

First-order phase transition

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- First-order phase transition typically happens reversibly (i.e., slowly) at constant temperature and pressure.
- During phase transition, the heat added or released do not change the temperature or pressure.
- This is because - during phase transition (let's say ice to water) both phases co-exist i.e., the system becomes inhomogeneous. The heat absorbed/released is utilized to make the mixture of ice and water to either fully water or ice before changing the temperature.
- Clausius - clapeyron equation: (2nd derivation)
 $S = S(T, V) \rightarrow$ gives 2nd T-dS equation.

In molar form,

$$dS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$\begin{cases} C_V = \text{molar specific heat} \\ V = \text{molar volume} \end{cases}$$

Since in 1st-order phase transition T & P remain constant,

$$T dS = T \left(\frac{\partial P}{\partial T} \right)_V dV$$

Since P & T remain constant $\left(\frac{\partial P}{\partial T} \right)_V = \frac{dP}{dT}$

$$\therefore \frac{dP}{dT} = \frac{dS}{dV} = \frac{T \Delta h}{T \Delta V} = \frac{h^f - h^i}{V^f - V^i}$$

$\Delta h =$ molar enthalpy difference = Latent heat
i.e. this heat/energy does not change the T or P during the phase transition.

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The change in molar enthalpy means that there will be change in molar entropies.

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

General expression.

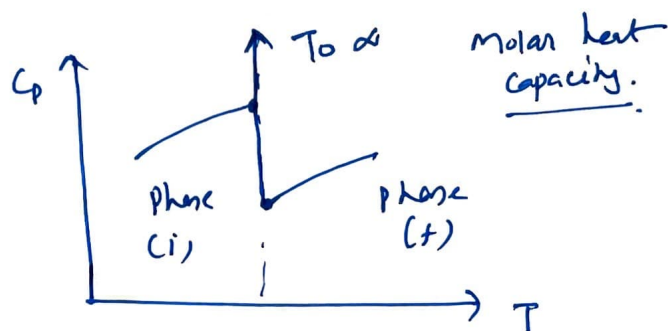
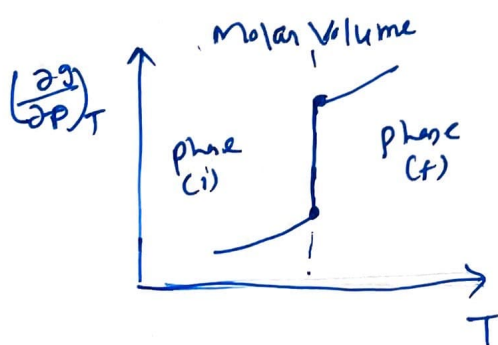
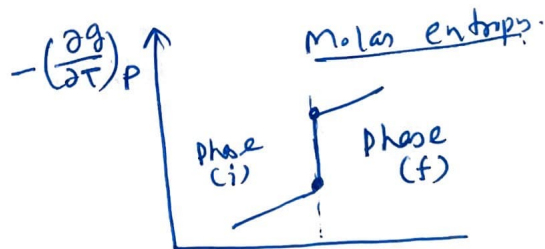
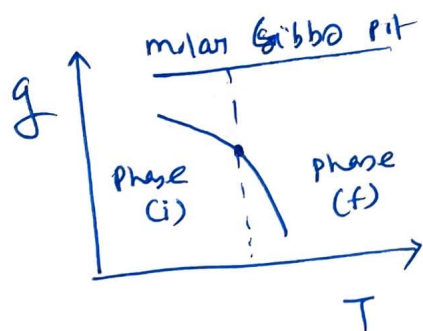
$$\therefore dg = -sdT + vdp$$

$$\therefore s = -\left(\frac{\partial g}{\partial T}\right)_p \quad \text{and} \quad v = \left(\frac{\partial g}{\partial p}\right)_T$$

Therefore, we define, first-order transition as the one where

- (i) there are changes of molar entropy and molar volume.
- (ii) the first-order derivative of the molar Gibbs potential change discontinuously.

For first-order phase transition, the temperature variations of g , s , v , and c_p are shown below. For liquid to vapour.



- The molar Gibbs potential has a singular value at the vaporization temperature, but the slope is discontinuous.

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- The molar heat capacity (C_p) of a mixture of two phases during the phase transition is infinite.

This is true because the transition occurs at constant T and P .

When P is constant, $dT=0$ or when T is constant, $dP=0$.

$$\therefore C_p = T \left(\frac{\partial S}{\partial T} \right)_P \rightarrow \infty$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \rightarrow \infty$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \rightarrow \infty$$

- ⑩ It should be noted that the above statements are true only when both phases are present. i.e., C_p of phase (i) remains finite right up to the transition temperature.

▮ We know, $dg = -sdT + v dP$ for single component system.

\therefore For a phase transition at constant T & P ,
 $dg = 0$ or $dg = 0$

\therefore The molar Gibbs potential are equal at the two end states.

$$g^{(i)} = g^{(f)}$$

And for a phase change at $T+dT$ and $P+dP$,

$$g^{(i)} + dg^{(i)} = g^{(f)} + dg^{(f)}$$

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Therefore, $dg(i) = dg(f)$

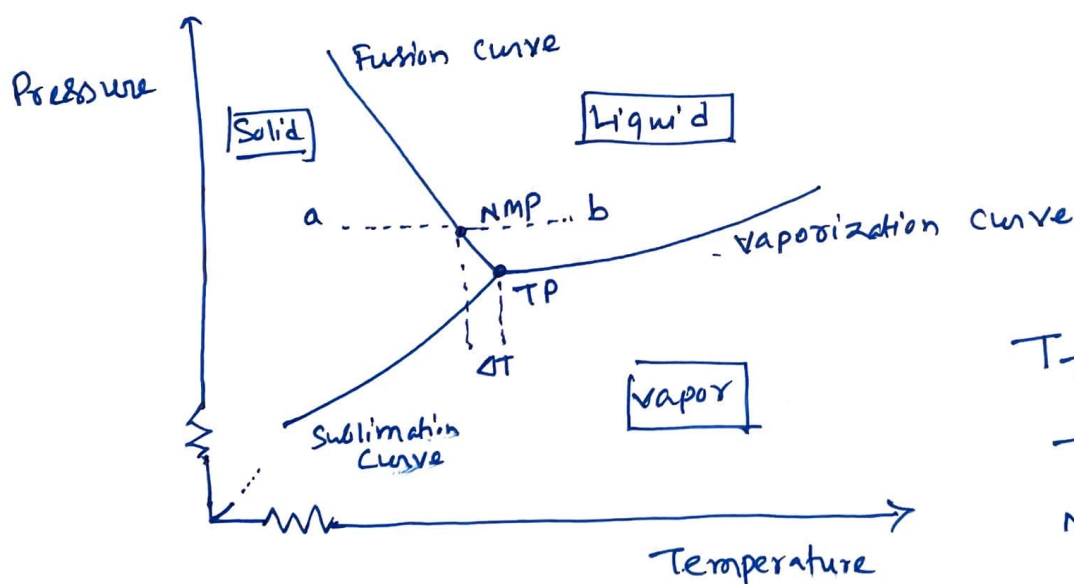
$$\text{or, } -s(i)dT + v(i)dp = -s(f)dT + v(f)dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{s(f) - s(i)}{v(f) - v(i)}$$

$$\boxed{\frac{dp}{dT} = \frac{h(f) - h(i)}{T(v(f) - v(i))}}$$

This is the
Clausius-Clapeyron
equation, (1st derivation).

▣ phase diagram of water:



$$T_{TP} = 273.16 \text{ K}$$

TP = Triple point

NMP = Normal melting point.

- Let "a" be the state of a system which moves horizontally upon heating (at const P) towards the state "b". Heating raises the enthalpy and hence the T until it reaches the normal melting point (NMP). Further increase in heat does not change the temperature until ice melts to water. After that temperature raises again.

Clausius - clapeyron relation (3rd derivation)

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Two phases (i & f) are in chemical equilibrium with each other at constant T and P.

∴ Their chemical potentials

$$\mu^{(i)} = \mu^{(f)}$$

∴ Along the co-existence curve $P = P(T)$,

$$d\mu^{(i)} = d\mu^{(f)}$$

Using the Gibbs - Duhem relation

$$-s^{(i)}dT + v^{(i)}dP = -s^{(f)}dT + v^{(f)}dP$$

$$\Rightarrow \frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}} = \frac{\Delta s}{\Delta v} = \frac{\frac{\Delta h}{T\Delta v}}{\Delta v} = \frac{L}{T\Delta v}$$

∴ This relation equates the slope of the co-existence curve to the latent heat (L) at a temperature T per molar volume change.