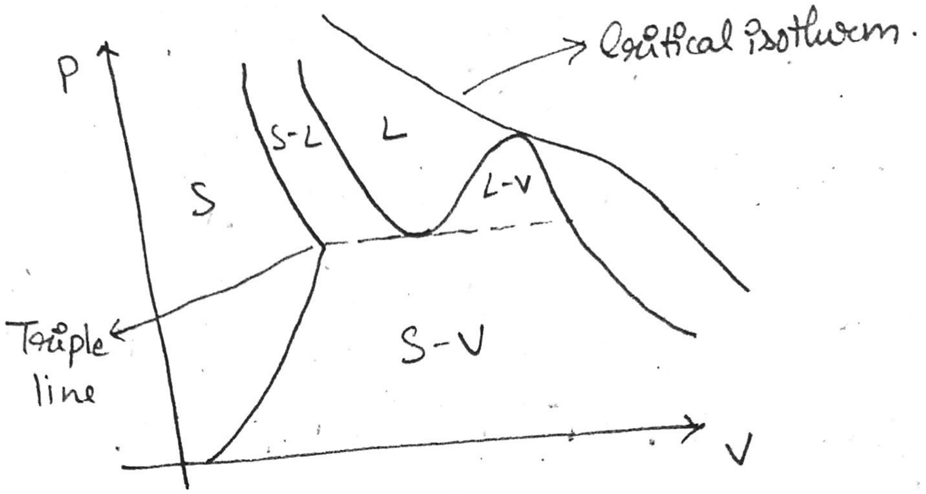
$\circledast$ Next tutorial will have 2 problems.

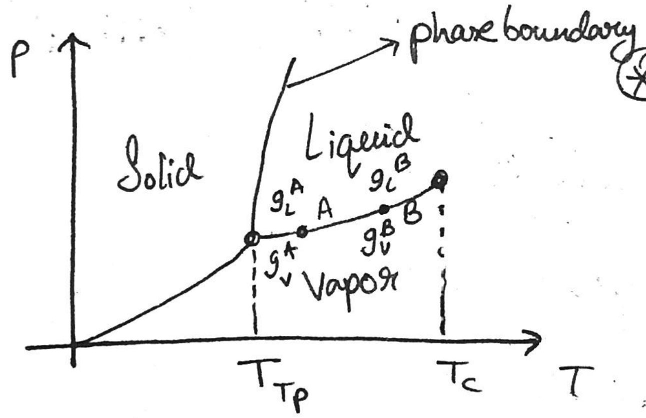
12th March 2024

Let us imagine a hydrostatic system described by (P, V, T).
It describes a 3D surface with the constraint of the equation of state — ~~...~~ but this constraint depends on the phase of the system.

Plot →



In physics we see P vs. T graphs.
Corresponding P-T diagram,



$\circledast$ Here, the nice thing is that each phase has a separate area, unlike the previous one.

Note: These are for standard liquid — not water.

Goal of condensed matter — predict phase plot from underlying physics.
There is some sort of interplay b/w thermal energy and some other energy at phase boundaries.

What does a curve on the P-T diagram mean?

At every point on the curve, two phases coexist at that temp and pressure. at equilibrium.

o Constant ~~volume~~ pressure and Constant temperature →

$$dG = -SdT + vdp$$

Gibbs free energy is minimized.

$$g = m_l g_l + m_v g_v$$

Free energy per unit mass.

m_l → Mass of liq, m_v → Mass of vapor

$$M = m_l + m_v = \text{constant}.$$

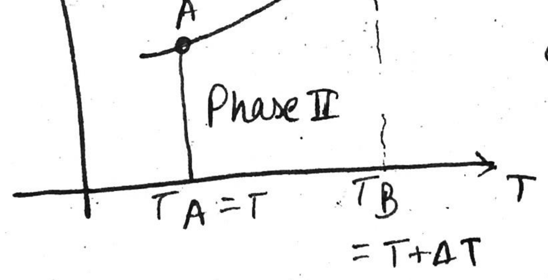
$$dg = d(m_l)\, g_l + d(m_v)\, g_v = 0$$

Using this,

$$\boxed{g_l = g_v}$$

✱ All points on the curve are eq points, but the lines are where two phases coexist.

Take a P-T diagram,



for equilibrium,

$$g_1^A = g_2^A$$

and,

$$g_1^B = g_2^B$$

$$\Rightarrow g_1^B - g_1^A = g_2^B - g_2^A$$

as $G = (p, T, m_l, m_v)$ and $g = g(P, T)$,

this is not just $0 = 0$., i.e, $g_1^A \neq g_1^B$

$$\Rightarrow dg_1 = dg_2$$

$$\Rightarrow \left(\frac{\partial g_1}{\partial p}\right)_T dp + \left(\frac{\partial g_1}{\partial T}\right)_P dT = dg_1$$

$$\Rightarrow v_1\, dp - s_1\, dT = dg_1 \quad \text{(maxwell)}$$

Similarly.

$$dg_2 = v_2\, dp - s_2\, dT$$

$$\Rightarrow v_1\, dp - s_1\, dT = v_2\, dp - s_2\, dT$$

Infinitesimal change despite being Δ

$$\Rightarrow \frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v} = \frac{đQ}{T\Delta V}$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{đQ}{T(\Delta V)}}$$

Clausius - Claypeyron equation.

Slope of P-T graph

Change in specific vol going from one phase to another.

Depending on this, slope may be +ve or -ve

$$T\left(\frac{\partial s}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V \quad \text{(maxwell eqn)}.$$

$$\Rightarrow \left(\frac{đQ}{dV}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V$$

During evaporation,

$$đQ = L\, dm$$

$\hookrightarrow$ Latent heat for evaporation.

$$dV = (v_{vap} - v_{liq})\, dm$$

$\hookrightarrow$ Specific volumes.

$$\therefore \frac{đQ}{dV} = \frac{L}{v_{vap} - v_{liq}} = T \frac{\partial p}{\partial T}$$

Something about Gibbs FE change being discontinuous at phase change.