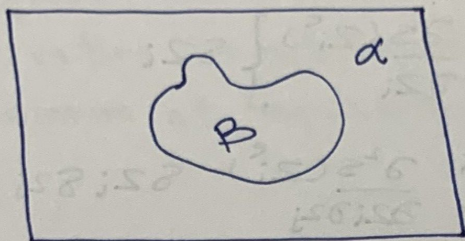


Stability of thermodynamic systems

Consider an isolated system with an imaginary subsystem β such that the complete system $\alpha + \beta$ is a single phase system of N -components.



The system can be described by $N+2$ coordinates at equilibrium. Let any equilibrium state be denoted by

$$Z_i^e = Z_i^e \quad (i = 1, 2, \dots, N+2) \quad - (1)$$

A small perturbation is introduced to the system. Under such conditions, the Taylor series expansion can be written as

$$S(Z_i) = \left[S(Z_i^e) + \left\{ \frac{\partial S(Z_i^e)}{\partial Z_1} \right\} (Z_1 - Z_1^e) \right.$$

$$+ \left\{ \frac{\partial S(Z_i^e)}{\partial Z_2} \right\} (Z_2 - Z_2^e) + \dots$$

$$+ \left\{ \frac{\partial S(Z_i^e)}{\partial Z_{N+2}} \right\} (Z_{N+2} - Z_{N+2}^e) +$$

$$\left\{ \frac{1}{2!} \frac{\partial^2 S(Z_i^e)}{\partial Z_1^2} \right\} (Z_1 - Z_1^e)^2 + \dots$$

$$+ \left\{ \frac{1}{2!} \frac{\partial^2 S(Z_i^e)}{\partial Z_1 \partial Z_{N+2}} \right\} (Z_1 - Z_1^e) (Z_{N+2} - Z_{N+2}^e)$$

(for $\alpha + \beta$ system) (with higher order terms)

-(2)

Eq. (2) can be written in a compact form as

$$S(2_i) - S(2_i^e) = \Delta S \\ = \delta S + \frac{1}{2!} \delta^2 S + \frac{1}{3!} \delta^3 S + \dots$$

where

$$\delta S = \sum_{i=1}^N \left\{ \frac{\partial S(2_i^e)}{\partial 2_i} \right\} \delta 2_i \quad - (3)$$

$$\delta^2 S = \sum_{i=1}^{N+2} \sum_{j=1}^{N+2} \frac{\partial^2 S(2_i^e)}{\partial 2_i \partial 2_j} \delta 2_i \delta 2_j \quad - (4)$$

$$\delta^3 S = \sum_{i=1}^{N+2} \sum_{j=1}^{N+2} \sum_{k=1}^{N+2} \frac{\partial^3 S(2_i^e)}{\partial 2_i \partial 2_j \partial 2_k} \delta 2_i \delta 2_j \delta 2_k \quad - (5)$$

where $\delta 2_i = 2_i - 2_i^e$ and so on.

The equilibrium criteria dictate that the first derivatives must vanish. For this condition to be true,

$$\delta S = 0 \\ \Rightarrow \sum_{i=1}^{N+2} \frac{\partial S(2_i^e)}{\partial 2_i} \delta 2_i = 0$$

Since 2_i 's are all independently variable all the coefficients of $\delta 2_i$'s must be individually zero for the above condition to be true.

$$\Rightarrow \frac{\partial S(2_i^e)}{\partial 2_i} = 0 \quad ; \quad i = 1, 2, \dots, N \quad - (6)$$

This means that the derivative of entropy with respect to every independent variable must be zero at equilibrium.

Eqⁿ (6) indicates that the derivative of entropy must be zero. This merely means that the equilibrium coordinates are extremas. They can be minima or maxima. For this analysis, we need to look at the stability criteria. Stability criteria in terms of entropy dictate the first non-vanishing derivative higher than the first derivative must be negative i.e. entropy must be maximum at equilibrium. Consider the second derivative.

$$\delta^2 S < 0$$
$$\Rightarrow \sum_{i=1}^{N+2} \sum_{j=1}^{N+2} \frac{\partial^2 S(z_i^e)}{\partial z_i \partial z_j} \delta z_i \delta z_j < 0 \quad - (7)$$

For $S = S(U, V, n_1, \dots, n_N)$ and α part of the system,

$$\delta^2 S^\alpha = \frac{\partial^2 S^\alpha}{\partial U^2} (\delta U^\alpha)^2 + \frac{\partial^2 S^\alpha}{\partial V^2} (\delta V^\alpha)^2$$
$$+ 2 \frac{\partial^2 S^\alpha}{\partial U \partial V} (\delta U^\alpha)(\delta V^\alpha) + \sum_{i=1}^N \sum_{j=1}^N \frac{\partial^2 S^\alpha}{\partial n_i \partial n_j} (\delta n_i^\alpha)(\delta n_j^\alpha)$$
$$+ 2 \sum_{i=1}^N \frac{\partial^2 S^\alpha}{\partial n_i \partial U} (\delta n_i^\alpha)(\delta U) + 2 \sum_{i=1}^N \frac{\partial^2 S^\alpha}{\partial n_i \partial V} (\delta n_i^\alpha)(\delta V^\alpha)$$

- (8)

A similar expression can be written for the β part with $\delta^2(S^\alpha + S^\beta) < 0$. Before perturbation, α and β have identical conditions. If n_T is the total number of moles of the complete system,

$$n_T^\alpha \left(\frac{\partial^2 S^\alpha}{\partial z_i \partial z_j} \right) = n_T^\beta \left(\frac{\partial^2 S^\beta}{\partial z_i \partial z_j} \right) \quad - (9)$$

The conditions of isolation can be written as

$$(\delta U^\alpha)^2 = (\delta U^\beta)^2$$

$$(\delta V^\alpha)^2 = (\delta V^\beta)^2$$

$$(\delta n_i^\alpha)^2 = (\delta n_i^\beta)^2$$

Using Eqⁿ (9) and the above isolation conditions,

$$\begin{aligned} \delta^2 S = \frac{n_T}{n_T^\beta} & \left[\frac{\partial^2 S^\alpha}{\partial U^2} (\delta U^\alpha)^2 + 2 \frac{\partial^2 S^\alpha}{\partial U^\alpha \partial V^\alpha} (\delta U^\alpha) (\delta V^\alpha) \right. \\ & + \frac{\partial^2 S^\alpha}{\partial V^2} (\delta V^\alpha)^2 + 2 \sum_{i=1}^N \frac{\partial^2 S^\alpha}{\partial U \partial n_i} (\delta U^\alpha) (\delta n_i^\alpha) \\ & + 2 \sum_{i=1}^N \frac{\partial^2 S^\alpha}{\partial V \partial n_i} (\delta V^\alpha) (\delta n_i^\alpha) \\ & \left. + \sum_{i=1}^N \sum_{j=1}^N \frac{\partial^2 S^\alpha}{\partial n_i \partial n_j} (\delta n_i^\alpha) (\delta n_j^\alpha) \right] < 0 \quad - (10) \end{aligned}$$

It is to be noted that the above condition of stability contains only α superscripts in the properties. Hence, the choice of region β is immaterial. Following the inequality of (10), every fluctuation should lead to a "stable" equilibrium.

The general stability criteria can be given in terms of thermodynamic potentials. In energy representation,

$$U = y^{(0)} = f(x_1, x_2, \dots, x_m); \quad m = N+2$$

$$x_i \in \{S, V, n_1, \dots, n_N\}$$

The stability criteria can be written as

$$S^2 y^{(i)} = k \sum_{i=1}^m \sum_{j=1}^m \frac{\partial^2 y^{(i)}}{\partial x_i \partial x_j} s_{xi} s_{xj} > 0 \quad - (11)$$

k is a multiplicative constant and since we are interested in inequality it may be dropped since it is a positive number. However, since s_{xi} 's and s_{xj} 's can be positive or negative, it is possible only to comment upon the summation in Eq (11) and not the individual coefficients. For a stable system, $S^2 y^{(i)} = 0$ gives rise to limit of stability.

The necessary and sufficient condition for the stability of a system is

$$\frac{\partial^2 y^{(m-2)}}{\partial x_{m-1}^2} > 0 \quad - (12)$$

A handy notation for the above is $y_{(m-1)(m-1)}^{(m-2)} > 0$.

Here $m = N + 2$ for an N -component system.

$y^{(m-2)}$ is a higher order Legendre transformation.

An m th order determinant L_i is defined as

$$L_i = \begin{vmatrix} y_{(i+1)(i+1)}^{(i)} & y_{(i+2)(i+2)}^{(i)} & \dots & y_{(i+v)(i+1)}^{(i)} \\ y_{(i+2)(i+1)}^{(i)} & y_{(i+2)(i+2)}^{(i)} & \dots & y_{(i+2)(m-1)}^{(i)} \\ \vdots & \vdots & \ddots & \vdots \\ y_{(m-1)(i+1)}^{(i)} & y_{(m-1)(i+2)}^{(i)} & \dots & y_{(m-1)(m-1)}^{(i)} \end{vmatrix} \quad - (13)$$

A few low order L_i 's are as given below

$$L_0 = \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} & \dots & y_{1(m-1)}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} & \dots & y_{2(m-1)}^{(0)} \\ \vdots & \vdots & \ddots & \vdots \\ y_{(m-1)1}^{(0)} & y_{(m-1)2}^{(0)} & \dots & y_{(m-1)(m-1)}^{(0)} \end{vmatrix}$$

$$L_i = \begin{vmatrix} y_{12}^{(i)} & y_{13}^{(i)} & \dots & y_{1(m-1)}^{(i)} \\ y_{22}^{(i)} & y_{23}^{(i)} & \dots & y_{2(m-1)}^{(i)} \\ \vdots & \vdots & \ddots & \vdots \\ y_{(m-1)2}^{(i)} & y_{(m-1)3}^{(i)} & \dots & y_{(m-1)(m-1)}^{(i)} \end{vmatrix}$$

i in Eqⁿ (3) varies from 1 to $m-2$. The necessary and sufficient condition for stability is

$$L_i > 0 \quad \forall i \in \{1, 2, \dots, m-2\}$$

Consider the case of a ternary system for example. $N = 3$. The stability conditions are

$$y_{(m-1)(m-1)}^{(m-2)} > 0$$

where $m = N+2 = 5$. Therefore,

$$y_{11}^{(0)} > 0$$

$$y_{22}^{(1)} > 0$$

$$y_{33}^{(2)} > 0$$

$$y_{44}^{(3)} > 0$$

If $y^{(0)} = U(S, V, n_1, \dots, n_N)$ then

$$y^{(1)} = A$$

$$y^{(2)} = G$$

$$y^{(3)} = \text{An unknown quantity say } B$$

Hence the conditions of stability are

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_{V, n_1, \dots, n_N} > 0$$

$$\left(\frac{\partial^2 A}{\partial V^2} \right)_{T, n_1, \dots, n_N} > 0$$

$$\left(\frac{\partial^2 G}{\partial n_i^2} \right)_{P, T, n_i^*} > 0$$

$$\left(\frac{\partial^2 B}{\partial n_i^2} \right)_{P, T, \mu_1, n_3, \dots} > 0$$

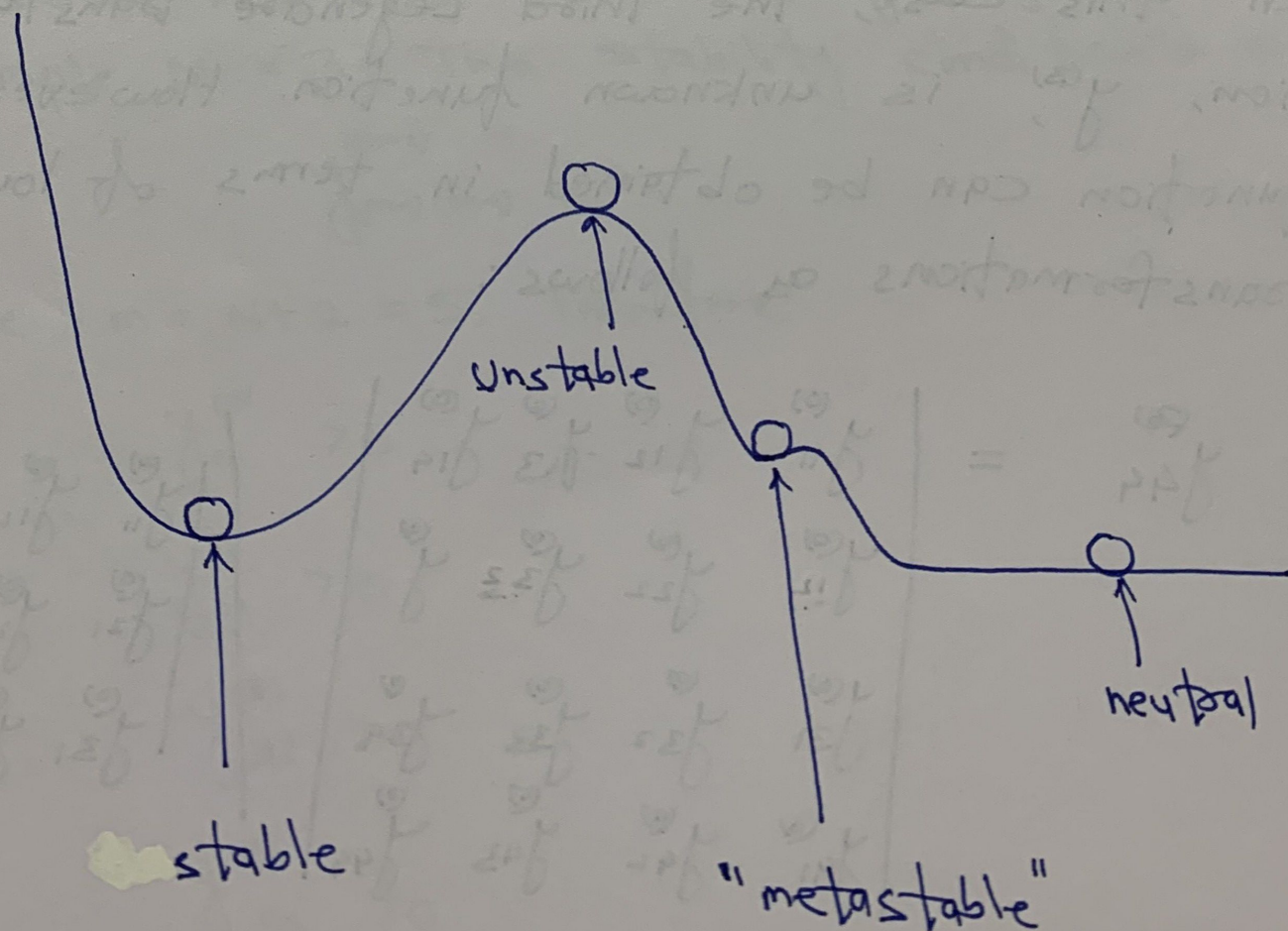
In this case, the third Legendre transformation, $y^{(3)}$, is unknown function. However, this function can be obtained in terms of lower transformations as follows:

$$y_{44}^{(3)} = \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} & y_{13}^{(0)} & y_{14}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} & y_{23}^{(0)} & y_{24}^{(0)} \\ y_{31}^{(0)} & y_{32}^{(0)} & y_{33}^{(0)} & y_{34}^{(0)} \\ y_{41}^{(0)} & y_{42}^{(0)} & y_{43}^{(0)} & y_{44}^{(0)} \end{vmatrix} \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} & y_{13}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} & y_{23}^{(0)} \\ y_{31}^{(0)} & y_{32}^{(0)} & y_{33}^{(0)} \end{vmatrix}$$

$$\Rightarrow \begin{vmatrix} U_{ss} & U_{sv} & U_{sn1} & U_{sn2} \\ U_{sv} & U_{vv} & U_{vn1} & U_{vn2} \\ U_{sn1} & U_{vn1} & U_{nn1} & U_{n2n1} \\ U_{sn2} & U_{vn2} & U_{nn2} & U_{n2n2} \end{vmatrix} > 0$$

If the form of the fundamental equation is changed then we obtain a completely different set of stability criteria. Test of only one set of criteria obtained by any one of the fundamental equations is sufficient.

On a thermodynamic potential landscape, the equilibria can be visualized as gravitational potential landscape as follows.



Stability criteria can be used to develop phase diagrams. Let us consider a pure component system. For any single component system,

$$U = y^{(0)} = f(s, v, n) \\ \Rightarrow y^{(0)} = f(x_1, x_2, x_3)$$

The conditions of stability require

$$L_i > 0$$

In this case $m = N + 2 = 3$. Therefore $i = 0, 1$.

$$\Rightarrow L_0 > 0$$

$$L_1 > 0$$

$$L_0 = \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} \end{vmatrix} > 0$$

$$\Rightarrow \begin{vmatrix} U_{ss} & U_{sv} \\ U_{rs} & U_{rv} \end{vmatrix} > 0 \quad - (14)$$

$$L_1 = y_{22}^{(1)} > 0 \quad - (15)$$

For the above ordering of variables $y^{(0)} = A$

$$\Rightarrow A_{vv} > 0 \quad - (16)$$

Equations (14) and (15) give all the criteria required to establish the stability of the system.

Eqⁿ (6) is called the criterion of mechanical stability of the system. It may be used to develop the P-V projection of the vapour-liquid equilibrium phase diagram. According to this criterion,

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n} > 0$$

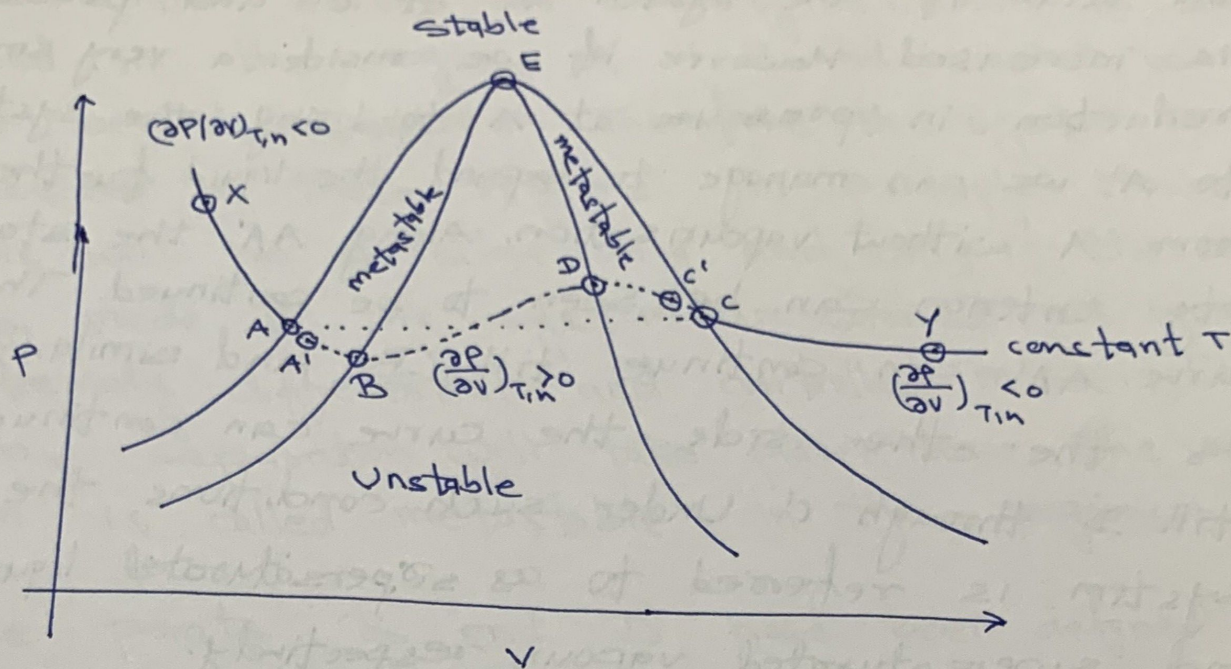
$$\Rightarrow \left\{ \left(\frac{\partial A}{\partial V}\right)_{T,n} \right\}_{T,n} > 0$$

$$\Rightarrow -\left(\frac{\partial P}{\partial V}\right)_{T,n} > 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_{T,n} < 0 \quad - (7)$$

Therefore, according to the criterion of mechanical stability, an increase in pressure of the system should result in a decrease in volume of the system at constant temperature and number of moles.

Now we can develop the P-V projection using the result in Eqⁿ (7). Consider a system at the coordinates given by X in the accompanying figure. According to the inequality given by (7), a reduction of pressure at constant temperature and total number of moles by volumetric expansion will follow a curve which will have a negative slope if the system is stable. At equilibrium, T and P are equal. Therefore, the points A and C show the phases at equilibrium.



Since $V_A < V_B$, V_A must correspond to the liquid phase volume while V_B must correspond to the vapour phase volume. Due to the stability criterion, slopes of XA and CY have to be drawn as negative.

They have different slopes due to different compressibilities of liquid and vapour phases. Pure liquid can be expanded till A and pure vapour can be compressed till C at constant T and n to obtain vapour liquid equilibrium.

Now suppose that the system is at A i.e. we have a saturated liquid. Large perturbations in the system pressure (resulting in further reduction of system pressure) will lead to the vapourisation of the liquid. Similarly, condensation

will occur if the system is at c and pressure is increased. However, if we consider a very small reduction in pressure at A to bring the system to A' , we can manage to expand the liquid further from A without vapourisation. Along AA' , the stability criterion can be seen to be continued. The curve AA' can continue till B and similarly for the other side, the curve can continue till D through c' . Under such conditions the system is referred to as supersaturated liquid and supersaturated vapour, respectively.

All along $AA'B$ and $cc'D$, the system is stable since $(\partial P / \partial V)_{T,n} < 0$. However, the slopes keep reducing so as to reach $(\partial P / \partial V)_{T,n} = 0$ at B and D . At these points where $(\partial P / \partial V)_{T,n} = 0$, slope inversion must take place so as to have $(\partial P / \partial V)_{T,n} > 0$. To summarise

Liquid phase: $X-A-A'-B \rightarrow (\partial P / \partial V)_{T,n} < 0$
 - stable

At $B \rightarrow (\partial P / \partial V)_{T,n} = 0$ - limit of stability

At $A \rightarrow$ saturated liquid

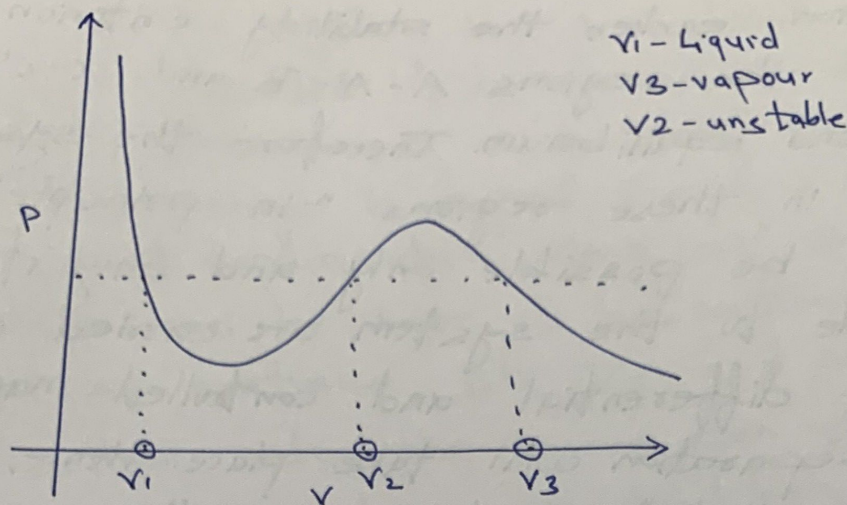
$A-A'-B \rightarrow$ supersaturated liquid.

A similar analysis can be done for the vapour phase also.

As mentioned earlier, the stability criterion is satisfied in the regions $A-A'-B$ and $C-C'-D$ which are beyond equilibrium. Therefore, the system can be observed in these regions "in principle". However, this will be possible only and only if the changes made to the system are carried out in an extremely differential and controlled manner. Else, phase separation will take place. Hence, the system is called "metastable" in these regions.

The points B and D have been defined as the limits of stability. Since the system is at extrema at these points, inversion in slope takes place between B and D i.e. between B and D , $(\partial P / \partial v)_{T, n} > 0$. Hence, the system is unstable in this region. If the system is at A' , and the pressure is reduced by such a value that the system crosses B then the system will enter the unstable region. In such a case, the system will cease to be in the liquid state and vaporisation will take place. Therefore, the amplitude of fluctuations is very important in metastable region.

The curve $X-A-A'-B-D-C'-C-Y$ is actually the solution to cubic equations of state like van der Waals equation of state. As can be seen from the next figure, mathematically three solutions (v_1, v_2, v_3) exist but only two are physical.



The above curve is obtained at a constant T . As T is increased, the difference between V_3 and V_1 decreases. The locus of points A & C gives rise to a bell shaped curve, called the "binodal curve". It is obtained by finding the saturation P and V for different T . The apex of the binodal curve where the two points A and C merge is the critical point E.

Similar to the binodal curve, a locus of points B and D can be traced. This also results in a bell-shaped curve with the same apex E. This curve is called the spinodal curve. Hence, the entire region can be divided into three regions:

Beyond binodal $\rightarrow$ stable system

Within spinodal $\rightarrow$ unstable system

Between binodal and spinodal curve
 $\rightarrow$ metastable system

P-T projection for a VLE system

Consider a vapour-liquid equilibrium system. At equilibrium,

$$\mu^{\text{vap}} = \mu^{\text{liq}} \quad - (1)$$

Similar equality will exist at standard state

$$\mu^{\text{ovap}} = \mu^{\text{oliq}} \quad - (2)$$

The relationship with fugacity is given as

$$\mu^{\text{vap}} = \mu^{\text{ovap}} + RT \ln f^{\text{vap}} \quad - (3)$$

$$\mu^{\text{liq}} = \mu^{\text{oliq}} + RT \ln f^{\text{liq}} \quad - (4)$$

From Eqⁿs (1) - (4), at equilibrium,

$$f^{\text{vap}} = f^{\text{liq}} \quad - (5)$$

$$\Rightarrow d(\ln f^{\text{vap}}) = d(\ln f^{\text{liq}})$$

For a pure component system, fugacity is a function of T and P. Therefore,

$$\begin{aligned} \left(\frac{\partial \ln f^{\text{vap}}}{\partial T} \right)_P dT + \left(\frac{\partial \ln f^{\text{vap}}}{\partial P} \right)_T dP \\ = \left(\frac{\partial \ln f^{\text{liq}}}{\partial T} \right)_P dT + \left(\frac{\partial \ln f^{\text{liq}}}{\partial P} \right)_T dP \end{aligned} \quad - (6)$$

$$\Rightarrow \frac{dP}{dT} = \frac{\left(\frac{\partial \ln f^{\text{liq}}}{\partial T} \right)_P - \left(\frac{\partial \ln f^{\text{vap}}}{\partial T} \right)_P}{\left(\frac{\partial \ln f^{\text{vap}}}{\partial P} \right)_T - \left(\frac{\partial \ln f^{\text{liq}}}{\partial P} \right)_T}$$

- (7)

Various derivatives of E_q^n (7) need to be determined.

$$\mu = \mu^0 + RT \ln f$$

$$\Rightarrow \frac{\mu^0}{T} = \frac{\mu}{T} - R \ln f \quad - (8)$$

At low pressures when the gas behaves ideally,
 $f = P$.

$$\Rightarrow \frac{\mu^0}{T} = \frac{\mu'}{T} - R \ln P' \quad - (9)$$

Primes in E_q^n (9) are used to denote limiting conditions. Since μ^0 is a function of T only, its value remains unchanged.

$$\frac{d}{dT} \left(\frac{\mu^0}{T} \right) = \frac{\partial}{\partial T} \left(\frac{\mu}{T} \right)_{P,n} - R \frac{\partial}{\partial T} (\ln f)_{P,n} \quad - (10)$$

$$\frac{d}{dT} \left(\frac{\mu^0}{T} \right) = \frac{\partial}{\partial T} \left(\frac{\mu'}{T} \right)_{P,n} - R \frac{\partial}{\partial T} (\ln P')_{P,n} \quad - (11)$$

Obviously the last term of E_q^n (11) is zero.

Further,

$$\mu = \frac{G}{n} = \frac{H}{n} - T \frac{S}{n}$$

$$\text{But } S = - \left(\frac{\partial G}{\partial T} \right)_{P,n} = - n \left(\frac{\partial \mu}{\partial T} \right)_{P,n}$$

$$\Rightarrow \mu = \frac{H}{n} + T \left(\frac{\partial \mu}{\partial T} \right)_{P,n}$$

$$\Rightarrow \frac{H}{n} = \mu - T \left(\frac{\partial \mu}{\partial T} \right)_{P,n}$$

$$\Rightarrow \frac{H}{T^2 n} = \frac{\mu}{T^2} - \frac{1}{T} \left(\frac{\partial \mu}{\partial T} \right)_{P,n}$$

$$\Rightarrow \frac{-H}{T^2 n} = \frac{\partial}{\partial T} \left(\frac{\mu}{T} \right)_{p,n} \quad - (12)$$

$$\therefore \frac{d}{dT} \left(\frac{\mu^0}{T} \right) = \frac{-H}{T^2 n} - R \frac{\partial}{\partial T} (\ln f)_{p,n} \quad - (13)$$

$$\frac{d}{dT} \left(\frac{\mu^0}{T} \right) = \frac{-H'}{T^2 n} \quad - (14)$$

From Eqⁿs (13) and (14),

$$\left(\frac{\partial (\ln f)}{\partial T} \right)_{p,n} = \frac{H' - H}{n R T^2} \quad - (15)$$

In general for an n-component system,

$$\left(\frac{\partial (\ln f_i)}{\partial T} \right)_{p,n} = \frac{\bar{H}_i' - \bar{H}_i}{R T^2}$$

Further,

$$\mu = \mu^0 + RT \ln f$$

$$\Rightarrow \left(\frac{\partial \mu}{\partial p} \right)_{T,n} = RT \left(\frac{\partial \ln f}{\partial p} \right)_{T,n}$$

$$\Rightarrow \left(\frac{\partial \ln f}{\partial p} \right)_{T,n} = \frac{V}{nRT} \quad - (16)$$

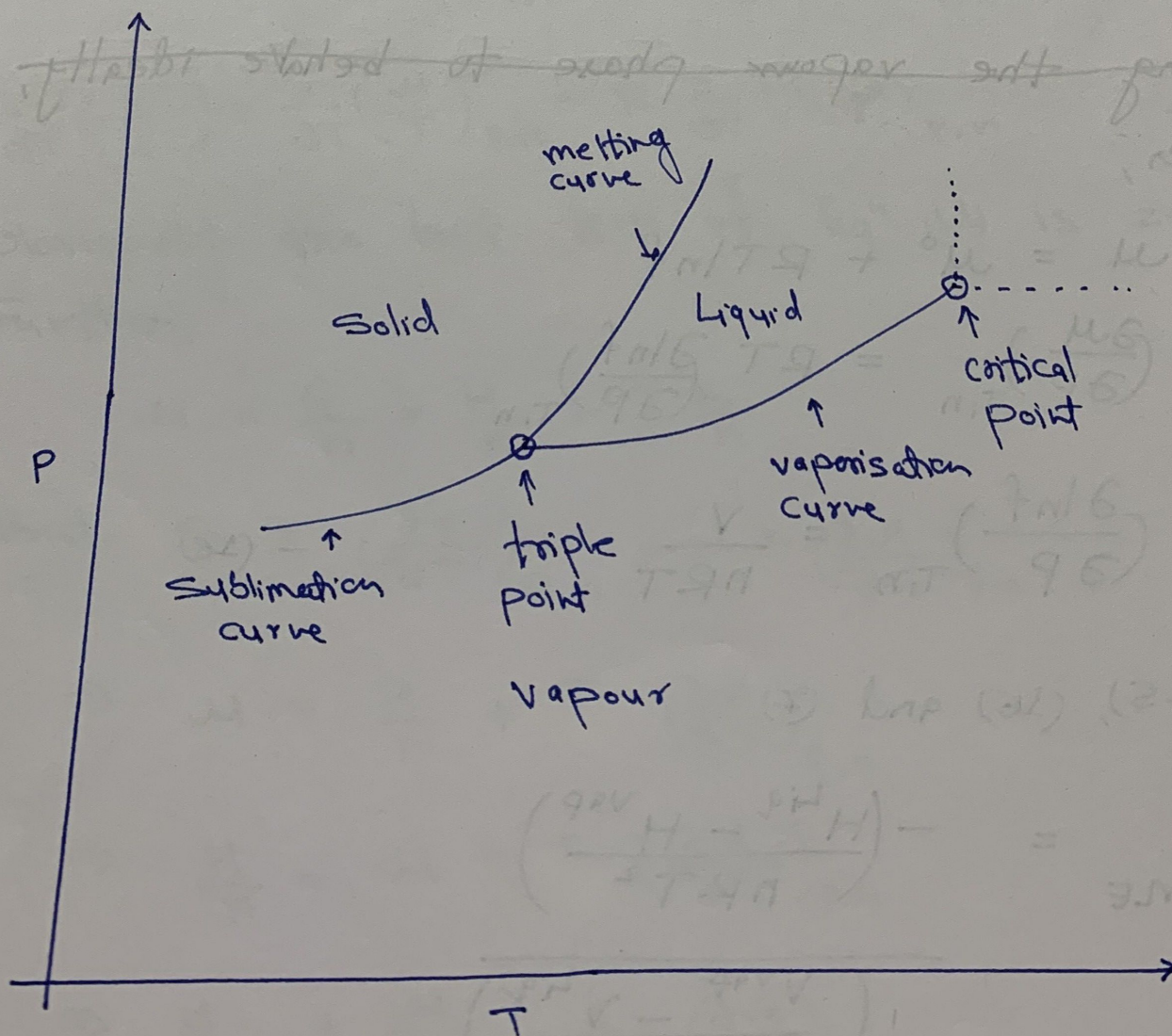
From (15), (16) and (7)

$$\left(\frac{dp}{dT} \right)_{VLE} = \frac{- \left(\frac{H^{Liq} - H^{Vap}}{n R T^2} \right)}{\left(\frac{V^{Vap} - V^{Liq}}{RT} \right)}$$

$$\Rightarrow \left(\frac{dP}{dT} \right)_{VLE} = \frac{H^{vap} - H^{Lq}}{T (V^{vap} - V^{Lq})}$$

$$\Rightarrow \left(\frac{dP}{dT} \right)_{VLE} = \frac{\Delta H}{T \Delta V} \quad (47)$$

Equation (47) is known as the Clausius-Clapeyron equation. It can be used to determine the P-T projection. Since at equilibrium, $P = P^{vap} = P^L$, it can be used to determine the vapour pressure as a function of temperature. A representative P-T projection for a pure fluid is shown below. Each curve represents coexistence of two phases.



It can be seen from the phase diagram that the system is invariant at the triple point. Three curves can be defined as follows:

Sublimation curve - co-existence of solid and vapour

Vapourisation curve - co-existence of liquid and vapour

Melting curve - co-existence of solid and liquid

Slopes of all three curves can be seen to be positive. This is following Eqⁿ (17). This means that $\Delta P / \Delta T > 0$ i.e. with an increase in temperature pressure also increases. Whereas this is true for sublimation and vaporisation curves of all substances, opposite trends may be observed for melting curves of certain substances, water for e.g. It is also to be noted that melting and sublimation curves do not terminate but the vaporisation curve terminates at a point called the critical point. We can move along the vaporisation curve with co-existence of vapour and liquid. However, there exists a temperature where liquid ceases to exist but the material is not vapour either. The properties of the material become such that vapour-liquid distinction is not possible. This state is called the super-critical state. Three cases arise:

$T > T_c$, $P > P_c$ - supercritical state

$T > T_c$, $P < P_c$ - gas

$T < T_c$, $P > P_c$ - compressed liquid-like

Now we focus our attention on multicomponent systems. Temperature, pressure and mole fraction are the generally measured variables in any multicomponent system. We develop relationships among these quantities here. Consider a two-phase two-component system.

Phases - α and β

Components - A and B

The conditions of equilibrium are

$$T^{\alpha} = T^{\beta}$$

$$P^{\alpha} = P^{\beta}$$

$$\mu_A^{\alpha} = \mu_A^{\beta}$$

$$\mu_B^{\alpha} = \mu_B^{\beta}$$

$$f_A^{\alpha} = f_A^{\beta}$$

$$f_B^{\alpha} = f_B^{\beta}$$

For multiphase-multicomponent system, fugacities are functions of T , P and x_i .

$$f_A = f(T, P, x_A)$$

$$\Rightarrow d(\ln f_A^{\alpha}) = \left. \frac{\partial (\ln f_A^{\alpha})}{\partial T} \right|_{P, x_A} dT^{\alpha} + \left. \frac{\partial (\ln f_A^{\alpha})}{\partial P} \right|_{T, x_A} dP^{\alpha} + \left. \frac{\partial (\ln f_A^{\alpha})}{\partial x_A} \right|_{T, P} dx_A^{\alpha}$$

$$\Rightarrow d(\ln f_A^{\alpha}) = - \left(\frac{\bar{H}_A - \bar{H}_A'}{RT^2} \right) dT^{\alpha} + \left(\frac{\bar{V}_A}{RT} \right) dP^{\alpha} + \left. \frac{\partial (\ln f_A^{\alpha})}{\partial x_A} \right|_{T, P} dx_A^{\alpha}$$

Similarly for the β phase,

$$d(\ln f_A^\beta) = -\left(\frac{\bar{H}_A^\beta - \bar{H}_A'}{RT^2}\right)dT + \left(\frac{\bar{V}_A^\beta}{RT}\right)dP + \frac{\partial(\ln f_A^\beta)}{\partial x_A}\bigg|_{T,P} dx_A^\beta \quad (19)$$

Expressions similar to Eq's (18) and (19) can be written for the component B. The corresponding equations can be equated following the equilibrium conditions to give

$$-\left(\frac{\bar{H}_A^\alpha - \bar{H}_A^\beta}{RT^2}\right)dT + \left(\frac{\bar{V}_A^\alpha - \bar{V}_A^\beta}{RT}\right)dP + \frac{\partial(\ln f_A^\alpha)}{\partial x_A} \frac{dx_A^\alpha}{dx_A^\beta} d x_A^\beta = 0 \quad (20)$$

$$-\left(\frac{\bar{H}_B^\alpha - \bar{H}_B^\beta}{RT^2}\right)dT + \left(\frac{\bar{V}_B^\alpha - \bar{V}_B^\beta}{RT}\right)dP + \frac{\partial(\ln f_B^\alpha)}{\partial x_B} \frac{dx_B^\alpha}{dx_B^\beta} d x_B^\beta = 0 \quad (21)$$

Eq's (20) and (21) involve three differentials, dT , dP and dx_A and two equations. By suitable eliminations, quantitative relationships relating two quantities can be obtained.

The Gibbs - Duhem equation at constant temperature and pressure in terms of fugacities and mole fractions can be written as

$$x_A^\pi \left(\frac{\partial \ln f_A^\pi}{\partial x_A} \right) + x_B^\pi \left(\frac{\partial \ln f_B^\pi}{\partial x_B} \right) = 0 \quad (22)$$

Since $x_A + x_B = 1$, $dx_A = -dx_B$. Hence, Eqⁿ (21) can be written in terms of dx_A by replacing all dx_B 's by $-dx_A$'s. We carry out the following operation.

$$\begin{aligned} & \text{Eqⁿ (20)} \times x_A^\alpha + \text{Eqⁿ (21)} \times x_B^\alpha \\ & - \left\{ \frac{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)}{RT^2} \right\} dT \\ & + \left\{ \frac{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)}{RT} \right\} dP \\ & - \left(x_A^\alpha - \frac{x_A^\beta x_B^\alpha}{x_B^\beta} \right) \left(\frac{\partial \ln f_A^\beta}{\partial x_A} \right) dx_A^\beta = 0 \quad - (23) \end{aligned}$$

$$\begin{aligned} \Rightarrow dP &= \frac{1}{T} \left\{ \frac{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\} dT \\ &+ RT \left\{ \frac{(x_A^\alpha - x_A^\beta x_B^\alpha / x_B^\beta) (\partial \ln f_A^\beta / \partial x_A)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\} dx_A^\beta \quad - (24) \end{aligned}$$

Eqⁿ (24) can be used to determine the slopes of various projections of the phase diagram. For example, the slope of P-T projection can be determined as

$$\left(\frac{\partial P}{\partial T} \right)_{x_A^\beta [\alpha-\beta]} = \frac{1}{T} \left\{ \frac{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^\beta) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^\beta)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^\beta) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^\beta)} \right\} \quad - (25)$$

Similarly,

$$\left(\frac{\partial P}{\partial x_A^B}\right)_{T[\alpha-\beta]} = RT \left\{ \frac{(x_A^\alpha - x_A^B x_B^\alpha / x_B^B) (\partial \ln f_A^B / \partial x_A^B)}{x_A^\alpha (\bar{V}_A^\alpha - \bar{V}_A^B) + x_B^\alpha (\bar{V}_B^\alpha - \bar{V}_B^B)} \right\} \quad - (26)$$

$[\alpha-\beta]$ in the above equations denotes the conditions at which phases α and β co-exist at equilibrium.

The variation in T with x_A^B can be determined using $\pi\gamma z-1$ rule.

$$\left(\frac{\partial T}{\partial x_A^B}\right)_P \left(\frac{\partial x_A^B}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{x_A^B} = -1$$

$$\Rightarrow \left(\frac{\partial T}{\partial x_A^B}\right)_{P[\alpha-\beta]} = -RT^2 \left\{ \frac{(x_A^\alpha - x_A^B x_B^\alpha / x_B^B) (\partial \ln f_A^B / \partial x_A^B)}{x_A^\alpha (\bar{H}_A^\alpha - \bar{H}_A^B) + x_B^\alpha (\bar{H}_B^\alpha - \bar{H}_B^B)} \right\} \quad - (27)$$

For an N -component π -phase system, for each component, $\pi-1$ equations of the following form can be written.

$$\frac{-(\bar{H}_i^\alpha - \bar{H}_i^B)}{RT^2} dT + \frac{(\bar{V}_i^\alpha - \bar{V}_i^B)}{RT} dP + \sum_{j \neq k}^N \left\{ \left(\frac{\partial \ln f_i^\alpha}{\partial x_j^\alpha}\right) dx_j^\alpha - \left(\frac{\partial \ln f_i^B}{\partial x_j^B}\right) dx_j^B \right\} = 0 \quad - (28)$$

slopes of various projections can be determined and the phase diagram can be drawn.

Let us now consider the case of a non-volatile solute dissolved in a volatile solvent. The vapour pressure in this case is purely of the solvent. If the system is maintained in such a manner that the solute concentration does not vary with T or P then for the solvent at equilibrium,

$$f_{\text{solvent}}^{\text{vap}} = f_{\text{solvent}}^{\text{Lq}} \quad - (29)$$

From Clausius-Clayperon equation,

$$\left(\frac{\partial P}{\partial T}\right)_{x[\text{vap-Lq}]} = \frac{H_{\text{solvent}}^{\text{vap}} - H_{\text{solvent}}^{\text{Lq}}}{T(V_{\text{solvent}}^{\text{vap}} - V_{\text{solvent}}^{\text{Lq}})} \quad - (30)$$

Eqⁿ (30) can be seen to be a limiting case of Eqⁿ (25). The numerator of Eqⁿ (30) RHS is the change in enthalpy of the system when one mole of the solvent is vaporised keeping the mole fraction of the solute in the liquid phase constant. Another way that the system can be maintained is by keeping the solution saturated with the solid all the time. For this, a small amount of undissolved solute must be present in the system all the time. The system now becomes a three-phase system.

Phase 1: Solution (liquid)

Phase 2: Solvent vapour

Phase 3: Solid solute

The equilibrium relations can be written as follows:

$$f_{\text{solvent}}^{\text{vap}} = f_{\text{solvent}}^{\text{liq}} \quad - (31)$$

$$f_{\text{solute}}^{\text{liq}} = f_{\text{solute}}^{\text{solid}} \quad - (32)$$

The fugacity of the vapour phase can be expanded in T and P while for the liquid phase, the expansion needs to be in T , P and x_{solvent} . From Eqⁿ (31),

$$d \ln f_{\text{solvent}}^{\text{vap}} = d \ln f_{\text{solvent}}^{\text{liq}}$$

$$\Rightarrow \frac{\partial}{\partial T} (\ln f_{\text{solvent}}^{\text{vap}})_P dT + \frac{\partial}{\partial P} (\ln f_{\text{solvent}}^{\text{vap}})_T dP$$

$$= \frac{\partial}{\partial T} (\ln f_{\text{solvent}}^{\text{liq}})_P dT + \frac{\partial}{\partial P} (\ln f_{\text{solvent}}^{\text{liq}})_T dP$$

$$+ \frac{\partial}{\partial x_{\text{solvent}}} (\ln f_{\text{solvent}}^{\text{liq}}) dx_{\text{solvent}} \quad - (33)$$

$$\Rightarrow - \left(\frac{H_{\text{solvent}}^{\text{vap}} - \overline{H}_{\text{solvent}}^{\text{liq}}}{RT^2} \right) dT + \left(\frac{V_{\text{solvent}}^{\text{vap}} - \overline{V}_{\text{solvent}}^{\text{liq}}}{RT} \right) dP$$

$$= \frac{\partial}{\partial x_{\text{solvent}}} (\ln f_{\text{solvent}}^{\text{liq}}) dx_{\text{solvent}} \quad - (34)$$

Similarly from Eqⁿ (32),

$$\begin{aligned}
 & - \left(\frac{H_{\text{solute}}^{\text{solid}} - \bar{H}_{\text{solute}}^{\text{liq}}}{RT^2} \right) dT + \left(\frac{V_{\text{solute}}^{\text{solid}} - \bar{V}_{\text{solute}}^{\text{liq}}}{RT} \right) dP \\
 & = \frac{\partial}{\partial x_{\text{solute}}} (\ln f_{\text{solute}}^{\text{liq}}) dx_{\text{solute}} \quad - (35)
 \end{aligned}$$

Eqⁿs (34) and (35) must be solved simultaneously to obtain the P-T relationship. We carry out the following operation:

$$\text{Eqⁿ (34)} \times x_{\text{solvent}}^{\text{liq}} + \text{Eqⁿ (35)} \times x_{\text{solute}}^{\text{liq}}$$

$$\begin{aligned}
 \Rightarrow & -x_{\text{solvent}} \left(\frac{H_{\text{solvent}}^{\text{vap}} - \bar{H}_{\text{solvent}}^{\text{liq}}}{RT^2} \right) dT + x_{\text{solvent}} \left(\frac{V_{\text{solvent}}^{\text{vap}} - \bar{V}_{\text{solvent}}^{\text{liq}}}{RT} \right) dP \\
 & - x_{\text{solute}} \left(\frac{H_{\text{solute}}^{\text{solid}} - \bar{H}_{\text{solute}}^{\text{liq}}}{RT^2} \right) dT + x_{\text{solute}} \left(\frac{V_{\text{solute}}^{\text{solid}} - \bar{V}_{\text{solute}}^{\text{liq}}}{RT} \right) dP \\
 & = \left\{ x_{\text{solvent}} \left(\frac{\partial \ln f_{\text{solvent}}^{\text{liq}}}{\partial x_{\text{solvent}}} \right)_{T,P} + x_{\text{solute}} \left(\frac{\partial \ln f_{\text{solute}}^{\text{liq}}}{\partial x_{\text{solute}}} \right)_{T,P} \right\} dx_{\text{solvent}} \quad - (36)
 \end{aligned}$$

From Gibbs-Duhem equation, the RHS of Eqⁿ (36) becomes zero. Therefore,

$$\left(\frac{dP}{dT} \right)_{[S-L-V]} =$$

$$x_{\text{solvent}} (H_{\text{solvent}}^{\text{vap}} - \bar{H}_{\text{solvent}}^{\text{liq}}) + x_{\text{solute}} (H_{\text{solute}}^{\text{solid}} - \bar{H}_{\text{solute}}^{\text{liq}})$$

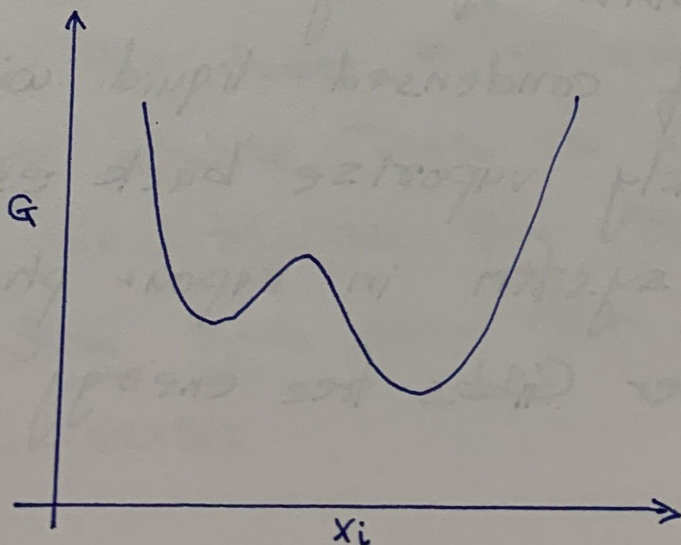
$$T \left\{ x_{\text{solvent}} (V_{\text{solvent}}^{\text{vap}} - \bar{V}_{\text{solvent}}^{\text{liq}}) + x_{\text{solute}} (V_{\text{solute}}^{\text{solid}} - \bar{V}_{\text{solute}}^{\text{liq}}) \right\}$$

$$- (37)$$

Phase transitions and critical phenomena

As has been discussed previously, the vapour-liquid co-existence curve does not extend indefinitely but terminates at the coordinates which is referred to as the critical point. When both temperature and pressure are higher than the critical values then the system is said to be in the supercritical state.

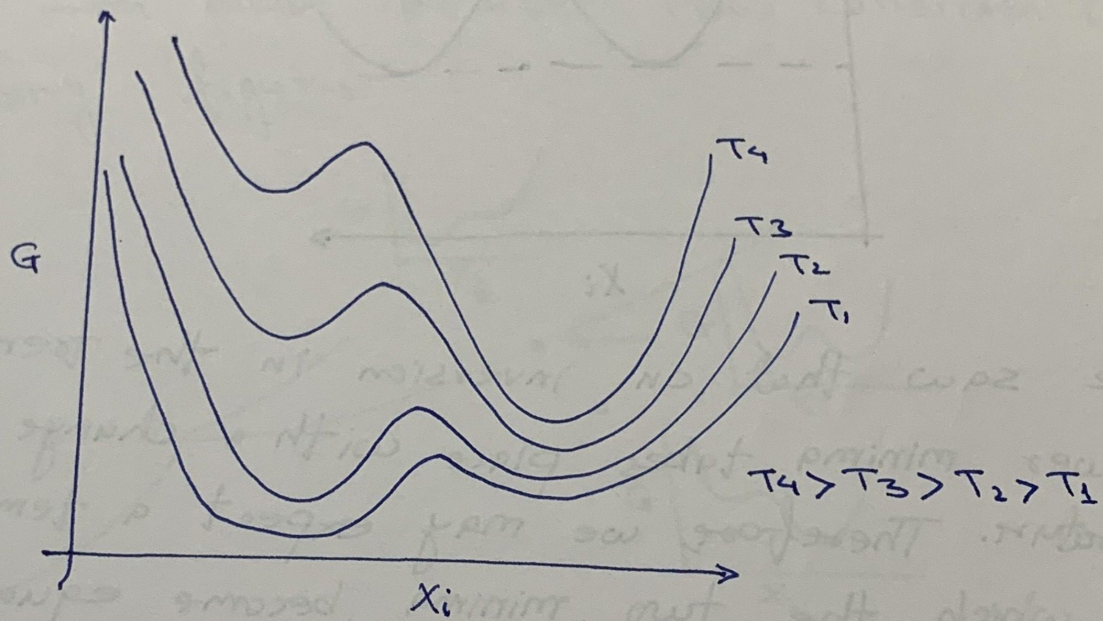
Consider water as an example to analyse the critical phenomena and phase transitions. Suppose we have a vessel full of water vapour at 1 atm. The vapour is present just above the boiling point. Consider a small section of the vapour. The macrostate of this system is described by specifying (T, P) . The Gibbs free energy therefore, is a suitable descriptor of this section. The Gibbs free energy as a function of the independent variables may not be a monotonous function and can have multiple minima. Consider the form of G shown in the figure below.



x_i is any descriptor of the system. If we consider x_i as the molar volume then it can be seen that for the accompanying figure, the system exhibits larger stability when the molar volume of the system is large. Now consider fluctuations induced to the system. If the fluctuations take the system to the minima of higher free energy by overcoming the barrier, then the system will experience a local minima.

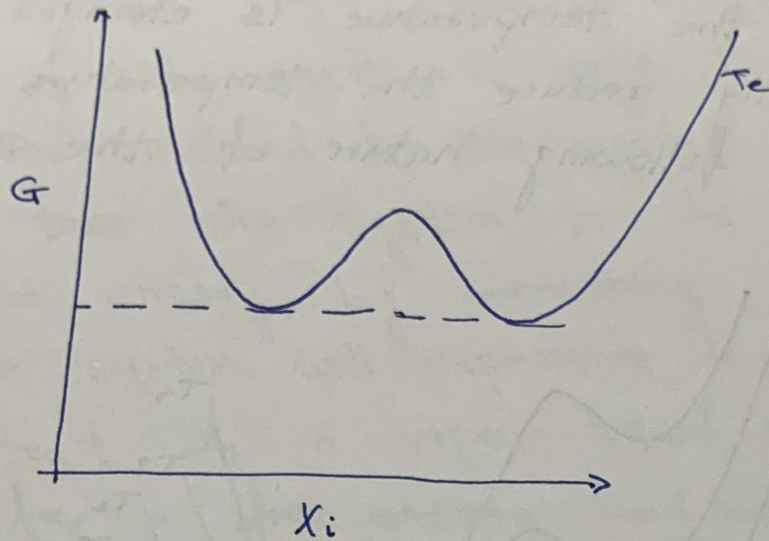
In context of a vapour-liquid equilibrium system, for a free energy landscape like the one shown in the accompanying figure, the system will be present as vapour as the vapour has higher molar volume than the liquid. Fluctuations may take the system (as a part of it) to another minima corresponding to the low molar volume liquid phase. However, if the fluctuations can result in overcoming the barrier, the same fluctuations will bring the system back to the state of higher stability. Hence, small pockets of condensed liquid within the vapour will quickly vaporise back essentially maintaining the system in vapour phase only which has a lesser Gibbs free energy at a given set of T and P .

The free energy landscape shown in the previous figure is for a given temperature. Now we need to analyse what happens to this landscape as the temperature is changed. As we systematically reduce the temperature, we observe the following nature of the curves.



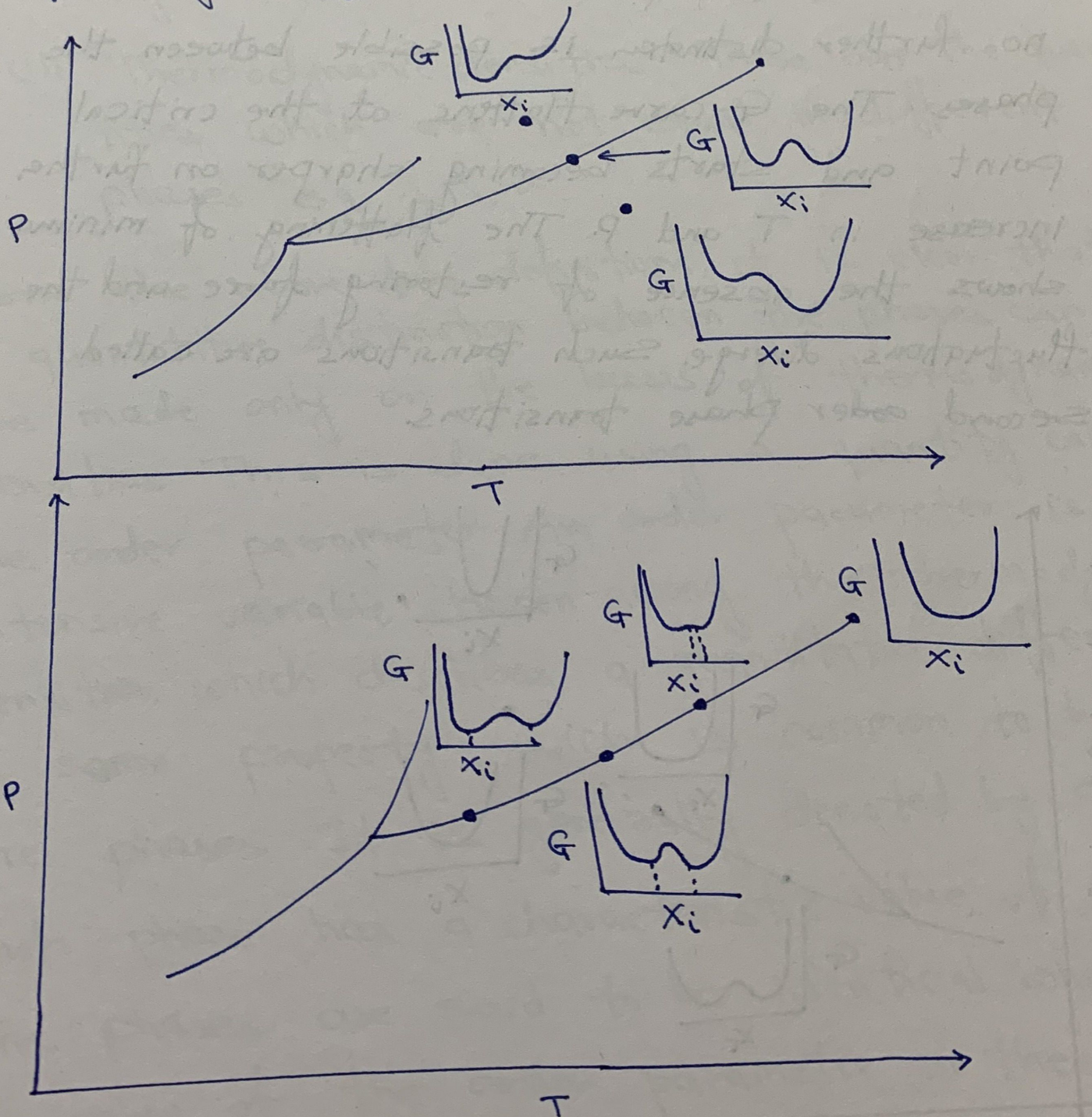
We can note from the above free energy landscape that with a reduction in temperature, the behaviour of G changes and the lower minima shifts to that corresponding to the lower molar volume. This means that at lower temperatures, the lower molar volume liquid phase is more stable. This is also what is observed in reality; as the temperature is reduced, condensation takes place from the vapour phase and vice-versa.

Now consider a temperature T_e at which the energy landscape looks like the one given below.

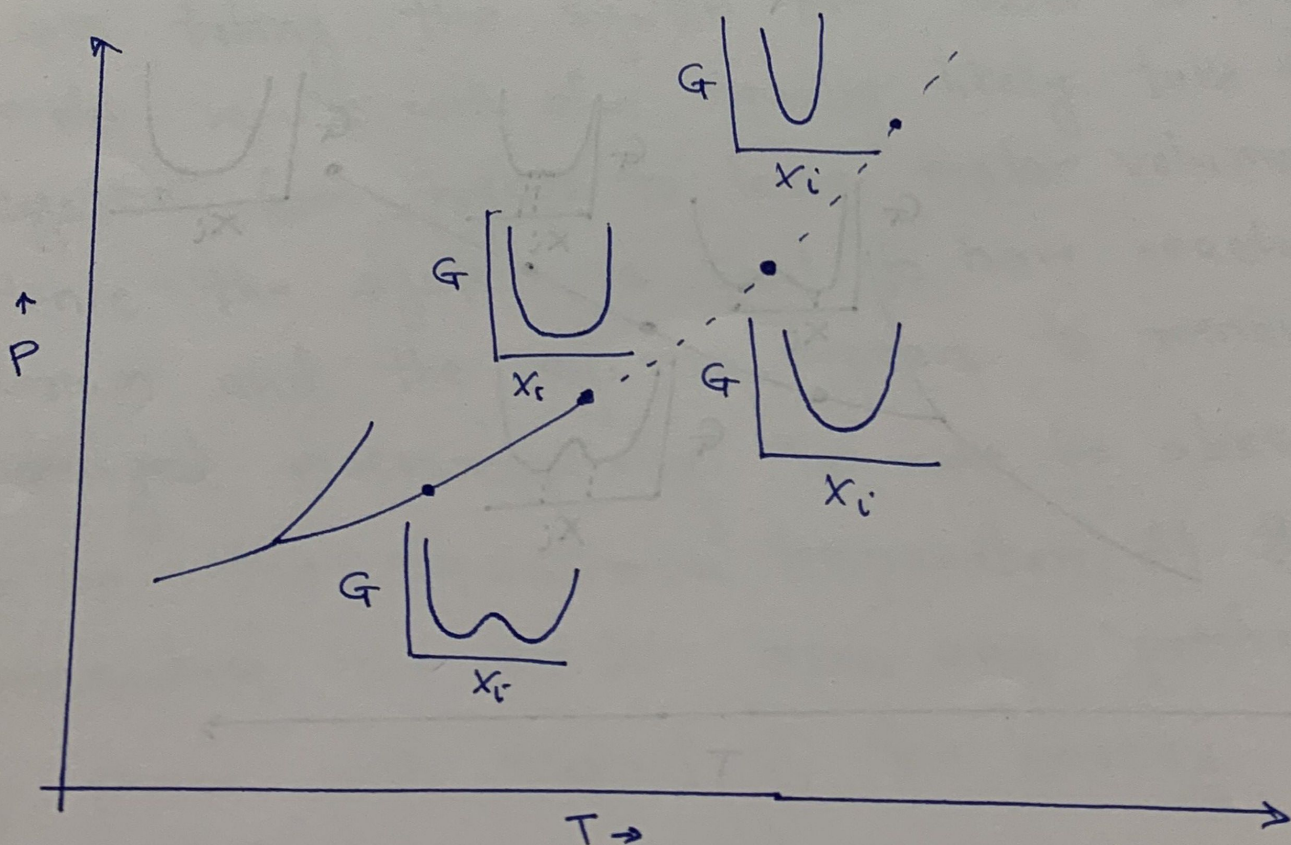


We saw that an inversion in the trend of lower minima takes place with a change in temperature. Therefore, we may expect a temperature at which the two minima become equal. In such a condition, a fluctuation which results into taking the system from lower to higher molar volume will also equally likely take the system from higher to lower molar volume. Hence, the system is said to have reached equilibrium and the system appears to remain unchanged macroscopically. T_e can be observed to be the equilibrium temperature. At this temperature, the system loses any "preference" of phase with respect to free energy.

The phase transition described above required the equality of Gibbs free energy. However, there was a finite difference in the molar volume of the two phases. Such phase transition taking place with equal Gibbs free energy but with discontinuous other variables is called first order phase transition. Now consider the following figures.



It can be seen that at equilibrium, G is equal in two phases. However, due to differences in the molar volume, the minima are separated. As we move along the equilibrium curve, the differences in the molar volumes decrease continuously with increments in temperature. At the critical point, the two minima merge i.e. the liquid and the vapour molar volumes become equal. The two phases then become alike and no further distinction is possible between the phases. The G -curve flattens at the critical point and starts becoming sharper on further increase in T and P . The flattening of minima shows the absence of restoring force and the fluctuations diverge. Such transitions are called second order phase transitions.



Landau theory of phase transitions:

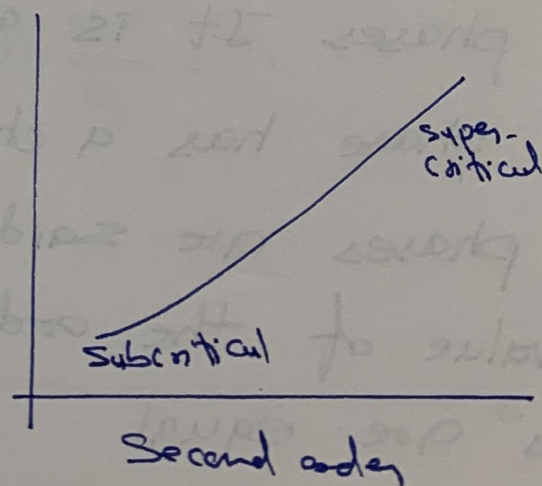
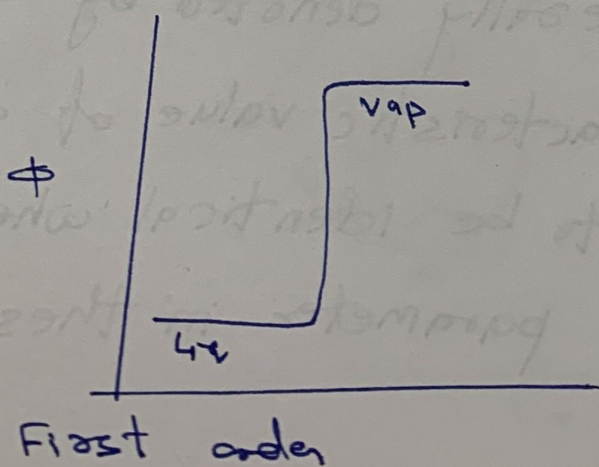
Landau explained phase transitions on the basis of order parameters and a quantity called the Landau potential. All intensive quantities associated with a multiphase system can be categorised into two classes:

- (i) Thermodynamic fields: These are the quantities which remain constant across the phases e.g. T, P, μ .
- (ii) Thermodynamic densities: These are the quantities which are not equal in different phases e.g. S, ρ, v .

From the above two definitions, it is clear that a quantitative distinction between the phases can be made only on the basis of thermodynamic densities. This is done using a quantity called the order parameter. An order parameter is an intensive variable, chosen among the thermodynamic densities, which describes a quantitative difference in some property which is common to both the phases. It is generally denoted by ϕ . Each phase has a characteristic value of ϕ . The phases are said to be identical when the value of the order parameter in these phases are equal.

The order parameter that can be used conveniently for the description of vapour-liquid equilibrium is the specific volume. Usually, since we are interested in difference in the order parameter across phases, the order parameter is set to zero in one of the phases while it has a non-zero value in the other phase. The phase change is identified by the change in the value of the order parameter. The phase with $\Phi = 0$ is called the disordered phase while the phase with $\Phi > 0$ is called the ordered phase.

The order parameter may change continuously with phase change or may change suddenly. The nature of continuity/discontinuity defines the order of phase transition. A phase transition is said to be first order if there is a sudden change in the order parameter while it is called second order phase transition if the order parameter changes continuously with a change in phase.



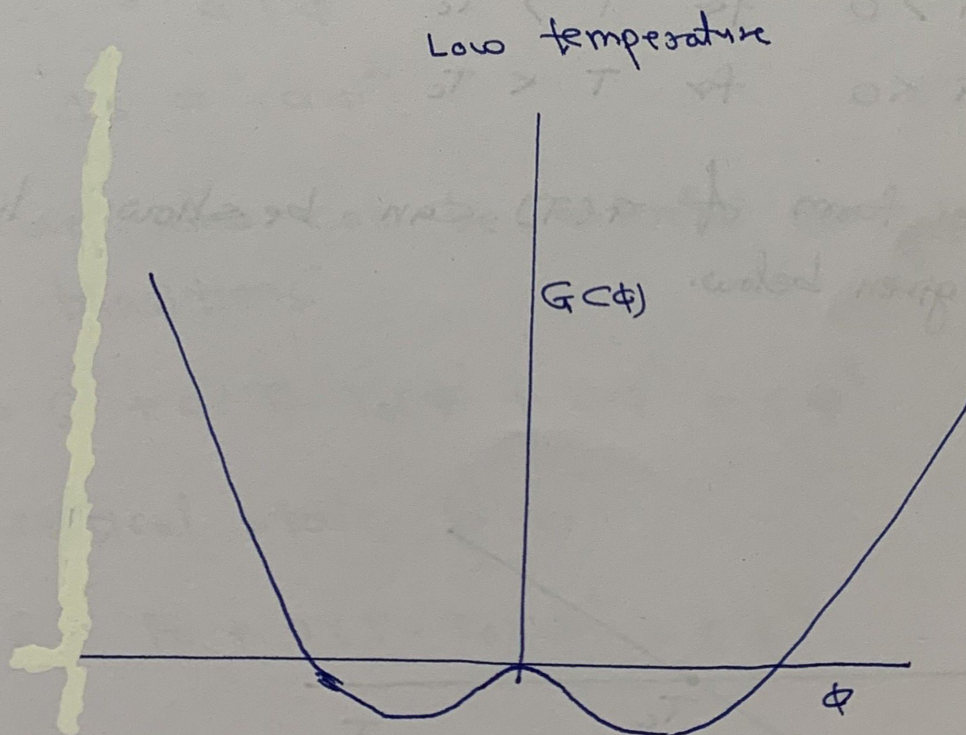
Landau defined a quantity called Landau potential which can be written as a function of the order parameter. To explain the phase transition, he proposed that the potential $F(\phi)$ can be expanded as a power series of ϕ .

$$F(\phi) = F_0 + a\phi + b\phi^2 + c\phi^3 + \dots \quad (1)$$

From the nature of the plots encountered previously, we require $F(-\phi) = F(\phi)$. Hence the series must have only even powers.

$$\text{Consider } F(\phi) = F_0 + (-a)\phi^2 + b\phi^4 \quad (2)$$

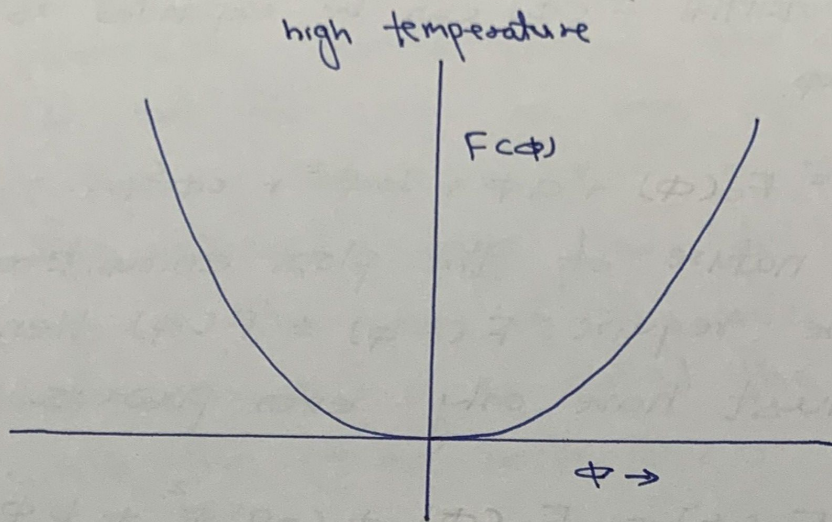
The variation of the above function for suitably chosen values of 'a' and 'b' is shown below.



The above nature looks similar to the curve at equilibrium.

Now consider the high temperature behaviour of the same function.

$$F(\phi) = F_0 + a\phi^2 + b\phi^4 \quad - (3)$$



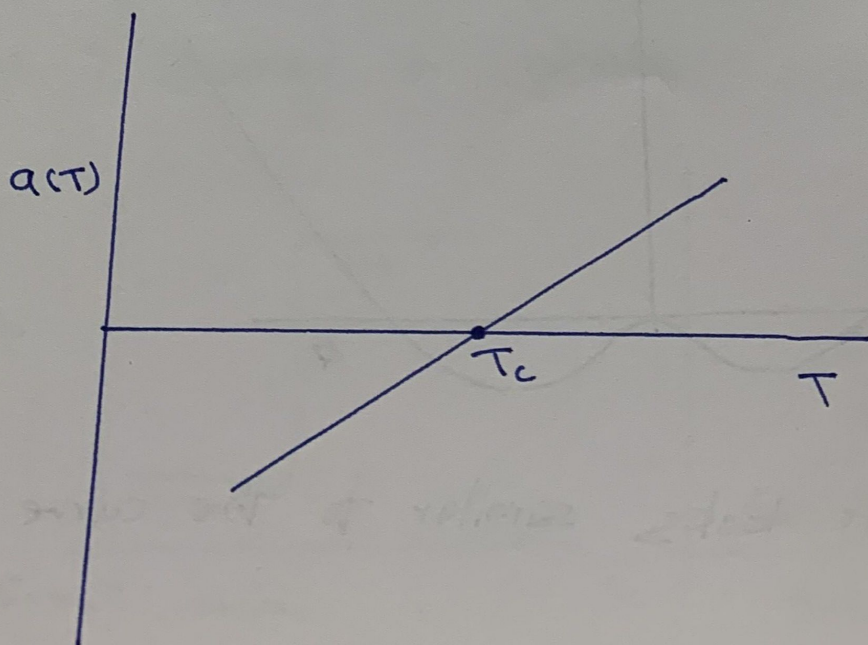
Hence, the potential can be generalised as

$$F(\phi) = F_0 + a\phi^2 + b\phi^4$$

with $a > 0$ for $T > T_c$

$a < 0$ for $T < T_c$

Thus, the form of $a(T)$ can be shown like the one given below.



$$\Rightarrow F(\phi) = F_0(\phi) + a(T-T_c)\phi^2 + b\phi^4 \quad - (4)$$

With this form of the equation, the coefficients can be assumed to be temperature independent.

We now need to analyze the extrema of Eqⁿ (4).

$$\frac{\partial F(\phi)}{\partial \phi} = 2a(T-T_c)\phi + 4b\phi^3 = 0$$

$$\Rightarrow 2b\phi^3 = a(T-T_c)\phi$$

$$\Rightarrow \phi = 0, \quad \phi^2 = \frac{a(T-T_c)}{2b}$$

Now if the potential is Gibbs free energy then

$$G = G_0 + a(T-T_c)\phi^2 + b\phi^4$$

$$= G_0 + \Delta H - T\Delta S$$

$$\Rightarrow \Delta H = aT_c\phi^2 + b\phi^4$$

$$-T\Delta S = aT\phi^2$$

$$\Rightarrow \Delta S = -a\phi^2$$

The above idea can be extended to get "tricritical phase transitions."

$$F = F_0 + a(T-T_c)\phi^2 + b\phi^4 + c\phi^6 \quad - (5)$$

For tricritical state, $b=0$

$$\Rightarrow F = F_0 + a(T-T_c)\phi^2 + c\phi^6 \quad - (6)$$