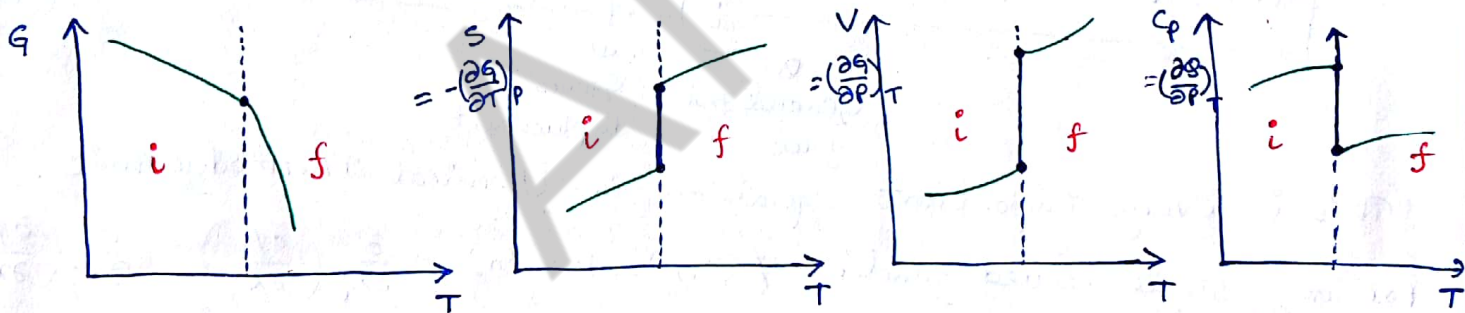# Phase Equilibria

In most of the daily encountered phase transition, e.g. melting of ice, vaporization of water or sublimation, we can write down the Clausius-Clapeyron's equation $\left(\frac{\partial P}{\partial T}\right)_{saturation} = \frac{L}{T(V_2 - V_1)}$.

This is classified as 1st order phase transition. This takes place at constant T and P while there is a transfer of latent heat that change the entropy and volume. As $dG = -SdT + VdP = 0$, so G is equal at two states $G^i = G^f$ and $S = -\left(\frac{\partial G}{\partial T}\right)_P$,

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

As T & P is constant, $dT = 0$ when $P = $ constant
                            $dP = 0$ when $T = $ constant

So $C_P = T\left(\frac{\partial S}{\partial T}\right)_P \rightarrow \infty$, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \rightarrow \infty$, $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \rightarrow \infty$.

A 1st order phase transition is where the 1st order derivative of the Gibbs function changes abruptly at the transition point.

Using $G = \mu N$ and $dG = -SdT + VdP + \mu dN$ we obtain

$$\mu dN + N d\mu = -SdT + VdP + \mu dN$$

or $d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$.

∴ Along an isotherm $dT = 0$ means $\mu_{liquid} - \mu_{gas} = \int_{gas}^{liquid} \frac{V}{N}dP = 0$

∴ $\mu_l = \mu_g$.

Note that T-ds equation $Tds = C_p dT - TV\beta dP$ gives indeterminate result because $C_p \to \infty$, $dT \to 0$, $\beta \to \infty$, $dP \to 0$. However the other T-ds equation $Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ can be integrated along the phase transition.

$$\therefore T(S^f - S^i) = T\left(\frac{\partial P}{\partial T}\right)_v (v^f - v^i) = T\frac{dP}{dT}(v^f - v^i)$$

$$\text{or} \quad H^f - H^i = T\frac{dP}{dT}(v^f - v^i)$$

$$\text{or} \quad \boxed{\frac{dP}{dT} = \frac{H^f - H^i}{T(v^f - v^i)}}$$

Clausius- Clapeyron's equation for 1st order transition

[One can reach to this conclusion starting from the fact that at constant temperature & pressure, G = constant.

So applying, $G^i = G^f$ and for a change of phase from (T, P) to $(T + dT$ & $P + dP)$ we have $G^i + dG^i = G^f + dG^f$

$$\text{or} \quad dG^i = dG^f \quad \text{or} \quad -S^i dT + v^i dP = -S^f dT + v^f dP$$

$$\text{&} \quad \frac{dP}{dT} = \frac{T(S^f - S^i)}{T(v^f - v^i)} = \frac{H^f - H^i}{T(v^f - v^i)} \quad]$$

2nd order Phase Transition

In 1st order phase transition (sublimation, vaporization, fusion) happening at a constant temperature & pressure, there is a transfer of (latent) heat & hence a change in entropy & volume. G remains fixed and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$ or the first order derivative of G changes abruptly. at the transition point.

However investigation on some liquid showed no evolution of latent heat or change in volume. T, P, G, S, V remain unchanged and therefore U, H, G etc remain unchanged. However, finite change is seen in C_p, K and β, which are,
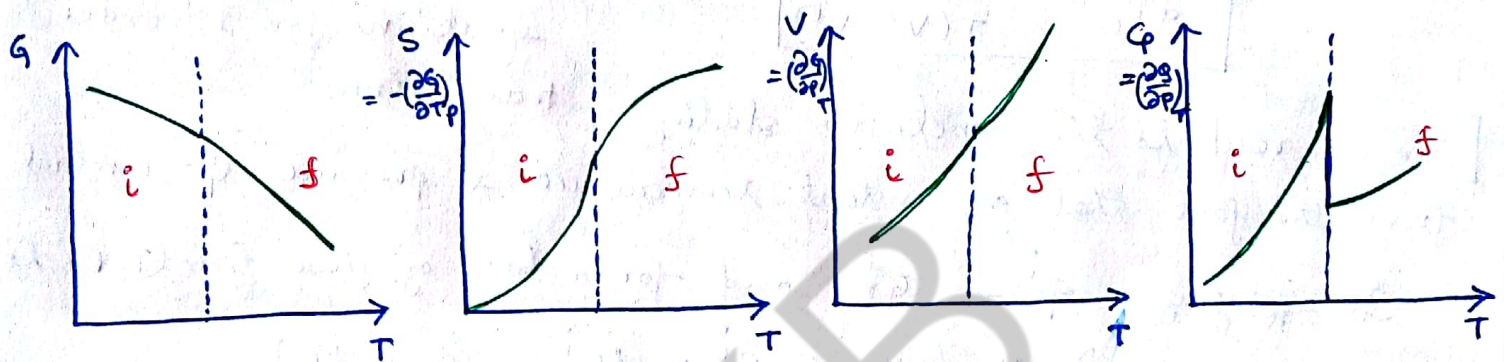
$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial P}\right)_T\right]_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_p = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P \partial T}\right)_{T,P}$$

This led Ehrenfest to conclude that in a 1st order phase transition the 1st order derivative of G changes discontinuously while in a 2nd order phase transition, the 2nd order derivative of G changes discontinuously.

Second order phase transition is an example of continuous phase transition.

As $S = $ constant, we have $dS^i = dS^f$

from $S = S(T, P)$, $\quad dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$$= \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dP = \frac{C_p}{T} dT - V\beta \, dP$$

we have, $\quad \frac{C_p^i}{T} dT - V\beta^i dP = \frac{C_p^f}{T} dT - V\beta^f dP$

$$\therefore \quad (C_p^i - C_p^f)\frac{dT}{T} = V dP(\beta^i - \beta^f)$$

$$\therefore \quad \boxed{\frac{dP}{dT} = \frac{C_p^i - C_p^f}{TV(\beta^i - \beta^f)}} \qquad \text{Ehrenfest's first equation for } 2^{nd} \text{ order phase transition.}$$

Similarly $V = $ constant yields $dV^i = dV^f$

But $V = V(T, P)$, $\quad dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$= \beta V dT - KV dP, \quad \text{we have}$$

$$\beta^i V dT - K^i V dP = \beta^f V dT - K^f V dP$$

or $\quad (\beta^i - \beta^f) dT = (K^i - K^f) dP$

or

$$\frac{dP}{dT} = \frac{\beta^i - \beta^f}{k^i - k^f}$$

Ehrenfest's second equation for 2nd order phase transition.

Paramagnetic to ferromagnetic transition is an example of 2nd order P.T. Ehrenfests classification gave birth to "critical phenomena" that phase transition can be classified as n^{th} order if n^{th} derivative of the free energy with respect to any of its arguments yields a discontinuity at the phase transition. It was found that $\rho_{lg} \propto (T - T_c)^\beta$ and $M_{pf} = \frac{1}{N}\sum_{i=1}^{N} S_i \propto (T_c - T)^\beta$
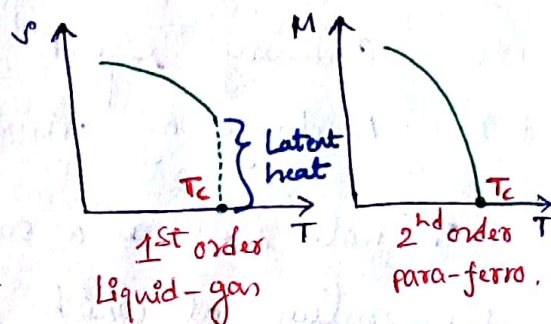
The fact that two apparently different physical systems may share precisely the same set of critical exponents is known as "universality." These led to many Nobel prizes including Landau's theory of 2nd order phase transition, Bragg-Williams theory of 1st order phase transition, Widom's scaling laws & Kadanoff's renormalisation group (RG) with two variant → GellMan - Low RG and Wilson-RG. which made the last significant contribution in the list of Nobel prizes in Statistical physics.

λ - Transition in He⁴

By far the most interesting higher order phase transition that is found in Helium is the Lambda Transition, which is characterized by:

(a) T, P, G remains constant.

(b) S, V (also U, H, F) remains constant.

(c) C_p, β, k tends to infinity at transition temperature.
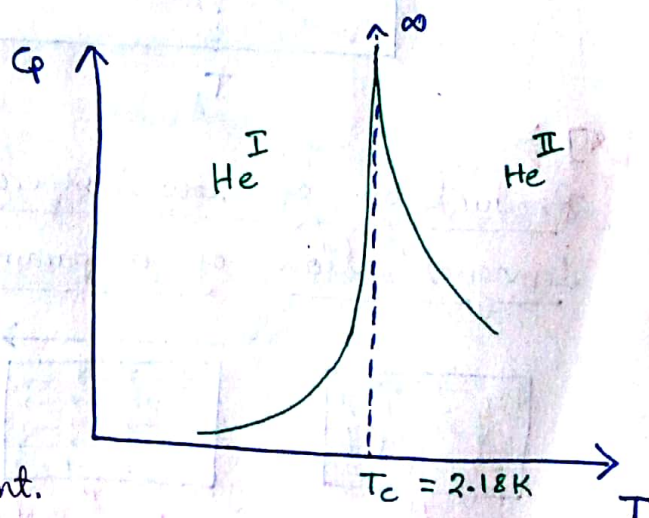
Examples of "λ" type phase transition is

(1) Order disorder transformation in alloys.

(2) Onset of ferroelectricity in Rochelle salt.

(3) Ferro to paramagnetism at the Curie point.

(4) Ordinary liquid Helium-I to superfluid liquid helium-II.

(5) A change of orientation of an ion in a crystal lattice.

To note that as a substance in any one phase approaches the temperature at which 1st order phase transition occurs, C_p remains finite upto the transition temperature. It becomes infinite only when a small amount of the other phase is present and its behaviour before this takes place shows no evidence of the happening of the event.

1st order
2nd order
λ type
shifted to
T_c
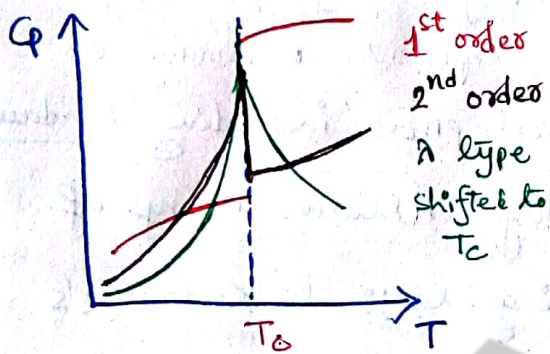
But in case of λ-type transition, C_p starts to rise before the transition point is reached and the substance anticipates the outcome of the phase transition.

$[He^4]$
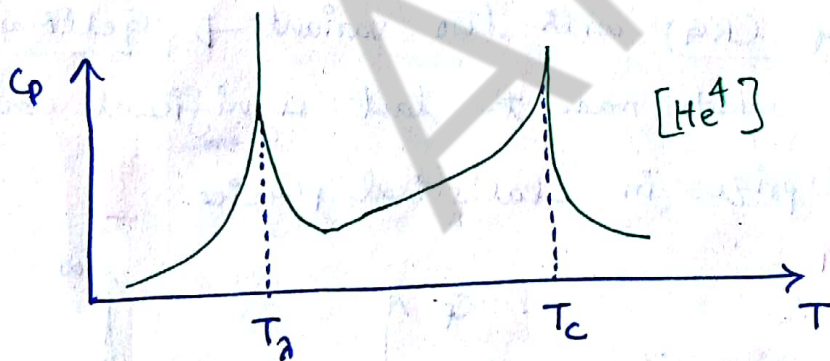
[*] ⇒ [Production of low temperature using the method of adiabatic demagnetisation of a paramagnetic substance.

$M = \sum_i^N S_i = 0$

$M = \sum_i^N S_i \neq 0$
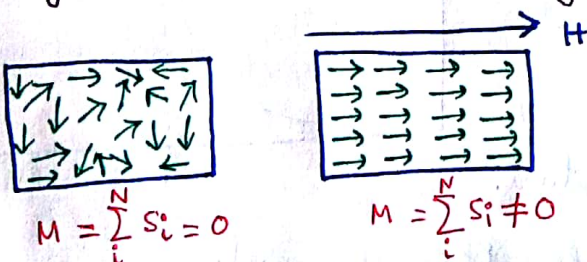
The atoms of a paramagnetic material possess a permanent magnetic moment 2mℓ. In the absence of an external field as a result of the thermal (Brownian) motion of the atoms, the orientation of magnetic moments is almost

random. Quantitatively disorder is confined in entropy $S = K_B \ln \Omega$, where Ω is the thermodynamic probability i.e. the number of ways N number of atoms of the paramagnetic sample can be distributed among the $(2J+1)$ sublevels into which every atomic level splits in a magnetic field. So $\Omega = (2J+1)^N$ and $\therefore S = K_B N \ln (2J+1)$

when the magnetic field is applied and its intensity is increased, more & more number of magnetic moments are oriented in the direction of the field, and the entropy is reduced. At the state of magnetic saturation, all moments are ordered & the entropy vanishes.

This process of magnetisation of a paramagnetic sample upto saturation is accompanied by the decrease of entropy. At a constant temperature T with a decrease in entropy ΔS, heat $\Delta Q = T \Delta S$ is generated & transmitted to the surrounding (immersing on a liquid Helium bath). After equilibriated, the bath is removed & the sample is left thermally insulated.

In such condition, the sample will quasistatically & adiabatically demagnetize with an increase in entropy ΔS. Heat is required to increase the entropy that is supplied by the thermal vibrations of the lattice. As the sample is thermally insulated, its temperature drops. Using this principle, it is possible to obtain temperature down to millikelving $\sim 10^{-3}$ °K. $\Big]$

Basis
lattice
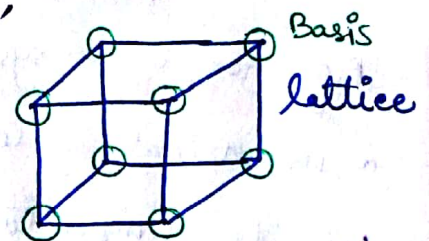
Gibbs Phase Rule

Gibbs published a series of papers on the equilibrium of heterogeneous substance. **Phase :** A homogeneous, physically distinct part of a system that is separated from other parts by definite bounding surfaces is called a phase. E.g. ice-water-vapour constitute a three-phase system. **Component :** The smallest number of independently variable constituents by means of which the composition of each phase can be expressed. In above example, density is that variable, so water phases is one component system. **Variance or d.o.f. :** The number of variable factors (e.g. pressure, temperature, concentration etc) that need to be fixed in order that the condition of system at equilibrium may be completely defined is called degree of freedom (d.o.f.).

If the equilibrium between any number of phases is not influenced by external forces (electromagnetic, gravity) but only influenced by pressure, temperature and concentration, then Gibb's phase rule provides the relation between number of d.o.f. F of the system to the components c and phases P as

$$F = C - P + 2$$

E.g for water system, $c = 1$, $P = 3$. $\therefore F = 1 - 3 + 2 = 0$ or it is a nonvariant system. So the three phases can only exist in contact at definite temperature & pressure, which is the "triple point."

[Read more about phase rule for heterogeneous substance from Wikipedia].