdT$ .....(iii)

Case I: At const. temp. $dT = 0$

Hence $dA = -pdv \Rightarrow \left(\frac{dA}{dv}\right)_T = -P$ ....(iv)

$$\int_{A_1}^{A_2} dA = -P\int_{V_1}^{V_2} dv = -\frac{nRT}{V}\,dv \quad \left(\because PV = nRT \Rightarrow V = \frac{nRT}{P}\right).$$

$$\text{or. } \Delta A = -nRT\int_{V_1}^{V_2}\frac{dv}{V} \Rightarrow \boxed{\Delta A = -nRT\ln\frac{V_2}{V_1} = -W_{max}} \quad ....(v)$$

Case II: At const. volume $dv = 0$

Hence eqn (iii) becomes $dA = -SdT$

$$\Rightarrow \boxed{\left(\frac{dA}{dT}\right)_V = -S} \quad .....(vi)$$

Problem: Calculate ΔA for the vapourisation of 0.1 mole of water at 1 atm. and 100°c. Given molar volume of water(l) at 100°c is 18.8 ml/mole and that of water is 30.6 lit/mole.

Ans. $V_1 = 18.8 \times 0.1 = 1.88\ ml/0.1mole$, $V_2 = \frac{30.6}{10} = 3.06L = 3060ml/0.1mole$

$n = 0.1$ mole $T = 100 + 273 = 373K$.

Hence $\Delta A = nRT\ln\frac{V_2}{V_1} = -2293.7J = 2.294KJ$.

Criteria of Spontaneity of a process:

We know that change in entropy :

$$ds = \frac{\delta q_{rev}}{T} = \frac{dU + Pdv}{T} \quad ....(i)$$

when the small change is brought about irreversibly then $q_{rev} < q_{irr}$

Hence for an irreversible process $Tds > q_{irr}$

Hence
$$\left.\begin{aligned} Tds &= dU + Pdv \text{ (for reversible process)} \\ Tds &> dU + Pdv \text{ (for irreversible process)} \end{aligned}\right\} \quad ....(ii)$$

Combining the above two equations, $Tds \geq dU + Pdv$ ....(iii)

Again $G = H - TS = U + PV - TS$

$dG = dU + Pdv + Vdp - Tds - SdT$ .....(iv)

$$\Rightarrow dU + pdV = dG - Vdp + TdS + SdT$$

Putting equation (iii) in (iv) we get

$$\cancel{TdS} \geq dG - Vdp + \cancel{TdS} + SdT$$

$$\Rightarrow \quad 0 \geq dG - Vdp + SdT$$

or $\quad dG - Vdp + SdT \leq 0$

At constant Temp. & pressure, $Vdp = SdT = 0$

$$(dG)_{T,P} \leq 0$$

Hence the criterion in terms of free energy is most useful criterion to decide the spontaneity of a process because most of the processes take place at const. temp. & process. To conclude :

(i) $(\Delta G)_{T,P} < 0 \Rightarrow$ Reacⁿ is spontaneous, process is irreversible

(ii) $(dG)_{T,P} = 0 \Rightarrow$ process is in equilibrium.

(iii) $(dG)_{T,P} > 0 \Rightarrow$ process is not feasible.

The limitation of Criteria for spontaneity are as follows:

(a) It does not tell about the extent to which the reaction take place

(b) It remains silent about the rate of reaction.

(c) It does not indicate the mechanism by which the reaction proceeds.

GIBB'S HELMHOLTZ EQUATION :

There are two forms of Gibb's Helmholtz equation.

(i) Interms of energy & enthalpy changes:

Let G_1, H_1, S_1 and G_2, H_2, S_2 are the free energy, enthalpy and entropy of the system in the initial & final states.

$$G_1 = H_1 - TS_1 \quad \text{(Initial)} \quad \ldots (i)$$

$$G_2 = H_2 - TS_2 \quad \text{(Final)} \quad \ldots (ii)$$

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or. $\quad \Delta G = \Delta H - T\Delta S$

Again we know that $\left(\frac{\partial G}{\partial T}\right)_P = -S$

Hence $\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1$ (initial) $\ldots (iii)$ and $\left(\frac{\partial G_2}{\partial T}\right)_P = -S_2$ (final) $\ldots (iv)$

So $\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -S_2 - (-S_1)$

$$\Rightarrow \left[\frac{\partial(G_2 - G_1)}{\partial T}\right]_P = S_1 - S_2 \Rightarrow \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -(S_2 - S_1) = -\Delta S \quad \ldots (v)$$

But $\quad \Delta G = \Delta H - T\Delta S \quad \ldots (vi)$

Putting eqn (v) in (vi) we get.

$$\boxed{\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p .}$$

It is the most common form of Gibb's Helmholtz equation.

Similarly Let A_1, U_1, S_1 and A_2, U_2, S_2 are the work function, internal energy & entropy of the system in the initial & final state respectively. We know that $\left(\frac{\partial A}{\partial T}\right)_V = -S$ ....(vii)

Since $\Delta A = A_2 - A_1$ and $\Delta S = S_2 - S_1$, $\Delta U = U_2 - U_1$

$$\left[\frac{\partial(\Delta A)}{\partial T}\right] = -\Delta S \qquad \text{But } A = U - TS \Rightarrow \Delta A = \Delta U - T\Delta S \quad ....(viii)$$

Combining eqn (vii) & (viii) we get,

$$\boxed{\Delta A = \Delta U + T\left\{\frac{\partial(\Delta A)}{\partial T}\right\}_V .} \quad ....(ix)$$

The above relation is Gibb's Helmholtz equation in terms of internal energy and work function.

Significance of Gibb's Helmholtz equation:

This equation helps towards a better understanding of the driving force behind chemical reaction. We know that $\Delta G = \Delta H - T\Delta S$

Case -I: For an exothermic reaction, ΔH is -ve. Hence ΔG = -ve. Hence exothermic reactions are always spontaneous even at ordinary temp. and pressure.

Case II: When ΔS = +ve, ΔG = -ve. This implies all the reactions proceeding with increase in entropy are spontaneous.

Hence to conclude for a spontaneous reaction,

$$\boxed{\Delta S = +ve, \Delta H = -ve \ \& \ \Delta G = -ve}$$

Application of Gibb's Helmholtz equation:

One of the important application is the study of electrochemical or galvanic cell. Let us consider $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

According to the G.H. equation, the electrical energy produced was equal to the decrease in free energy accompanying the cell reaction.

Let the no. of electrons taking part in the reaction is 'n'.

Then the quantity of electricity produced = nF (1F = 96500 C)

Let the emf of the cell = E

So electrical energy produced by the cell = nFE

Hence decrease in free energy $-\Delta G = nFE \Rightarrow \Delta G = -nFE$

Putting the ΔG value in G.H. equation we get

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p \Rightarrow \boxed{nFE = -\Delta H + nFT\left(\frac{\partial E}{\partial T}\right)_p}$$

Hence the electrical energy produced (nFE) is equal to heat evolved only when the temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p$ is z

Problem:

The free energy change (ΔG) accompanying a given process is -80.77 KJ/mole at 25°C and -78.68 KJ at 36°C. Calculate the change in enthalpy (ΔH) for the process at 30.5°C.

Ans:

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

ΔG at 30.5°C may be the average value at 25°C & 36°C.

Given ΔG at $298 = -80.77$ KJ and at $309 = -78.68$ KJ.

$$\text{So } \left\{\frac{\partial(\Delta G)}{\partial T}\right\}_p = \frac{-78.68 - [-(80.77)]}{309 - 298} = 0.19 \text{ KJ}.$$

$$\Delta G \text{ at } 30.5°C = \frac{-78.68 - 80.77}{2} = -79.725 \text{ KJ}.$$

$$\text{Hence } -79.725 = \Delta H + (303.5 \times 0.19) \Rightarrow \Delta H = -137.39 \text{ KJ}.$$

Criteria of Thermodynamic Equilibrium:

(a) In terms of extensive thermodynamic state function:

We know that $ds = \frac{dq}{T}$ or $dq = Tds$ (2nd law)

According the 1st law $dq = dU + dW$ $(\because dU = dq \mp P\Delta V)$.

or. $dq = dU + pdv$

Equilibrium Constants, K_c, K_p and K_x.

(i) K_c : If the active mass of each reactant and product in a reaction is taken to be molar concentration (no. of moles / Lit), the equilibrium constant is represented as K_c. Let us consider the following general reaction:

$$aA + bB + cC + \cdots\cdots \rightleftharpoons lL + mM + nN + \cdots\cdots$$

For the above reaction,

$$K_c = \frac{C_L^l \times C_M^m \times C_N^n \times \cdots\cdots}{C_A^a \times C_B^b \times C_C^c \times \cdots\cdots} \quad \cdots\cdots (i)$$

where C_L, C_M, C_N ···· and C_A, C_B, C_C ····· are the molar concentration of L, M, N, ···· and A, B, C, ····· respectively. The Unit of K_c is equal to $(\text{mole lit}^{-1})^{\Delta n}$ where Δn is the change in no. of moles and

$$\Delta n = \text{no. of moles of products} - \text{no. of moles of reactants.}$$

(ii) Chemical equilibria in ideal gas (K_p): If all the reactants and products at equilibrium are ideal or nearly ideal, then the active mass may be taken as partial pressure. for the above reaction in gaseous phase,

$$K_p = \frac{p_L^l \times p_M^m \times p_N^n \times \cdots\cdots}{p_A^a \times p_B^b \times p_C^c \times \cdots\cdots} \quad \cdots\cdots (ii)$$

where p_L, p_M, p_N ···· and p_A, p_B, p_C ····· are the partial pressures of L, M, N ···· and A, B, C ····· respectively. The unit of $K_p = (\text{atm})^{\Delta n}$.

When Δn is zero (0), K_p & K_c are dimensionless.

(iii) Equilibrium Constants in terms of mole fraction (K_x) : Here the equilibrium constant is expressed in terms of mole fraction (x). For the above equation;

$$K_x = \frac{x_L^l \times x_M^m \times x_N^n \cdots\cdots}{x_A^a \times x_B^b \times x_C^c \cdots\cdots} \quad \cdots\cdots (iii)$$

where x_L, x_M, x_N ···· and x_A, x_B, x_C ···· are the mole fractions of L, M, N, ···· and A, B, C ···· respectively. K_x is always dimensionless that is it has no units.

(iv) Relationship between K_p & K_c :

$$K_p = \frac{p_L^l \times p_M^m \times p_N^n \times \cdots\cdots}{p_A^a \times p_B^b \times p_C^c \times \cdots\cdots}$$

We know that $PV = nRT \Rightarrow P = \frac{n}{V} RT = CRT$ (where C is the conc.)

putting the value of P in the above equation,

$$K_p = \frac{(C_L RT)^l (C_M RT)^m (C_N RT)^n \cdots\cdots}{(C_A RT)^a (C_B RT)^b (C_C RT)^c \cdots\cdots}$$

$$\Rightarrow K_p = \frac{(C_L^l \times C_M^m \times C_N^n \times \cdots\cdots)}{(C_A^a \times C_B^b \times C_C^c \times \cdots\cdots)} \times (RT)^{(l+m+n+\cdots)-(a+b+\cdots)}$$

$$\Rightarrow \boxed{K_p = K_c \times (RT)^{\Delta n}}$$

EXP: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$\Delta n = 2-2 = 0$. so $K_p = K_c \cdot (RT)^0$.

or. $K_p = K_c$.

(v) Relationship between K_p & K_x :

$$K_p = \frac{p_L^l \times p_M^m \times \cdots\cdots}{p_A^a \times p_B^b \times \cdots\cdots}$$

We know that $PV = nRT$. If p_i is the partial pressure, $p_iV = n_iRT$

Hence $\frac{p_iV}{PV} = \frac{n_iRT}{nRT} \Rightarrow \frac{p_i}{P} = \frac{n_i}{n} \Rightarrow p_i = Px_i \; (\because x_i = \frac{n_i}{n})$

where x_i is the mole fraction of gas 'i'.

Now we can write $p_L = x_LP$, $p_M = x_MP$ ...

Hence
$$K_p = \frac{(x_LP)^l\,(x_MP)^m \cdots}{(x_AP)^a\,(x_BP)^b \cdots\cdots} = \left[\frac{x_L^l \times x_M^m \times \cdots\cdots}{x_A^a \times x_B^b \times \cdots\cdots}\right] \times P^{(l+m+\cdots)}_{(a+b+\cdots)}$$

$$\Rightarrow \boxed{K_p = K_x\, P^{\Delta n}}$$

VANTHOFF ISOTHERM:

Let us consider a general reaction,

$$aA + bB \longrightarrow cC + dD \quad \cdots\cdots (i)$$

We know that $dG = Vdp - SdT$

At const. temperature $(dG)_T = Vdp = \frac{RT}{P}dp \quad (\because PV = RT \Rightarrow V = \frac{RT}{P})$

$$\Rightarrow \int_{G_0}^{G} dG = RT\int \frac{dp}{P} \Rightarrow G - G_0 = RT \ln p.$$

$$\Rightarrow \boxed{G = G_0 + RT \ln P} \quad \cdots\cdots (ii)$$

where G_0 is the standard free energy and $G = G_0$ at 1 atm.

Let P_A, P_B, P_C, P_D and G_A, G_B, G_C, G_D are the partial pressures and free energies of A, B, C, D respectively in equation (i). The free energy change for equation (i) is :

$$\Delta G = G_{product} - G_{reactant} = (cG_C + dG_D) - (aG_A + bG_B) \quad \cdots (iii)$$

$$\Rightarrow \Delta G = [cG_C^0 + cRT\ln P_C + dG_D^0 + dRT\ln P_D] - [aG_A^0 + aRT\ln P_A + bG_B^0 + bRT\ln P_B]$$

$$\Rightarrow \Delta G = [(cG_C^0 + dG_B^0) - (aG_A^0 + bG_B^0)] + [(cRT\ln P_C + dRT\ln P_D) - (aRT\ln P_A + bRT\ln P_B)]$$

$$\Rightarrow \Delta G = \Delta G^\circ + RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \quad \cdots\cdots(iv)$$

When the reaction is in equilibrium $\Delta G = 0$.

Hence we can write $\Delta G^\circ = -RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

$$\Rightarrow \boxed{\Delta G^\circ = -RT\ln K_{eq}} \quad \cdots\cdots(v)$$

Putting the value of ΔG° in equation (iv) we get.

$$\Delta G = -RT\ln K_{eq}. + RT\ln\frac{(P_C)^c(P_D)^d}{[P_A]^a[P_B]^b}.$$

or.

$$\boxed{-\Delta G = RT\ln K_{eq}. - RT\ln\frac{[P_C]^c[P_D]^d}{[P_A]^a[P_B]^b}.}$$

The above equation is called Van't Hoff isotherm. It gives quantitative relation for free energy change accompanying a chemical reacn.

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

$$\Rightarrow \ln K_{eq} = \frac{-\Delta G^\circ}{RT} = \frac{-(\Delta H^\circ - T\Delta S^\circ)}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\cancel{T}\Delta S^\circ}{R\cancel{T}}$$

$$\Rightarrow \ln K_{eq} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Now we can write $\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$

similarily $\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}.$

Hence $\ln K_2 - \ln K_1 = \frac{-\Delta H^\circ}{RT_2} + \cancel{\frac{\Delta S^\circ}{R}} + \frac{\Delta H^\circ}{RT_1} - \cancel{\frac{\Delta S^\circ}{R}}$

$$\Rightarrow \ln\frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\Delta H^\circ}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \boxed{\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

The above expression is known as Van't Hoff isochore and is used to calculate equilibrium constant at T_2 if T_1 is known.

Equilibrium Constants & their quantitative dependence on T & P, Concentration: Dependence on temperature (Van't Hoff equation):

The equation for reaction isotherm when reactants and products are in gaseous and standard states is

$$\Delta G^\circ = -RT\ln K_p. \quad \cdots\cdots(i)$$

Differentiating w.r.t. T at const. P, $\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P = -R\ln K_p - RT\frac{d\ln K_p}{dT}$ $\cdots\cdots(ii)$

Multiplying both the sides by T, we get

$$T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P = -RT\ln K_p - RT^2\frac{d\ln K_p}{dT} \quad \dots (iii)$$

$$\Rightarrow \quad T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P = \Delta G^\circ - RT^2\frac{d\ln K_p}{dT} \quad \dots\dots (iv)$$

The Gibb's Helmholtz equation is $\Delta G^\circ = \Delta H^\circ + T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P$ ...(v)

Comparing equation (iv) & (v) we get,

$$\Delta H^\circ = RT^2\frac{d(\ln K_p)}{dT}$$

$$\Rightarrow \boxed{\frac{d\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}} \quad \dots\dots\dots (vi)$$

The above equation is known as Vant Hoff's equation, where ΔH° is the enthalpy change for the reaction at constant pressure when both the reactants and products are in standard states. Since ΔH for a reaction does not change appreciably with partial pressure, ΔH may be taken as ΔH°. Hence Vant Hoff's equation can be written as

$$\boxed{\frac{d\ln K_p}{dT} = \frac{\Delta H}{RT^2}} \quad \dots\dots\dots (vii)$$

Prediction of the effect of temperature on equilibrium Constant:

When the reaction is endothermic, $\Delta H^\circ = +ve$. Hence $T_2 > T_1$. Hence $\Delta H^\circ/RT^2$ is positive. Hence $K_{p_2} > K_{p_1}$. Hence value of constant increases with increase in temperature for endothermic reaction. Thus proofs that endothermic reactions are favoured by increase in temp. Similarly exothermic reactions are favoured by decrease in temperature. These results are in agreement with Le-chatelier's principle.

But equilibrium constant of a reaction is indepedent of temperature if $\Delta H = 0$.

Dependence on Pressure:

For an ideal gas at a given temperature, the values of K_p and K_c are indepedent of pressure. But the value of K_x may change. We know that $K_x = K_p(P)^{-\Delta n}$ ....(i)

Where Δn is the change in number of moles of the reactants & products. Taking ln of both the sides we get

$$\ln K_x = \ln K_p - \Delta n \ln P$$

Differentiating the above equation partially w.r.t. P,

$$\left[\frac{\partial(\ln K_x)}{\partial P}\right] = -\frac{\Delta n}{P} \quad \dots\dots (ii)$$

we know that $PV = nRT$

$$\Rightarrow P\Delta V = \Delta n RT \Rightarrow \Delta n = \frac{P\Delta V}{RT}.$$

Putting the value of Δn in eq^n(ii) we get

$$\left[\frac{\partial(\ln K_x)}{\partial P}\right] = -\frac{\cancel{P}\Delta V}{\cancel{P}RT} = \frac{-\Delta V}{RT}$$

where ΔV is the change in partial molar volume at temp. T and pressure P. The above equation shows that the value of K_x depends on Δn or ΔV.

(i) If Δn or ΔV is negative, K_x increases with increase in P.

(ii) If Δn or ΔV is positive, K_x decreases with increase in P.

(iii) If Δn or ΔV is zero, K_x is indepedent of P.

Problems:

①Q Calculate ΔG° for the following reaction at 298K

$$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$$

Given ΔG° for C_6H_6, O_2, CO_2, H_2O are +125 KJ, +205 KJ, −395 KJ, −237 KJ mol^{-1}. Ans. $\Delta G^\circ = \Sigma \Delta G^\circ_{products} - \Sigma \Delta G^\circ_{Reactants}$..

② ΔG for a reaction at 300K is −16 Kcal, ΔH for the reaction is −10Kcal. What is the entropy of the reaction? What will be ΔG at 330K?

Ans. (i) $\Delta G = \Delta H - T\Delta S. \Rightarrow \Delta S = \frac{\Delta G - \Delta H}{-T} = 0.02\,KCal\,K^{-1} = 20\,cal K^{-1}$

(ii) ΔG at 330K $= \Delta H - T\Delta S = -10\,Kcal - 330K \times 0.02\,Kcal\,K^{-1} = 16.6\,Kcal.$

Clausius - Clapeyron Equation :- 2021 - 2 mark
2022 - 2 mark

→ Clausius - clapeyron eqn basi-cally show the relationship betn the change in pressure with change in temp for a one component two phase system.

→ Let us consider two phases A $ B are equilibrium with each other.

Phase A $\rightleftharpoons$ Phase B (at temp T $ pressure p)

→ The condition of eqn for pure substance present in two phases A $ B at temp T and pressure P.

$$\begin{tikzcd} A \arrow[r, shift left] \arrow[d] & B \arrow[l, shift left] \\ \mu_A = \mu_B & \end{tikzcd}$$

$G_A = G_B$ (since they are in equilibrium)

$\Delta G = 0$

→ For a small change in temp, the temp changes from T to T+dT $ Pressure changes from P to P+dP.

→ The equilibrium also changes where the new gibbs free energy for the 2 phases remain equal to eachother.

i.e; $G_A + dG_A = G_B + dG_B$

As G_A $ G_B are equal

so, $G_A + dG_A = G_B + dG_B$

$\boxed{dG = VdP - SdT}$

$\Rightarrow dG_A = dG_B$ ——— (1)

→ As we know From thermodynamics for any pure substance the variation in free energy is given by

$$dG = VdP - SdT$$

$$dG_A = V_A dP - S_A dT \quad \text{———} \quad ②$$

$$dG_B = V_B dP - S_B dP \quad \text{———} \quad ③$$

Putting eqn (2) & (3) in eqn (1)

$$dG_A = dG_B$$

$$\Rightarrow V_A dP - S_A dT = V_B dP - S_B dT$$

$$\Rightarrow V_A dP - V_B dP = -S_B dT + S_A dT$$

$$\Rightarrow dP(V_A - V_B) = S_A dT - S_B dT$$

$$\Rightarrow dP(V_A - V_B) = dT(S_A - S_B)$$

$$\Rightarrow \cancel{-}dP(V_B - V_A) = \cancel{-}dT(S_B - S_A)$$

$$\Rightarrow \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{\Delta V}$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

$$\Rightarrow \frac{dP}{dT} = \frac{q}{T\Delta V}$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

2022 2-mark

⇒ When clapeyron eqn is applied to liquid-vapour or solid-vapour equilibria with the ~~adjum-~~ ~~ption~~ assumption that the volume of liquid & solid is negligible as compare to the vapour phase is called clausius-clapeyron equation.

Application :-

(1) Solid – Liquid Equilibria :- Solid $(H_2O) \rightleftharpoons$ Liquid (H_2O)

For this equilibrium $q = \Delta H_f$

ΔH_f = Enthalpy change of fusion

V_l = Volume of liquid phase

V_s = Volume of solid phase

So, Clapeyron eqn will be

$$\frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)}$$

The eqn is called Clapeyron eqn for solid-liquid equilibria.

(2) Solid – Vapour Equilibria :-

$$\text{Solid } (H_2O) \rightleftharpoons \text{Vapour } (H_2O)$$

$q = \Delta H_s$ = enthalpy change of sublimation

V_2 = Volume of vapour phase = V_g

V_1 = Volume of solid Phase = V_s

So, clapeyron eqn will be

$$\frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)}$$

For this equilibrium, $V_g >> V_s$

So, we can write $\frac{dP}{dT} = \frac{\Delta H_s}{TV_g}$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta H_s}{T} \times \frac{P}{RT}$$

$$\boxed{\begin{matrix} PV = RT \\ V = \frac{RT}{P} \end{matrix}}$$

$$\Rightarrow \frac{dP}{P} = \frac{\Delta H_s}{RT^2} dT$$

Integrating both sides,

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_s}{R}\int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\Rightarrow [\ln P]_{P_1}^{P_2} = \frac{-\Delta H_s}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\Rightarrow \ln P_2 - \ln P_1 = \frac{-\Delta H_s}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Rightarrow \ln \frac{P_2}{P_1} = \frac{-\Delta H_s}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\Rightarrow \ln \frac{P_2}{P_1} = \frac{\Delta H_s}{R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

The eqn is called clausius-clapeyron eqn for solid vapour equilibria.

(3) Liquid-Vapour Equilibria:-

For this equilibria

$$\text{liquid } (H_2O) \rightleftharpoons \text{Vapour } (H_2O)$$

$q = \Delta H_v$ = Enthalpy change of vaporisation

V_2 = Volume of vapour phase (V_g)

V_1 = Volume of liquid Phase (V_l)

So, Clapeyron eqn will be:-

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)}$$

For this equi, $V_g >> V_l$

$$\frac{dP}{dT} = \frac{\Delta H_v}{T \cdot V_g} \text{ (Ignoring } V_l)$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta H_v}{T} \times \frac{P}{RT}$$

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

$$\Rightarrow \int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R} \left[\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = -\frac{\Delta H_v}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Rightarrow \ln \frac{P_2}{P_1} = -\frac{\Delta H}{R} \cdot \frac{T_1 - T_2}{T_1 \cdot T_2}$$

$$\Rightarrow \ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \cdot \frac{T_2 \cdot T_1}{T_1 \cdot T_2}$$

The eq^n is called clausius-clapeyron eq^n for liquid-vapour equilibria.