Clausius Clapeyron Equation

An important equation was derived for one-component tow-phase systems by Clapeyron from Second Law of thermodynamics. It is known as the Clapeyron equation. The two phases in equilibrium may be any of the following.

i. Solid and Liquid, S⇌L, at the melting point of solid
ii. Liquid and Vapor, L⇌V , at the boiling point of liquid
iii. Solid and Vapor, S ⇌V, at the sublimation temperature of Solid.
iv. One crystalline form and another crystalline form eg. Rhombic and monoclinic $S_R \rightleftharpoons S_M$, at the transition temperature of two allotropic forms.

Consider any two phases, (liquid and vapor) of one and the same substance in equilibrium with each other at the given temperature and pressure. It is possible to transfer any definite amount of the substance from one phase to another in thermodynamically reversible manner i.e. infinitesimally slowly, the system remaining in equilibrium all along and the free energy change is zero. It can also be stated that *the equal amounts of a given substance must have exactly the same free energy in the two phases at equilibrium with each other.*

Let us consider a system where a substance changes from state A to B phase in equilibrium at a given temperature and pressure. Considering free change for A (initial phase) and B (final phase) be G_A and G_B respectively. And $G_A = G_B$ and therefore,

$$G_A - G_B = 0$$

Let the temperature raised from *T to T+dT* and pressure increases from *P to P+dP*. Therefore, Gibbs free energy change per mole of the substance in phase A and B changes as $G_A + dG_A$ and $G_B + dG_B$ respectively. Since both the phases are in equilibrium, therefore,

$$G_A + dG_A = G_B + dG_B$$

According to the thermodynamics,

$$dG = VdP - SdT$$

And hence phase A & B equations can be rewritten as,

$$dG_A = V_A dP - S_A dT$$

$$dG_B = V_B dP - S_B dT$$

Since G_A=G_B

$$dG_A = dG_B$$

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

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}$$

Or, $^{dP}/_{dT} = {}^{\Delta S}/_{\Delta V}$

If q is the heat exchanged reversibly per mole of the substance during the phase transformation at the temperature T. The entropy change of the process is given by $\Delta S = {}^{q}/_{T}$

Hence, $\dfrac{dP}{dT} = \dfrac{q}{T\Delta V}$

Thus, $\dfrac{dP}{dT} = \dfrac{q}{T(V_B - V_A)}$

This is known as **Clapeyron equation**.

This equation gives change in pressure *dP,* which must accompany the change in temperature *dT* or vice versa, for two phases of pure substance in equilibrium with each other. Let us consider a system of water in two different phases; liquid and vapor, in equilibrium with each other at temperature T.

Water (liquid) ⇌ Water (Vapor)

Then, q= Molar heat of vaporization, ΔH_{vap}

V_B= Volume of one mole of water in vapor form

V_A= Volume of one mole of water in vapor form

The equation therefore becomes,

$$dP/dT = \Delta H_{vap} / T(V_g - V_l)$$

Let us consider a system of water in two different phases; liquid and vapor, in equilibrium with each other at temperature T.

Water (solid) ⇌ Water (liquid)

And the equation becomes,

$$dP/dT = \Delta H_{fus} / T(V_l - V_s)$$

q= Molar heat of vaporization, ΔH_{fus}