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for Hons II, Paper III, Gp A, Lec (11)

~~Clausius clapeyron equation : & its application~~

Second law of thermodynamics :— Already we have seen there are three factors i.e ΔH, ΔS & ΔG which are responsible for Spontaneous changes. In General Sign of ΔH = −ve, ΔS = +ve, & ΔG = −ve is responsible for spontaneous changes. 2nd law of thermodynamics can be explained pointwise which is as follow.

I. All the spontaneous changes are thermodynamically irreversible. Means the process is so fast it can not maintain to equilibrium.

II. Spontaneous changes can not be reversed untill any external agency has worked. for example water can fall (from top to bottom but when we want to uplift water we have to use motor automatically water can not go to first floor or above.

III) Entropy of universe is increasing day by day.
Entropy of universe = Entropy of System + Entropy of Surrounding.

iv) Heat can not be converted completely in to work done somewhere without leaving some effect elsewhere.

Clausius clapeyron equation: →

Actually clausius and clapeyron equation express the change in boiling point a melting point with change in pressure. As for example normal boiling point of water is 100°C at 1atm but as pressure increases boiling point of water also increases, practically it happens inside pressure cooker.

In this equation first of all we will take a pure substance which changes their phase from initial (1) to final (2) at equilibrium with a given temperature & pressure.

G_1 = Free energy per mole of substance in initial phase
G_2 = Free energy per mole of substance in final phase

~~At equilibrium~~ $$\underset{G_1}{A} \underset{P}{\overset{T}{\rightleftharpoons}} \underset{G_2}{B}$$

At Equilibrium, $\Delta G = G_2 - G_1 = 0$.

If the temperature is raised from very small value dT, then temperature becomes $T + dT$ and in the mean time pressure will also change and it becomes P to $P + dP$.

Now $G_1 + dG_1$ = free energy per mole of substance in initial phase at new T & P.

& $G_2 + dG_2$ = free energy per mole of substance in final state (phase) at new T & P.

The phase 1 and 2 are in equilibrium (means the new T & P) could not change equilibrium.

So, $G_1 + dG_1 = G_2 + dG_2$

When system undergoes reversible change of temperature dT & pressure dp the change of free energy can be expressed as follows:

$$dG = Vdp - SdT \quad \text{(General eqn).}$$

For Initial phase (1) :-

$$dG_1 = V_1 dp - S_1 dT$$

$$dG_2 = V_2 dp - S_2 dT$$

As $G_1 = G_2$, So $dG_1 = dG_2$

Means, $= V_1 dp - S_1 dT = V_2 dp - S_2 dT$

$$= (V_2 - V_1) dp = (S_2 - S_1) dT$$

or

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} \longrightarrow 1$$

As we know $\Delta \cancel{S_{rev}} = \cancel{q}$

$$\Delta S = \frac{q_{rev}}{T} \quad \text{— II}$$

Now we put the value of ΔS from Eqn II to eqn I we have:

$$\frac{dp}{dT} = \frac{q}{T\Delta V} = \frac{q}{T(V_2 - V_1)} \quad \text{——— III}$$

This equation III is called Clausius & Clapeyron equation. In different phase transformation the formula can be written in different way.

i.e liquid - vapour phase

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

It is also called integrated form of Clausius clapeyron equation.

In solid - vapour phase:

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

In solid - liquid phase

$$\frac{dT}{dp} = \frac{T(V_1 - V_2)}{\Delta H_f}$$

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