Phase Transition –

We discuss for a PVT system i.e. a liquid at fixed no. of particles
Two special points in the fig

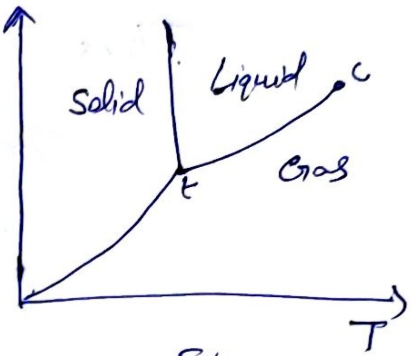

Fig
Solid / Liquid / Gas
Phase ~~transition~~ diagram

Tripal point → P_t, T_t

Critical Point → P_c, T_c

At equilibrium Gibbs free energy is minimized. Lowest energy state is solid.

* First order transition :

$$G = E - TS + PV$$

$$dG = -SdT + VdP + \mu dN$$

* First derivative of G is discontinuous

for a fixed mole = 1.

$$dG = -SdT + VdP$$

$$\left.\frac{\partial G}{\partial T}\right|_P = -S \quad \text{and} \quad \left.\frac{\partial G}{\partial P}\right|_T = V$$

↑ Latent heat ↑ Specific volume

* Second order phase transition !

Second derivative of G is discontinuous.

From above expressions.

$$\left.\frac{\partial^2 G}{\partial T^2}\right|_P = -\left.\frac{\partial S}{\partial T}\right|_P \propto C_p \quad \text{specific heat}$$

$$\left.\frac{\partial^2 G}{\partial P^2}\right|_T = \left.\frac{\partial V}{\partial P}\right|_T \propto \text{isothermal compressibility } K_T$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T}\Big|_P \propto \text{ thermal expansivity } \alpha$$

At coexistence line, two phases coexist

Thus $dG_{liquid} = dG_{gas}$

or $-S_l\, dT + V_l\, dP = -S_g\, dT + V_g\, dP$

$(S_g - S_l)\, dT = (V_g - V_l)\, dP$

or $\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{L}{T \Delta V}$

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

Clausius - Clapeyron equation