Phase Transition part-2

Triple Point

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Introduction

- Till now we have studied different phases and thermodynamics of transition between different phases.
- We also learned regarding the order of phase transition
- Different lines in the curves indicates that which two phases are in equilibrium with each other in particular range of p and T.

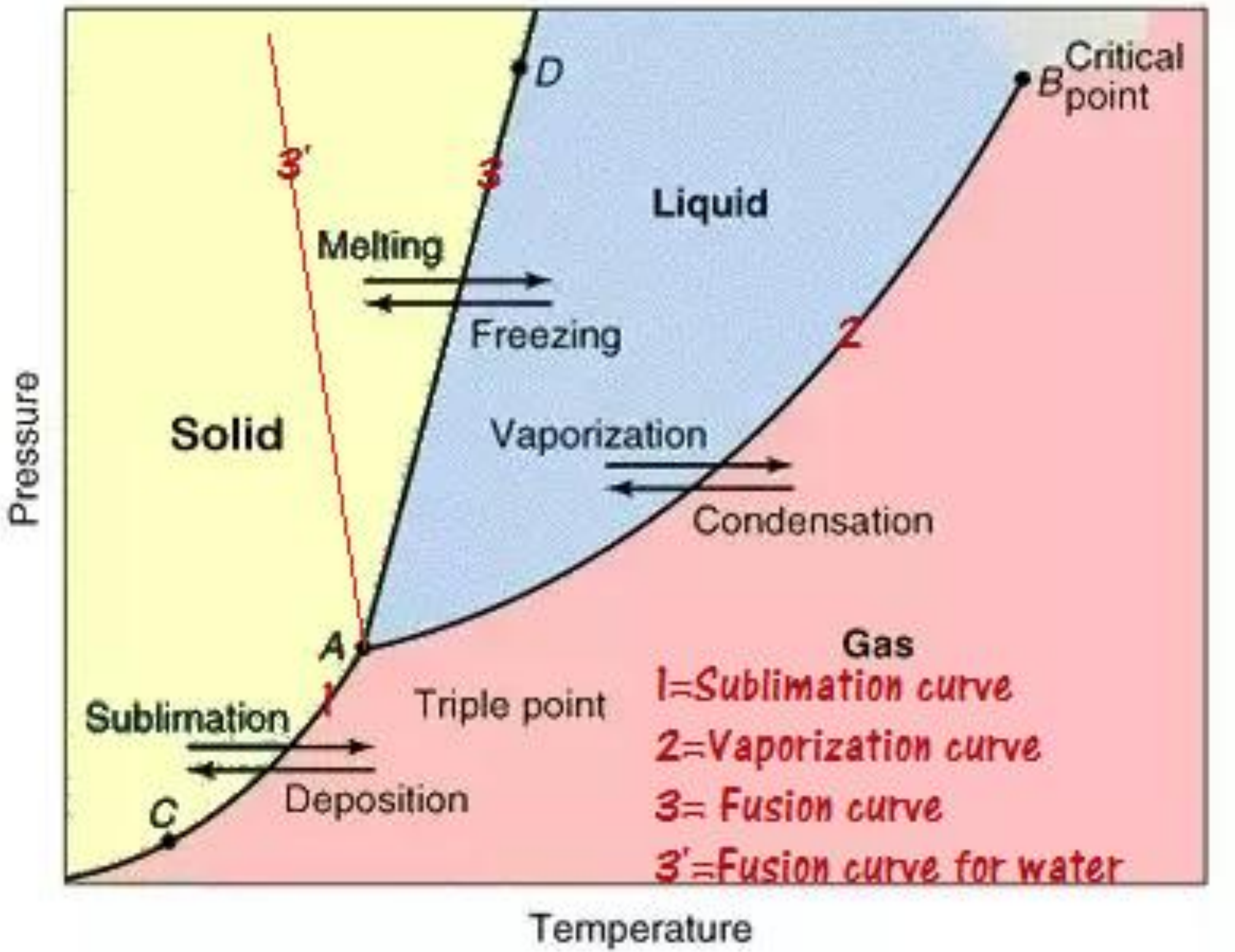
Phase diagram

- What is the phase diagram: It is a curve showing the thermodynamical condition of substance at different temperature and pressure.

- Some times it is given as three dimensional diagram, where volume is also considered as on parameter but generally P-T curve is known as phase diagram.

- Different lines in the curves indicates that which two phases are in equilibrium with each other in particular range of p and T.

A Typical phase diagram indicating different phases and processes



Another figure of Phase diagram defining supercritical fluid, critical temperature and critical pressure

(No difference from previous figure, just few more things are shown here)

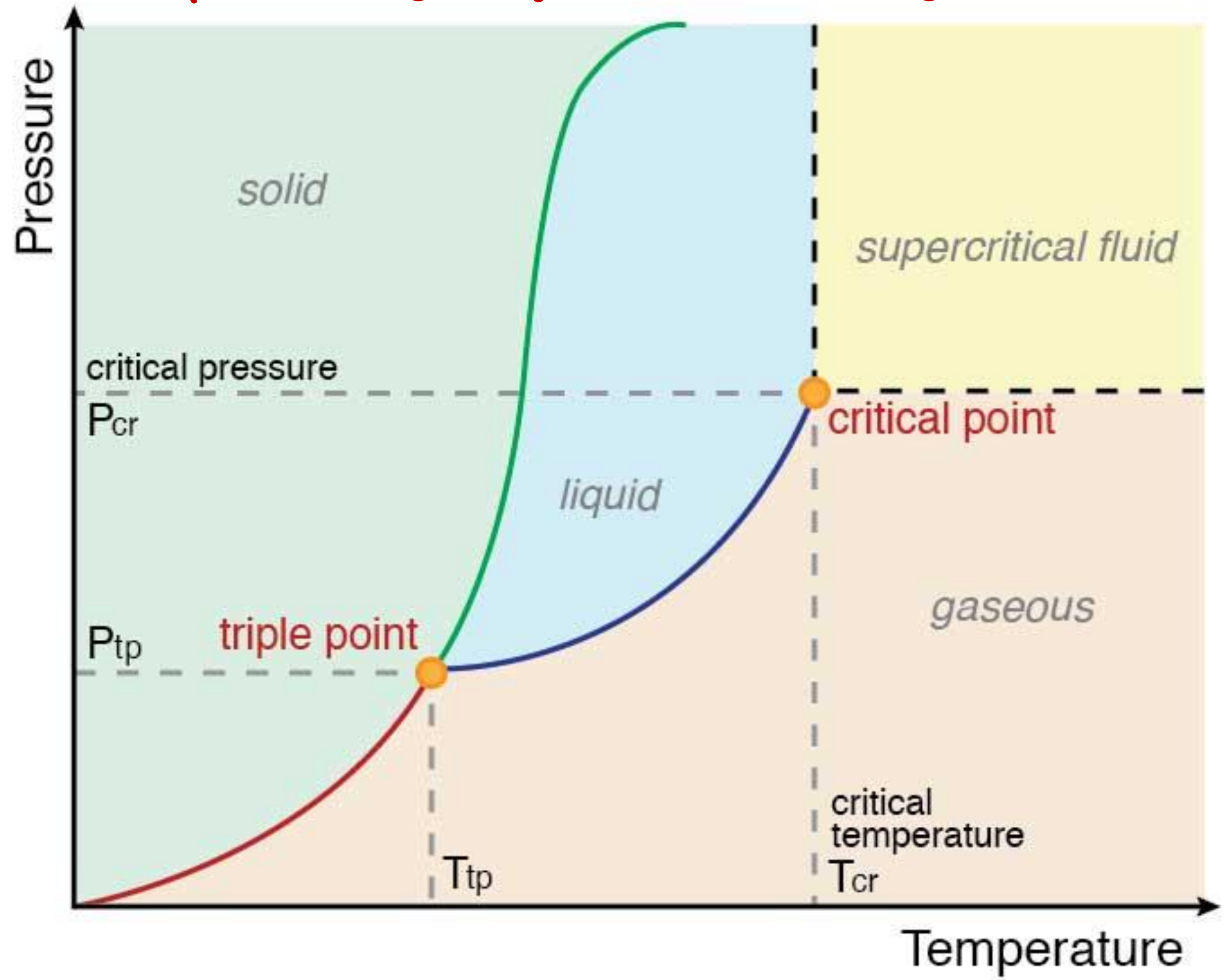


Figure taken from: https://www.learner.org/series/chemistry-challenges-and-solutions/the-behavior-of-atoms-phases-of-matter-and-the-properties-of-gases/

- In case of water different lines on phase diagram are defined in following way also
- 1-Hoar Frost line
- 2-Steam line
- 3'-Ice line

Triple Point

- What is TRIPLE POINT: Triple point on phase diagram is a unique point on the phase diagram where all the three phases coexists.
- Let us understand the thermodynamics of the triple point and see why it is a point and why it can't be an area on phase diagram

Thermodynamics of triple point

- Let us consider three states of a system having following mass, specific internal energy, specific entropy and specific volume

State of matter	Mass	Specific Internal Energy	Specific Volume	Specific Entropy
Solid	m_1	u_1	v_1	s_1
Liquid	m_2	u_2	v_2	s_2
Gas	m_3	u_3	V_3	s_3

- So we will have

Total Mass M	$=m_1+m_2+m_3$	$=\sum m_i$
Total internal energy	$=u_1+u_2+u_3$	$=\sum u_i$
Total Volume	$=v_1+v_2+v_3$	$=\sum v_i$
Total entropy	$=s_1+s_2+s_3$	$=\sum s_i$

- If the three phases coexist and are in equilibrium then the entropy of the total system should be maximum

- that means $dS=0$ and $d^2S<0$

- Although a continuous phase changes may be taking place but the equilibrium of isolated system demands

- $\delta M=0$, $\delta U=0$ and $\delta V=0$

- That means

$$\delta M = \sum \delta m_i$$

$$\delta V = \sum m_i \delta v_i + \sum v_i \delta m_i$$

$$\delta S = \sum m_i \delta s_i + \sum s_i \delta m_i$$

$$\delta U = \sum m_i \delta u_i + \sum u_i \delta m_i$$

- We can write $$\delta s_i = \frac{\delta u_i}{T_i} + \frac{p_i \delta v_i}{T_i}$$

- The thermodynamical equilibrium can be represented in terms of constraints by multiplying the constraints with lagrangian multipliers λ, μ and ν

- $\delta S + \lambda\, \delta M + \mu\, \delta U + \nu\, \delta V = 0$ ....(A)

- So we can write it as

$$\sum m_i \left(\frac{\delta u_i}{T_i} + \frac{p_i \delta v_i}{T_i} \right) + \sum s_i \delta m_i + \lambda \sum \delta m_i + \sum \mu \delta m_i u_i$$
$$+ \sum \mu m_i \delta u_i + \sum \nu m_i \delta v_i + \sum \nu v_i \delta m_i = 0$$

$$\sum \delta m_i (s_i + \mu u_i + \nu v_i + \lambda) + \sum \delta u_i \left(\mu m_i + \frac{m_i}{T_i} \right) + \sum \delta v_i \left(\nu m_i + \frac{m_i p_i}{T_i} \right) = 0 \quad \text{.................(B)}$$

- Since δm_i, δv_i and δu_i are arbitrary variation of mass, volume and internal energy of three phases, hence any two can be chose independently

- So let us start by considering

$$\delta m_i \neq 0, \text{ but } \delta v_i = 0 \text{ and } \delta u_i = 0$$

Then equation 'B' will give

$$s_i + \mu u_i + \nu v_i + \lambda = 0 \text{.....................(C)}$$

- Now let us consider δm_i=0, but $\delta v_i \neq 0$ and δu_i =0

$$\frac{m_i p_i}{T_i} + v m_i = 0 \qquad \text{.............(D)}$$

- Similarly by choosing δm_i=0, but δv_i =0 and $\delta u_i \neq 0$

$$\frac{m_i}{T_i} + \mu m_i = 0 \qquad \text{..................(E)}$$

- Equation 'E' gives

$$\mu = -\frac{1}{T_i} = -\frac{1}{T_1} = -\frac{1}{T_2} = -\frac{1}{T_3} \text{ or we can say } T_1 = T_2 = T_3 = T(say)$$

- Equation 'D' gives

$$\nu = -\frac{p_i}{T_i} = -\frac{p_1}{T_1} = -\frac{p_2}{T_2} = -\frac{p_3}{T_3} \text{ or we can say } p_1 = p_2 = p_3 = p\ (say)$$

- Hence from equation 'C' we get

$$\lambda = -s_i - \mu u_i - \nu v_i$$

- or $\lambda = -s_i + \frac{u_i}{T} + \frac{pv_i}{T} = -s_1 + \frac{u_1}{T} + \frac{pv_1}{T} = -s_2 + \frac{u_2}{T} + \frac{pv_2}{T} = -s_3 + \frac{u_3}{T} + \frac{pv_3}{T}$

- Or we will get $\frac{pv_1 + u_1 - Ts_1}{T} = \frac{pv_2 + u_2 - Ts_2}{T} = \frac{pv_3 + u_3 - Ts_3}{T}$ ....(F)
- we know that Gibbs free energy is given as
- G=U-TS+PV and Specific Gibbs energy g=G/m so we have

$$pv_1 + u_1 - Ts_1 = g_1$$

$$pv_2 + u_2 - Ts_2 = g_2$$

$$pv_3 + u_3 - Ts_3 = g_3$$ ....(G)

- From equation 'F' and 'G' we get $g_1=g_2=g_3$
- Thus the equilibrium condition demands that p, T, specific Gibbs free energy are same for all three co-existing phases

- At the triple point, we have

$$L_{31} = T(S_1 - S_3) \qquad L_{23} = T(S_3 - S_2) \qquad L_{12} = T(S_2 - S_1)$$

- So we will get

$$L_{23} + L_{31} + L_{12} = 0$$

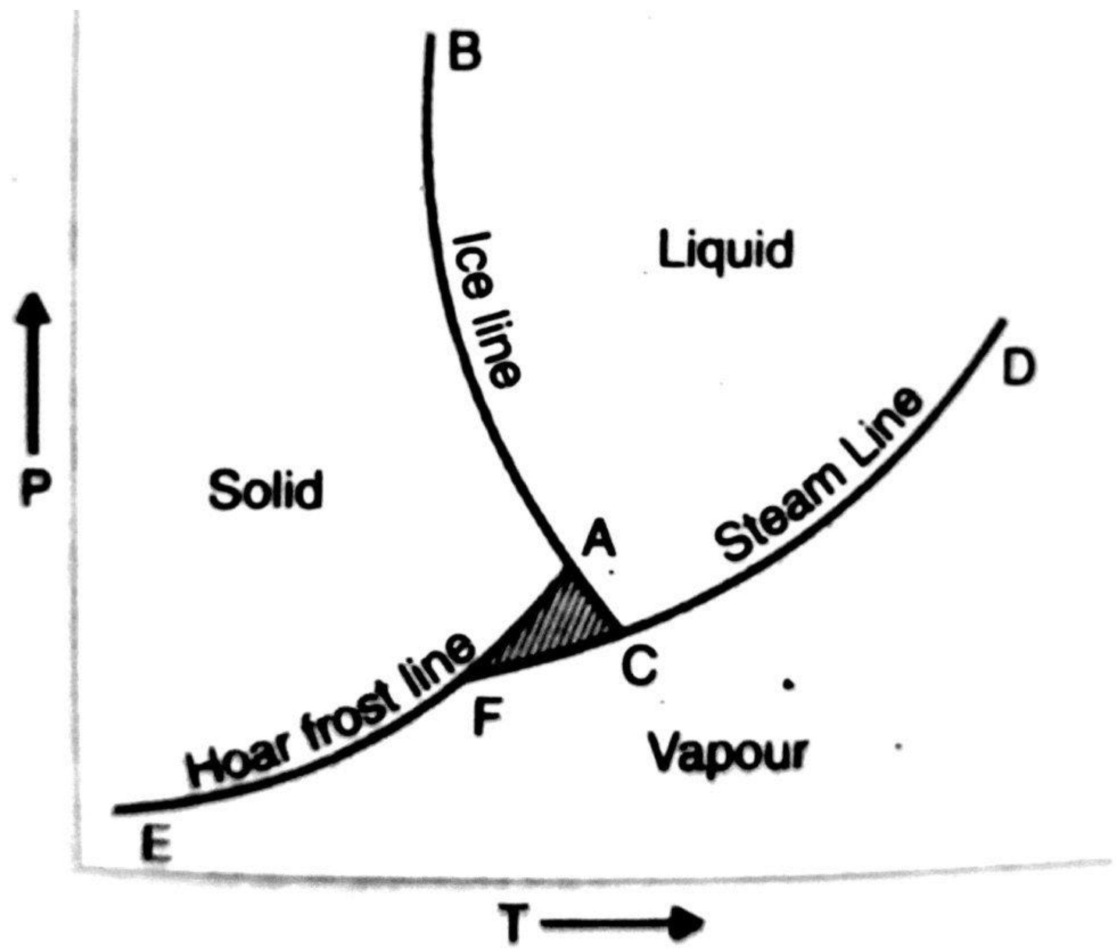
$$or\ -L_{31} = L_{23} + L_{12}$$

$$or\ L_{13} = L_{23} + L_{12}$$

- That means latent heat of sublimation (L_{13})

= latent heat of fusion (L_{12}) + latent heat of vaporization (L_{23})

Let us suppose that the three curves don't meet at one point, instead they enclose an area as shown in figure



- According to Hoar frost line the material should be in vapour phase in the enclosed area

- According to steam line the material should be in liquid phase in the enclosed area

- According to ice line the material should be in solid phase in the enclosed area

- That means if the curves don't meet at single point and instead they enclose an area then within that area all the three phases should coexist which is not possible and hence triple point is a point.

Phase diagram –Is there anything else to know??

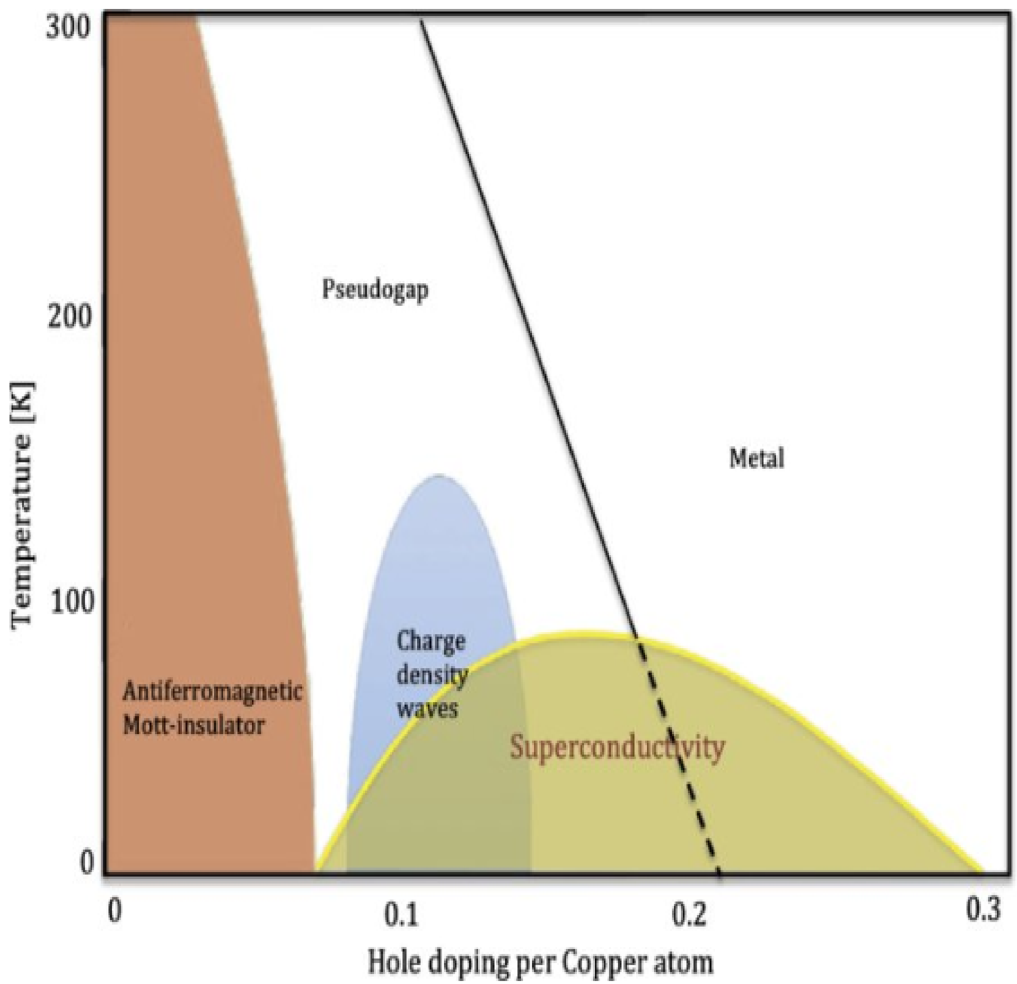
- Yes, a lot, and the most important one is to know that there are many other phase diagrams.

- What we have studied till now, was phase diagram related to First order phase transition.

- As we know that there are different phases and phase transition of different orders.

- And whenever there is a phase transition there will be a phase diagram. Of course the axis may be something else than P and T.

Phase diagram of superconducting material- just to give you an idea. It is not part of your course BPT-201



Figure

Caption

FIG. 7. A rough illustration of high Tc superconductors phase diagram. The yellow area is the superconducting phase obtained from equation 21 directly. The rest of the graphs and values are estimates and should not be taken literally. Salient features of this diagram are as follows. There are four distinct phases starting with Mott-insulator at low ... Read more

Taken from :

https://www.researchgate.net/publication/334759331_A_potential_justifying_superconductivity_and_pseudogap_formation_in_high-Tc_superconductors/figures?lo=1

Some Important definitions just for revision

- Sublimation: Phase transition from solid to gas state without going in liquid state
- Deposition: reverse process of sublimation i.e. it is a process where substance goes from a gas state to a solid state, without passing through liquid state
- Melting: It is the change of process where a substance goes from a solid to a liquid state.
- Fusion: It is opposite to melting that means when a substance goes from a liquid to a solid state.
- Vaporization/ evaporation: A phase change from a liquid to a gaseous state.

- Condensation: This is the reverse process of vaporization it occurs when a substance changes from gaseous phase to a liquid phase.

- Triple Point occurs when both the temperature and pressure of the three phases of the substance coexist in equilibrium.

- Critical Point – the point in temperature and pressure on a phase diagram where the liquid and gaseous phases of a substance merge together into a single phase. Beyond the temperature of the critical point, the merged single phase is known as a supercritical fluid.

Supercritical fluid

- Supercritical fluid: It is phase of material when the temperature and pressure is above its critical value.

- Supercritical fluid phenomenon was first observed by French engineer and physicist, Charles Cagniard de La Tour in 1822 but the phrase "supercritical fluid" was first time used by Irish chemist, Thomas Andrews.

- In phase diagram the vaporization curve is interrupted at the critical point, after which a continuum of physico-chemical properties exists.

- In this phase material exhibits an intermediate behavior between that of a liquid and a gas. In this state the densities are liquid-like but the viscosity is that of a gaseous state whereas the diffusities indicate an intermediate behavior that of a liquid and a gas.

- ***A nice series having videos and study material to understand the phase in detail :*** https://www.learner.org/series/chemistry-challenges-and-solutions/the-behavior-of-atoms-phases-of-matter-and-the-properties-of-gases/
- ***Supercritical fluid:*** http://www.supercriticalfluid.org/Supercritical-fluids.146.0.html
- https://theory.physics.manchester.ac.uk/~judith/stat_therm/node39.html
- https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_Matter/Phase_Transitions/Phase_Diagrams
- https://study.com/academy/lesson/phase-diagrams-critical-point-triple-point-and-phase-equilibrium-boundaries.html