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Equilibrium between Phases

- Thermodynamic criterion of phase equilibria

Considering a system in which a pure substance is present in two phases (e.g. liquid-vapour, solid-vapour or, solid-liquid etc.) in equilibrium with each other, the Gibb's function of the system can be written as,

$$G = f(T, P, n_\alpha, n_\beta) \text{ - - - - - - - - - } ①$$

where n_α and n_β are the amount of the pure substance in the phases α and β respectively.

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_\alpha, n_\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_\alpha, n_\beta} dP + \left(\frac{\partial G}{\partial n_\alpha}\right)_{T, P, n_\beta} dn_\alpha + \left(\frac{\partial G}{\partial n_\beta}\right)_{T, P, n_\alpha} dn_\beta .$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_\alpha, n_\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_\alpha, n_\beta} dP + \mu_\alpha dn_\alpha + \mu_\beta dn_\beta \text{ - - - - } ②$$

Chemical potential $\left[\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} = \mu_i\right]$

when the amount of the substance (dn) is transferred from one phase (α) to the other (β) at const. T and P, then

$$dG = \mu_\alpha(-dn) + \mu_\beta dn$$

$$dG = (\mu_\beta - \mu_\alpha) dn .$$

If the transfer takes place reversibly, then $dG = 0$

$$(\mu_\beta - \mu_\alpha) dn = 0$$

Since $dn \neq 0$, it follows that

$$\mu_\alpha = \mu_\beta . \quad \text{[at const. T and P]} \text{ - - - - - } ③$$

Hence, if a substance is in equilibrium between two phases, its chemical potential must have the same value in both the phases.

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Clapeyron Equation

At equilibrium we have (at const. T. and P)

$\mu_\alpha = \mu_\beta$. for any two phases of a pure substance.

Let the temperature of the system is changed by an infinitesimal amount. As the system is in equilibrium the pressure also undergoes a change by infinitesimal amount. Under this condition,

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \text{ - - - - } ④$$

as $\mu_\alpha = \mu_\beta$, $d\mu_\alpha = d\mu_\beta$.

writing $d\mu$ in the explicit form in terms of dT and dP. [as $d\mu = -SdT + VdP$] where,

$$d\mu_\alpha = -S_{m,\alpha}dT + V_{m,\alpha}dP.$$

and $d\mu_\beta = -S_{m,\beta}dT + V_{m,\beta}dP$.

$$-S_{m,\alpha}dT + V_{m,\alpha}dP = -S_{m,\beta}dT + V_{m,\beta}dP$$

or, $$\frac{dP}{dT} = \frac{S_{m,\beta} - S_{m,\alpha}}{V_{m,\beta} - V_{m,\alpha}}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta_{trs}S_m}{\Delta_{trs}V_m}} \text{ - - - } ⑤$$

Δ_{trs} is the change in property of the system when 1 mole of a pure substance is transferred from one phase (α) to another phase (β).

This is the mathematical form of

Clapeyron Equation

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Clapeyron - Clausius Equation

Now, the Clapeyron equation is

$$\frac{dP}{dT} = \frac{\Delta_{trs} S_m}{\Delta_{trs} V_m}$$

at the transformation temperature T,

$$\frac{dP}{dT} = \frac{\Delta_{trs} H_m}{T\,\Delta_{trs} V_m} \quad \text{- - - -} \textcircled{6}$$

where $\Delta_{trs} H_m$ is either the molar enthalpy of vapourization of the liquid or the molar enthalpy of sublimation of the solid and

$$\Delta_{trs} V_m = V_{m(g)} - V_{m(s\,or\,l)}$$

Clausius Simplification,

Clausius clapeyron equation is used for Solid-Vapour or liquid-vapour equilibrium, hence the following two approximations are introduced

approx 1. $V_{m,(g)} - V_{m(s\,or\,l)} \approx V_{m(g)}$

Since volume of gaseous substance is much higher than liquid or solid.

approx 2. The gaseous substance is assumed to be ideal, so, V_m can be written as RT/p.

$$\frac{dP}{dT} = \frac{\Delta_{trs} H_m}{RT^2}\cdot P$$

$$\boxed{\frac{dP}{P} = \frac{\Delta_{trs} H_m}{R}\cdot\frac{dT}{T^2}} \quad \text{- - - -} \textcircled{7}$$

This equation relates the vapour pressure of a condensed phase (solid or liquid) with its molar enthalpy of phase transformation (Sublimation or vapourization) and the temperature of transformation.

Integration of eqn. (7) gives,

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta_{trs.} H_m}{R} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{trs.} H_m}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

[Considering $\Delta_{trs} H_m$ to be independent of temperature]

[P_1 and P_2 are the vapour pressures of the Condensed phase at temp T_1 and T_2 respectively.]

When, $P_1 = 1$ atm, T_1 represents normal sublimation point of the solid (normal boiling point of the liquid), then we get,

$$\ln \left(\frac{P_2}{1 atm} \right) = - \frac{\Delta_{trs.} H_m}{R} \left(\frac{1}{T_2} - \frac{1}{T_0} \right)$$

So, $$\ln \left(\frac{P}{1 atm} \right) = - \frac{\Delta_{trs.} H_m}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad \text{----} ⑧.$$

Dividing the numerator and denominator of left side of eqn. (7) by unit vapour pressure (P^0) we get,

$$\frac{(1/P^0)\, dP}{(P/P^0)} = \frac{\Delta_{trs} H_m}{R} \frac{dT}{T^2}.$$

Integrating we get,

$$\ln \left(\frac{P}{P^0} \right) = \frac{\Delta_{trs.} H_m}{R} \frac{1}{T} + I \quad \text{----} ⑨.$$

where I is the integration constant. It's value may be determined if the value of vapour pressure P at some known temperature T is known.

If we can plot $\ln\left(\frac{P}{P^o}\right)$ vs. $(1/T)$, we will get a linear curve with slope $-\left(\Delta_{trs}.H_m/R\right)$, intercept = $\frac{\Delta_{trs}.H_m}{RT_0}$. From the determined values of slope and intercept, we can determine both $\Delta_{trs}.H_m$ and T_0 of the substance.

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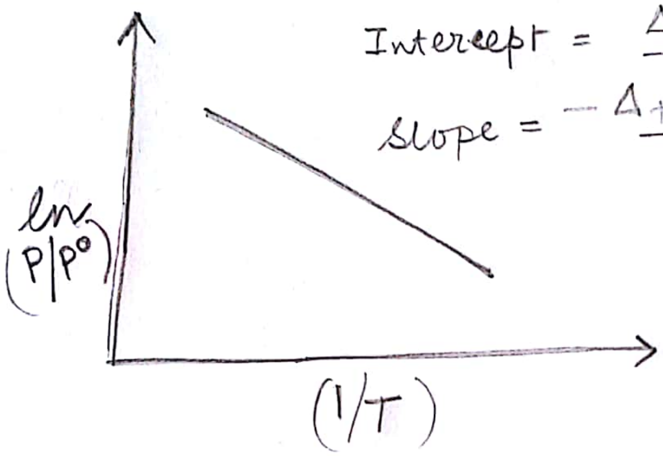

$$\text{Intercept} = \frac{\Delta_{trs}.H_m}{RT_0}.$$

$$\text{Slope} = -\frac{\Delta_{trs}.H_m}{R}.$$

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