STUDY MATERIAL

VIVEKANANDA COLLEGE
THAKURPUKUR

NAAC Accredited Grade—A

Subject: Physical Chemistry

Topic: Phase Transition

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Introduction:

Boiling, freezing and the ferromagnetism are all examples of changes of phase without change of composition. The guiding principle is the tendency of systems at constant T and P to shift to lower Gibbs free energy. Since we are dealing with pure substances, so we must consider it in terms of chemical potential (i.e. molar Gibbs free energy) and so the tendency to change is in the direction of decreasing chemical potential. It must never be forgotten, however, that three alternative ways of expressing the direction: for all the systems, the tendency of the Universe to greater disorder: e.g. while freezing, there is a compensating increase of entropy in the surroundings (as result of heat release) and overall effect is the entropy of the Universe will increase.

Consider a system in which the chemical potential is not uniform and suppose that at one point its value is μ_1 and at another μ_2. When an amount of the substance say dn is transferred from one point to the other, the overall change in molar Gibbs free energy = $(\mu_2 - \mu_1)$. dn. If $\mu_1 > \mu_2$, then it has the tendency to occur spontaneously but when $\mu_1 = \mu_2$, then there is no change in molar Gibbs free energy and the system is in internal equilibrium.

Stability of the phases of a pure substance:

Based on the third law of thermodynamics, the entropy of a substance is always positive.

We know that, $d\mu = -\bar{S}\,dT + \bar{V}\,dP$, therefore $(\delta\mu / \delta T)_{P} = -\bar{S}$; $(\delta\mu / \delta P)_{T} = \bar{V}$

For the three phases of a single substance, we have

$(\delta\mu_{solid} / \delta T)_{P} = -\bar{S}_{solid}$; $(\delta\mu_{liquid} / \delta T)_{P} = -\bar{S}_{liquid}$; $(\delta\mu_{gas} / \delta T)_{P} = -\bar{S}_{gas}$

At any temperature, $\bar{S}_{gas} >> \bar{S}_{liquid} >> \bar{S}_{gas}$. Thus, for the μ vs T plot, the solid has a slight negative slope. The μ vs T curve for the liquid is slightly more negative than that of the solid. As the entropy of the gas is higher than liquid, so μ vs T curve has the highest negative slope.

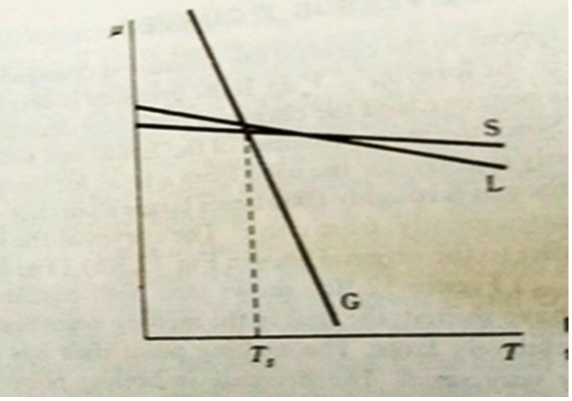


Fig1

A phase is thermodynamically stable over the range of temperature at which it has lower a lower chemical potential than any other phase. At lower temperature the solid is the most stable. Again, the liquid phase is stable at higher temperature. If the temperature is too high, then the vapour phase / gaseous state will exist.

PRESSURE DEPENDENCE OF μ VERSUS T CURVES

As $(\delta\mu / \delta P)_T = \bar{V}$, then $d\mu = \bar{V}dP$. If the pressure is decreased, then dP is negative and the chemical potential decreases proportionately to the volume of the phase. Since the molar volumes of the liquid and the solid are very small, the value of μ is decreased only slightly i.e. for the solid from a to a′ and for the liquid b to b′. Since the coefficient of compressibility of gas is highly negative, so μ of the gas decreases greatly from c to c′ [Fig.2a]. Pictorially this can be presented as

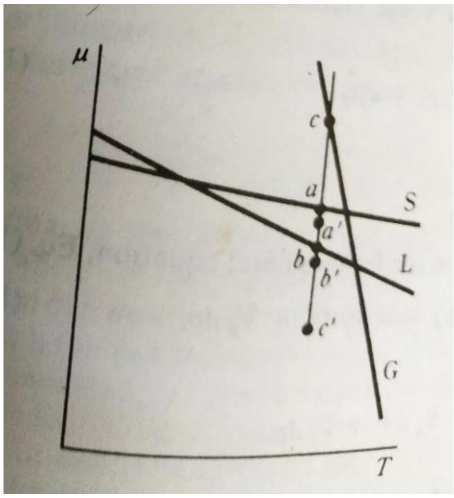


Fig 2a

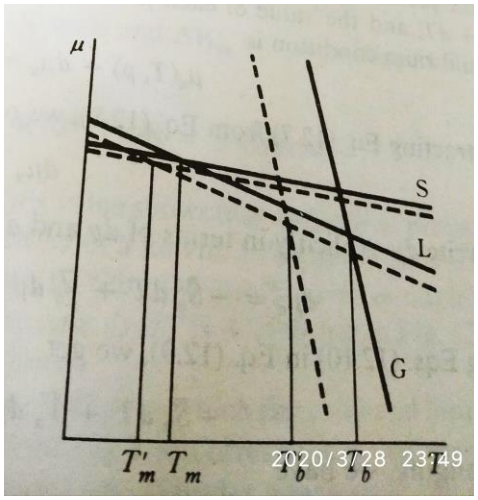


Fig 2b

The curves at the lower pressure show [Fig 2b] dashed lines which are parallel to the original lines. Hence shift in the melting point is very small where as shift in the boiling point is comparatively larger.

THE CLAPEYRON EQUATION:

The condition of equilibrium between two phases, α and β, of a pure substance is
$\mu_\alpha(T, P) = \mu_\beta(T, P)$; $d\mu_\alpha = d\mu_\beta$
So, when two phases α and β are in equilibrium that means when phase transformation takes place between α and β, then we can write $d\mu_\alpha = -S_\alpha\, dT + \bar{V}_\alpha\, dP$ and $d\mu_\beta = -S_\beta\, dT + \bar{V}_\beta\, dP$
As during phase transformation between α and β, $d\mu_\alpha = d\mu_\beta$
For the transformation $\alpha \rightarrow \beta$,
We have $(\bar{S}_\beta - \bar{S}_\alpha).\, dT = (V_\beta - V_\alpha)\, dP$

Therefore, **$dP / dT = \Delta S / \Delta V$** is called Clapeyron equation.

The Clapeyron equation is fundamental to any discussion of the equilibrium between two phases of a pure substance.

The Solid – Liquid Equilibrium:

So, applying The Clapeyron equation in the case of solid → liquid phase transformation, we have

$\Delta S = (\bar{S}\ \text{liquid} - \bar{S}\ \text{solid}) = \Delta S_{fus}$
and $\Delta V = (\bar{V}_{liquid} - \bar{V}_{solid}) = \Delta V_{fus}$
Generally, $\bar{V}_{liquid}$ is slightly greater than $\bar{V}_{solid}$, therefore when we plot P vs T curve for the solid → liquid phase transformation, then the slope, dP / dT will be nearly vertical.

The Liquid - Gas Equilibrium:

Applying the Clapeyron equation for the liquid → gas transformation, yields

$$dp / dT = \Delta S / \Delta V = (\bar{S}_{gas} - \bar{S}\ l_{iquid}) / (Ve_{gas} - \bar{V}_{liquid}) = \Delta \bar{H}_{vap} / T\, \Delta \bar{V};\ \text{where } \Delta S = \Delta \bar{H}_{vap} / T$$

Generally, $\bar{V}_{gas} >> \bar{V}_{liquid}$, hence for the P vs T plot, slope i.e. dP / dT is positive and gives a curved line.

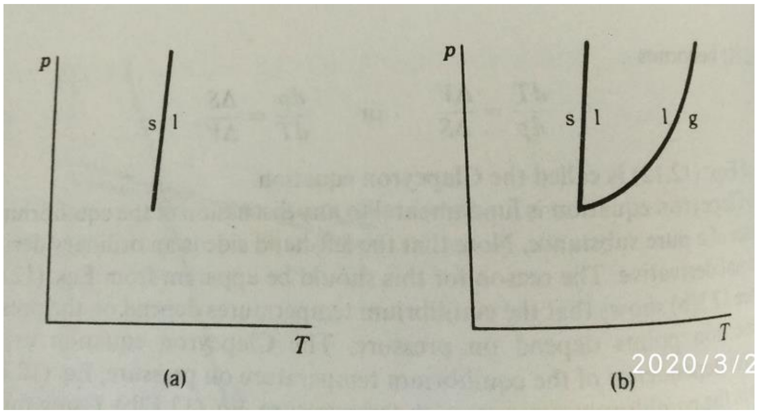


Figure 3a and 3b

Figure (3a) and (3b) shows the s → l as well as transformations. In figure (b), curve l → g is the locus of all points (T, P) at which liquid and gas coexist in equilibrium. Points just left of the l → g curve are below the boiling point under which the liquid state is stable and points to the right of l → g curve are condition under which the gas is stable.

The intersection of s → l and l → g curves corresponds to a temperature and pressure at which solid, liquid and gas all coexist in equilibrium. The values of T and P at this point can be determined by

$\mu\ \text{solid}\ (T, P) = \mu\ \text{liquid}\ (T, P)$ and $\mu\ \text{liquid}\ (T, P) = \mu\ \text{gas}\ (T, P)$ ……. (1)

Equation (1) can be solved by definite numerical values of T and P i.e. $T = T_t$ and $P = P_t$ where T_t and P_t are the triple-point temperature and pressure. There is only one such triple point at which all three phases can coexist in equilibrium.

Phase diagram of a simple substance is given below [Fig.4]:

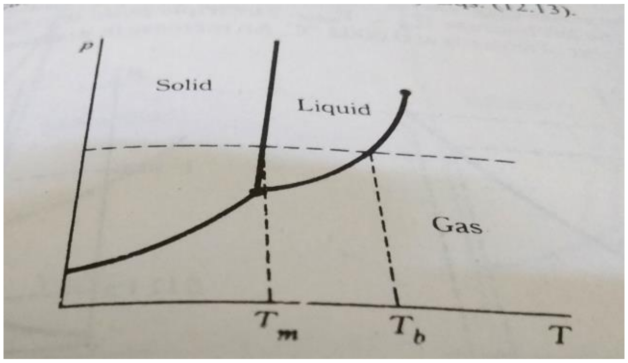


Figure 4

The Solid - Gas Equilibrium:

$\Delta S = (\bar{S}_{gas} - \bar{S}_{solid}) = \Delta\bar{H}_{sub} / T$ is positive and $\Delta\bar{V} = (\bar{V}_{gas} - \bar{V}_{gas})$ is also positive.

Therefore, $(dP/dT)_{s\rightarrow g} = \Delta\bar{H}_{sub} / T\,\Delta\bar{V}$

As $\Delta\bar{H}_{sub} = \Delta\bar{H}_{fus} + \Delta\bar{H}_{vap}$, so slope of the s → g curve is steeper than that of the l → g curve.

The transformation of phase is classified as –

(i) First order phase transformation
(ii) Second order phase transformation

Characteristics of First and Second Order Phase Transformations

(a) First order phase change ($\alpha \rightarrow \beta$) is associated with

(i) $\Delta\mu = 0$ i.e. $\mu_\alpha = \mu_\beta$ during phase change.

(ii) Sudden change of entropy and volume at the transition point during the change of state i.e. discontinuous change of the first order derivatives of μ with respect to temperature and pressure.

At the transition temperature and pressure for the phase equilibrium between α and β.

$$\text{So, } (\delta\mu_\beta / \delta T)_P - (\delta\mu_\alpha / \delta T)_P = -(\bar{S}_\beta - \bar{S}_\alpha) \neq 0$$

$$\therefore (\delta\mu_\alpha / \delta T)_P \neq (\delta\mu_\beta / \delta T)_P$$

Similarly in the case of $(\delta\mu / \delta P)_T = \bar{V}$

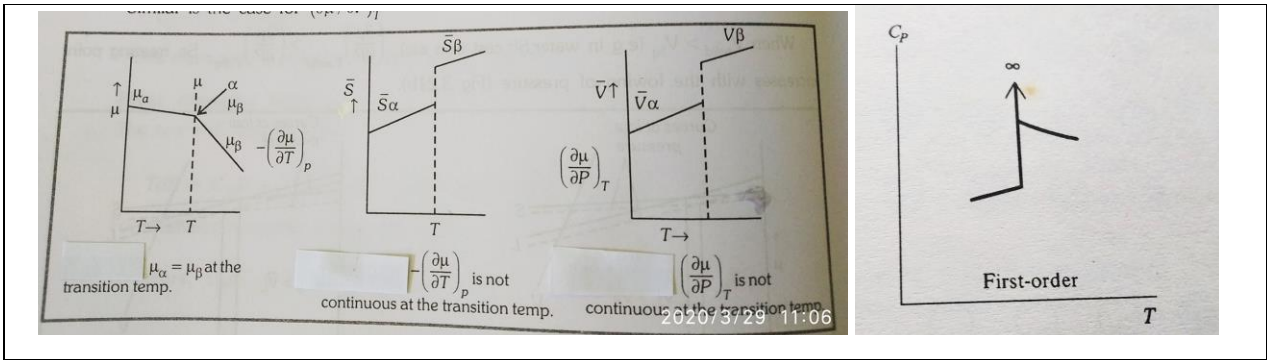


Figure 5: First order phase transitions

Examples of first order phase transition:

(i) Ice → Water; water → vapour; $S_\alpha \rightarrow S_\beta$; $CO_{2\,(S)} \rightarrow CO_{2\,(V)}$ etc.
(ii) Heat change associated with during phase change i.e. latent heat of transformation ≠ 0

N.B. For the first order phase transition C_p is infinite (∞) since the non-zero latent heat is absorbed by the system with no temperature change.

(b) Second order phase change (α → β) is associated with

(i) No change in entropy and volume during the phase change at the transition temperature i.e. $\bar{S}_\alpha = \bar{S}_\beta$ and $\bar{V}\alpha = \bar{V}\beta$ and latent heat of phase change is zero and C_p does not become infinite at the transition temperature but does change by a finite amount.

(j) Sudden change of heat capacity, expansion coefficient (α) and coefficient of compressibility (β). So,
the second order derivative becomes discontinuous at the transition temperature since

$$\left[\delta^2\mu / \delta T^2\right]_P = \left[\delta / \delta T(\delta\mu / \delta T)_P\right]_P = -\left(\delta\bar{S} / \delta T\right)_P = -\left(C_p / T\right)$$

and

$$\left[\delta^2\mu / \delta P^2\right]_T = = \left[\delta / \delta P(\delta\mu / \delta P)_T\right]_T = \left(\delta\bar{V} / \delta P\right)_T = -\beta\,\bar{V}$$

and

$$\delta^2\mu / \delta P\delta T = \left[\delta / \delta T\,(\delta\mu / \delta P)_T\right]_T = \left(\delta\bar{V} / \delta P\right)_T = \alpha\bar{V}$$

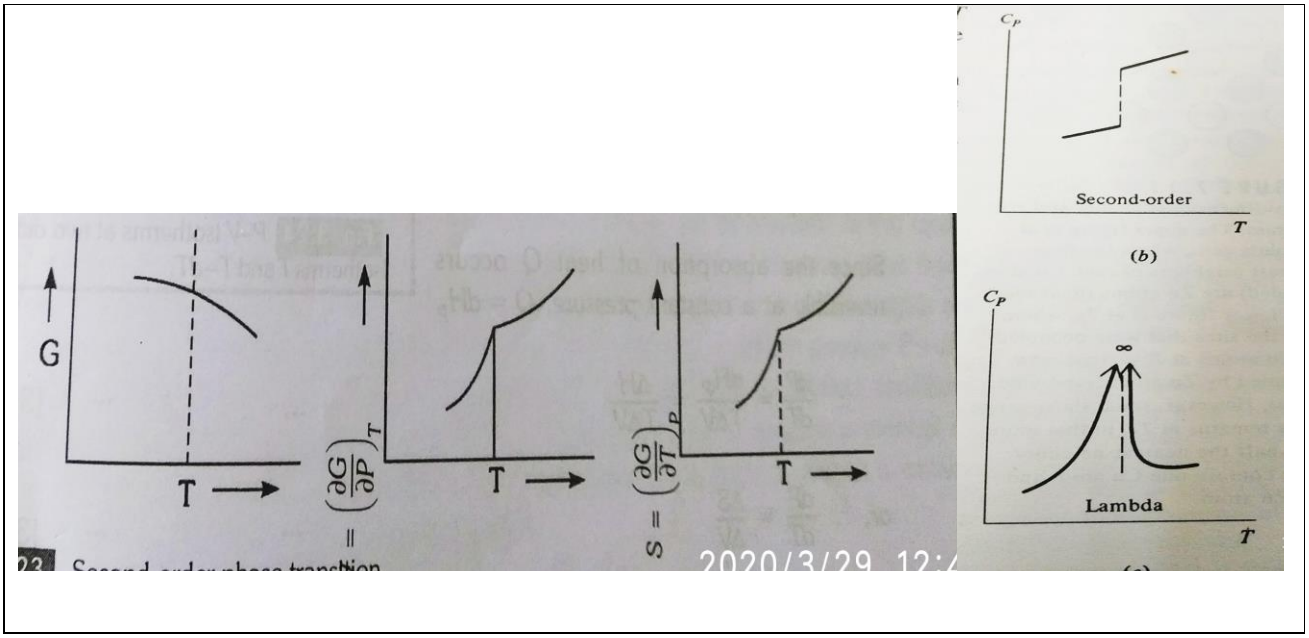


Figure 6: Second order phase transition and lambda transition

The only known second order transitions are those between liquid ^{3}He B and ^{3}He N, between ^{3}He A and liquid ^{3}He N and between normal conductivity and super conductivity in certain metals.

A **lambda transition** is one where C_p goes to infinity at lambda- point temperature (T_λ). The shape of the Cp vs T curve resembles the Greek letter λ (lambda). Examples of lambda transitions include liquid He I and liquid He II in ^{4}He; the transition between ferro magnetism and para magnetism in metals like Fe or Ni and order – disorder transitions in certain alloys e.g. β brass and in certain compounds like NH_4Cl, HF and CH_4.

Use of THE CLAPEYRON EQUATION:

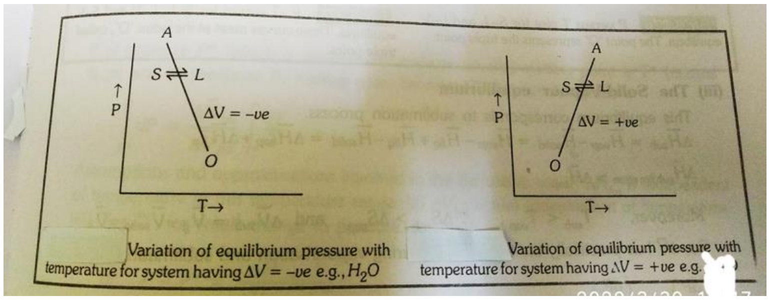
(i) The Solid – Liquid Equilibrium:

Here $\Delta\bar{S} = \bar{S}_{liq} - \bar{S}_{solid} = \Delta\bar{H}_{fus} / T$

$\therefore dP / dT = \Delta\bar{H}_{fus} / T (\bar{V}_{liq} - \bar{V}_{solid}) = \Delta\bar{H}_{fus} / T \Delta\bar{V}$

In the special case $\Delta\bar{V}$ may be negative and most of the cases $\Delta\bar{V}$ becomes positive.

So, P vs T plot will be:



Variation of equilibrium pressure with temperature for system having $\Delta V = -ve$ e.g., H_2O

Variation of equilibrium pressure with temperature for system having $\Delta V = +ve$ e.g.

Figure 7

Any point on the left of the line represents the solid phase and the space on right side of the solid line specifies the liquid state.

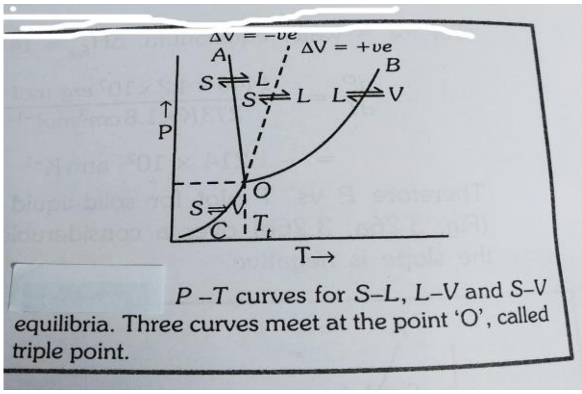
Integrated form of Clapeyron equation gives:

$$\boldsymbol{\Delta P = \Delta\bar{H}_{fus} \,.\, \Delta T / T \, \Delta\bar{V}}$$

Similarly, for the liquid – vapour equilibrium, integrated form of Clapeyron equation gives:

$$\ln\left(P / P^*\right) = -\Delta\bar{H}_{vap} / R \left(1 / T - 1 / T^*\right)$$

So, phase diagram can be represented as



P –T curves for S–L, L–V and S–V equilibria. Three curves meet at the point 'O', called triple point.

Figure8

Trouton's Rule:

For liquid – vapour equilibrium, the integrated form of Clausius – Clapeyron equation becomes

$$\ln P = - \Delta\bar{H}_{vap} / RT + Z$$

At normal boiling point of liquid, P = 1 atm

Hence $\Delta\bar{H}_{vap} / T = RZ = \text{constant}$

Or $\Delta\bar{S}_{vap} = \text{constant} = 21$ e.u.

This is Trouton's rule which states that at normal boiling point molar entropy change of vaporisation is constant and it is nearly 21e.u. But the fact that the law fails in case of associated liquid and also in case of high boiling and low boiling liquids. For this **Hilderbrand modified Trouton's rule by stating that instead of considering $\Delta\bar{S}_{vap}$ at normal boiling point, $\Delta\bar{S}$** is to be considered at a temperature where the vapour has very low concentration namely 0.005 moles/lit at 1 atm pressure. Under this condition $\bar{S}_v$ becomes so large compared to $\bar{S}_{liq}$ that **$\Delta\bar{S}_v$ remains more or less constant. Therefore** to compare **$\Delta\bar{S}_v$** , temperature will be different in different cases.

Derivation of Ehrenfest Equations:

Let the **second order** phase transition occurs between two phases say 1 and 2 at the transition temperature T and pressure P under the condition that

$\bar{S}_1 = \bar{S}_2$

As the temperature is raised inf……….(1) initesimally from T to T + dT, the equilibrium pressure changes also from P to P + dP. So, under the new equilibrium condition the above equation (1) becomes

$$\bar{S}_1 + d\,\bar{S}_1 = \bar{S}_2 + d\,\bar{S}_2 \;\ldots\ldots(2)$$

Comparing equations (1) & (2), we can write

$$d\,\bar{S}_1 = d\,\bar{S}_2$$

Now $S = f(T, P)$ for a closed system

Then, $dS = (C_P / T).dT - V\left[(\delta V/\delta T)_P / V\right]dP$.

Therefore, $dS_1 = C_{P1}/T - V\alpha 1.dP$ and $dS_2 = C_{P2}/T - V\alpha 2.dP$

$$\boxed{\text{or} \quad (dP/dT)_S = (C_{P2} - C_{P1})/VT(\alpha 2 - \alpha 1)}$$

This **Ehrenfest** equation for the second order phase transformation considering entropy remains constant at the transition point.

Let us consider now volume (V) of the system remains constant at the transition point.

Therefore at T,P ; $V1 = V2$, so $dV1 = dV2$ also.

Like the previous case if T becomes T + dT and P goes to P + dP. Then under the new equilibrium condition

$V1 + dV1 = V2 + dV2$

Now, $V = f(T,P)$

Then $dV = V.1/V\left[(\delta V / \delta T)_P \right].dT + V.\ 1/V\left[(\delta V / \delta P)_T \right].dV$

At new equilibrium, we can write $V\ \alpha 1.dT - V\beta 1.dP = V\ \alpha 2.dT - V\beta 2.dP$

$$\boxed{\text{or}\quad \mathbf{(dP/dT)_V = (\alpha 2 - \alpha 1) / (\beta 2 - \beta 1)}}$$

This is another form of **Ehrenfest** equation containing coefficients of volume expansion and coefficients of compressibility when volume, V remains constant.

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