

Lecture 4-6

Equilibrium

Discontinuity in the free energy, G versus T graph is an indication of phase transition.

For one-component system, existing in two phases, the chemical potentials of each of these phases is the same at equilibrium.

μ of phase A = μ of phase B

$\mu = G/n$, partial molar free energy is the chemical potential for a pure

substance

How do we understand this μ ? If it is possible to write down an analytical expression for μ , it should be possible to solve this equation and find T at which phase transition occurs. In the absence of this, we need to go for an alternate method.

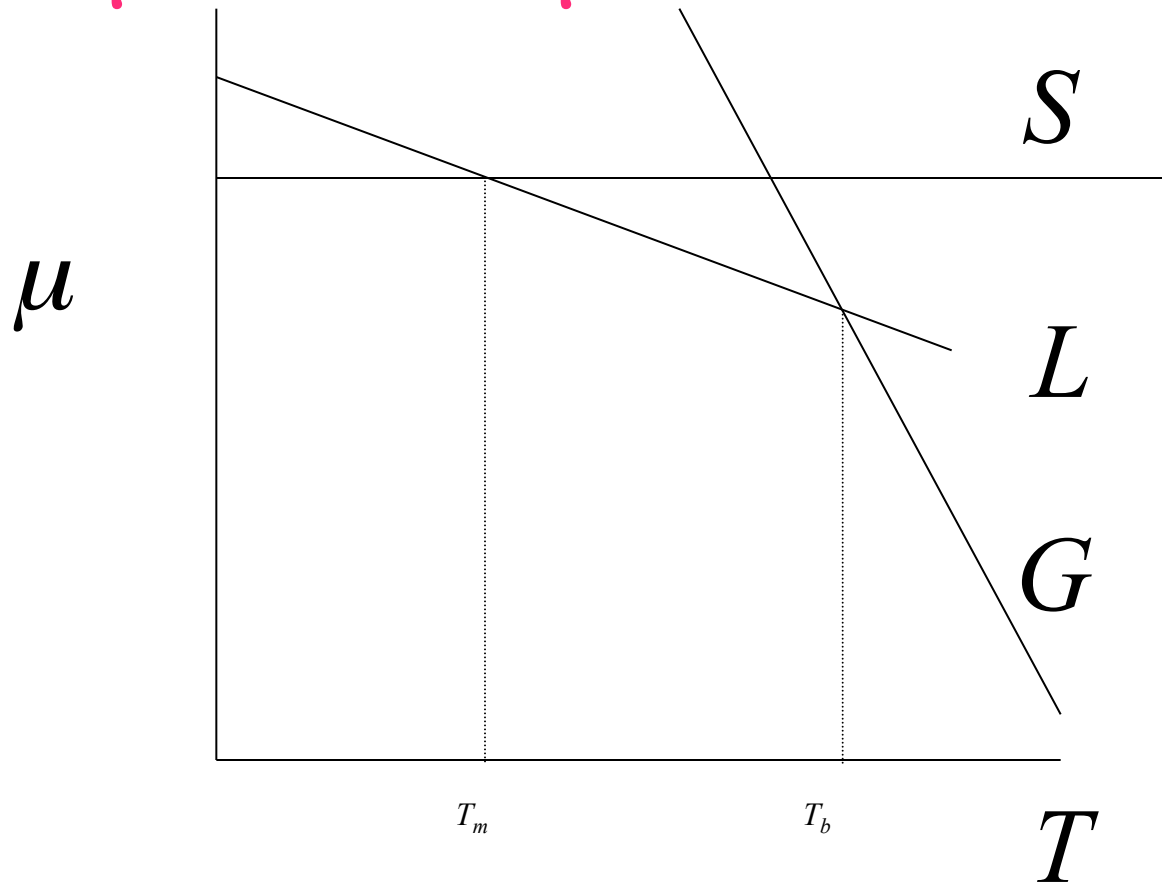
One way that we can understand it is under the condition of constant pressure. The variation in chemical potential with temperature is this $\partial\mu/\partial T$ or it is $(\partial G/\partial T)_P$

Chemical potential of each constituent must be the same everywhere. The simple way to write this for a one-component system, $d\mu = -SdT + \left(\frac{\partial\mu}{\partial P}\right)_T dP$
(One component)

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -S ; \left(\frac{\partial\mu}{\partial P}\right)_T = \left(\frac{\partial\mu}{\partial P}\right)_T V$$

If you have to talk about variation in μ Vs. T , the slope of that graph is going to get you the entropy i.e. you can get absolute entropies of solids, liquids or gases depending upon how you plot this graph. As we said earlier, S is large when it comes to gases. S of liquids it is much larger than that of solids.

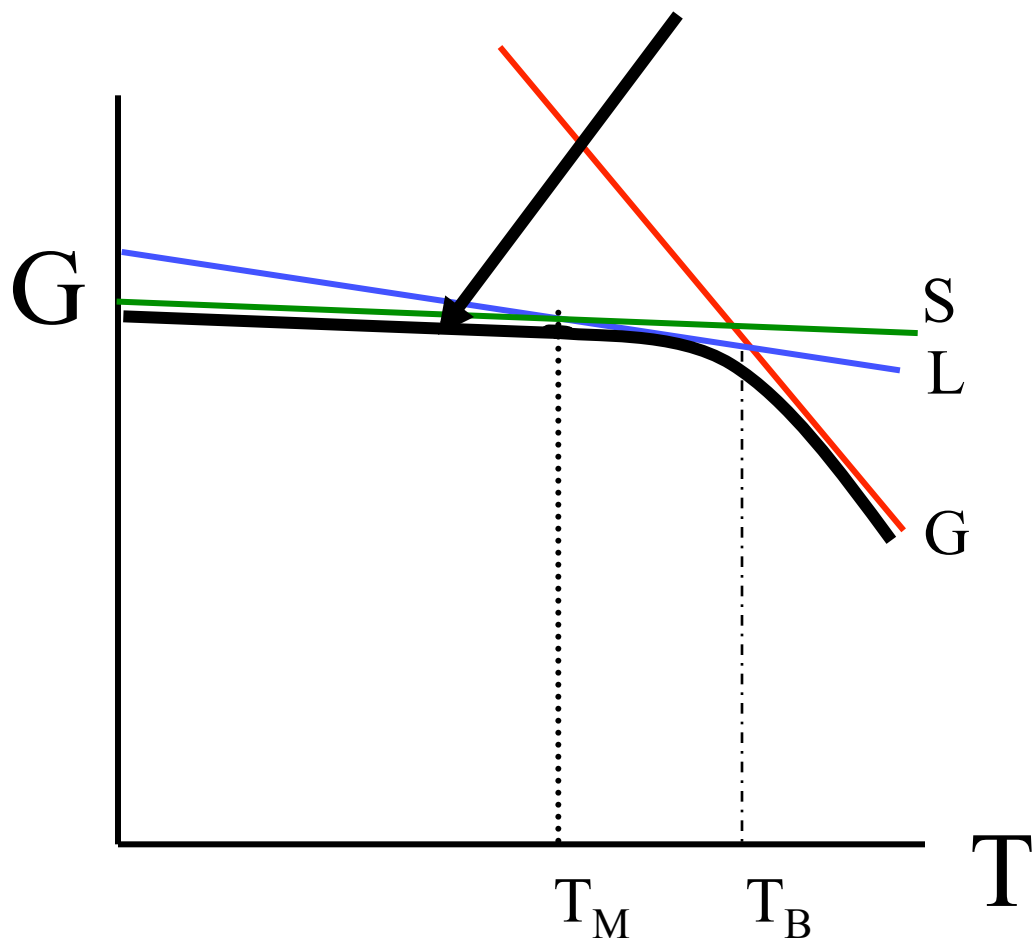
Slopes of μ Vs. T and μ Vs. P



Phase transitions occur when chemical potentials change discontinuously.

Why don't you see sublimation?

Which path will the system take?



Metastability

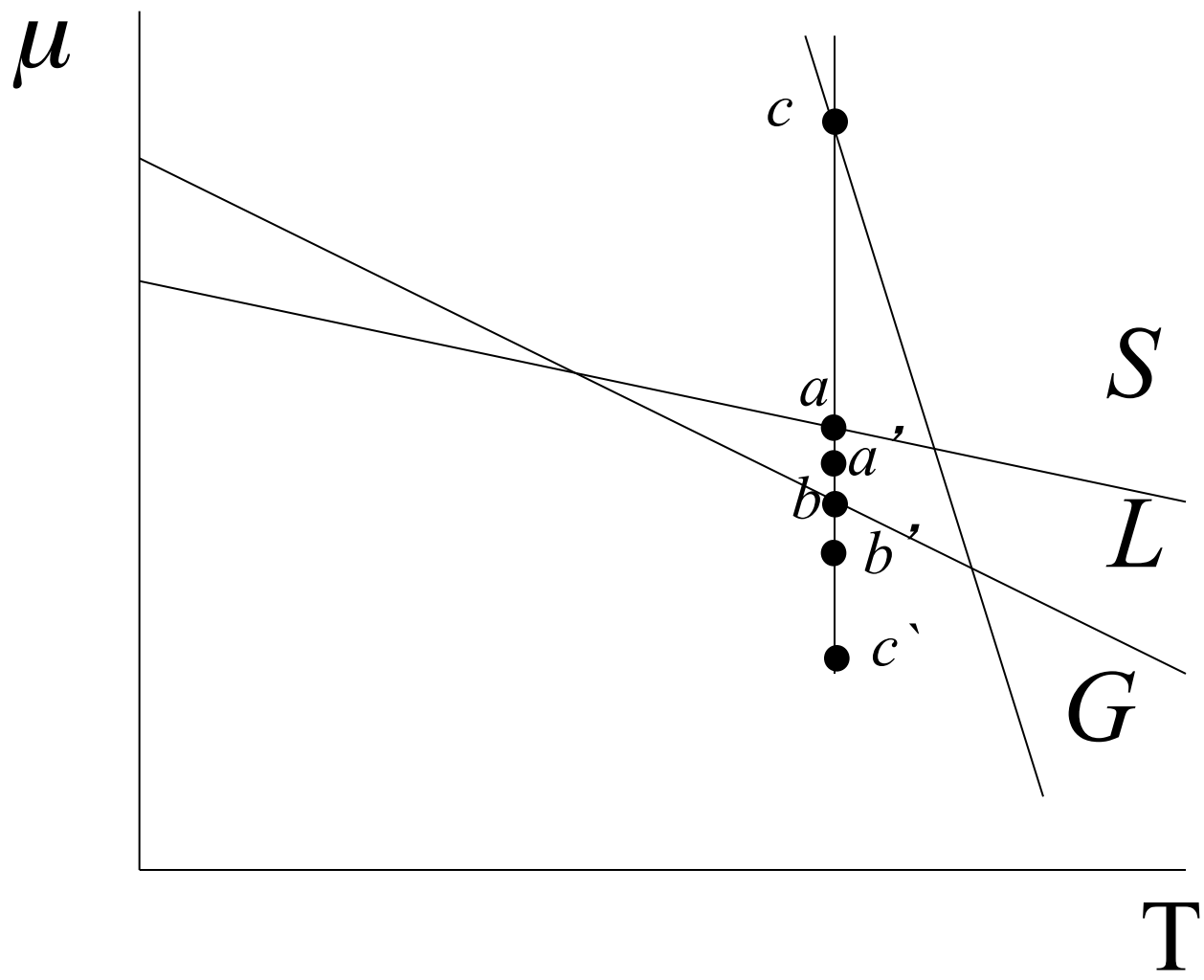
Pressure Dependence of μ Vs. T Curves

Change in pressure changes the free energy.

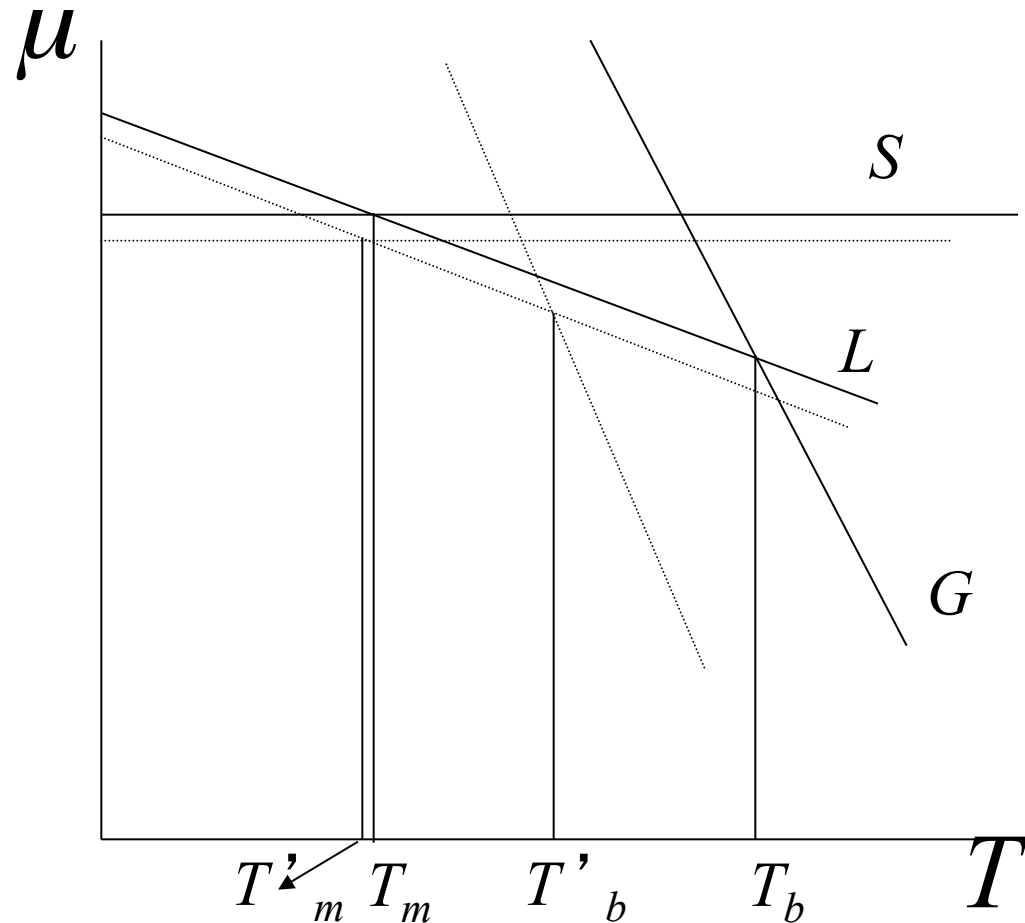
Since $(\partial\mu/\partial P)_T = V$, a decrease in pressure can only decrease the free energy as V is always positive (V is molar volume).

This decrease is depicted in figure when P is changed to P' .

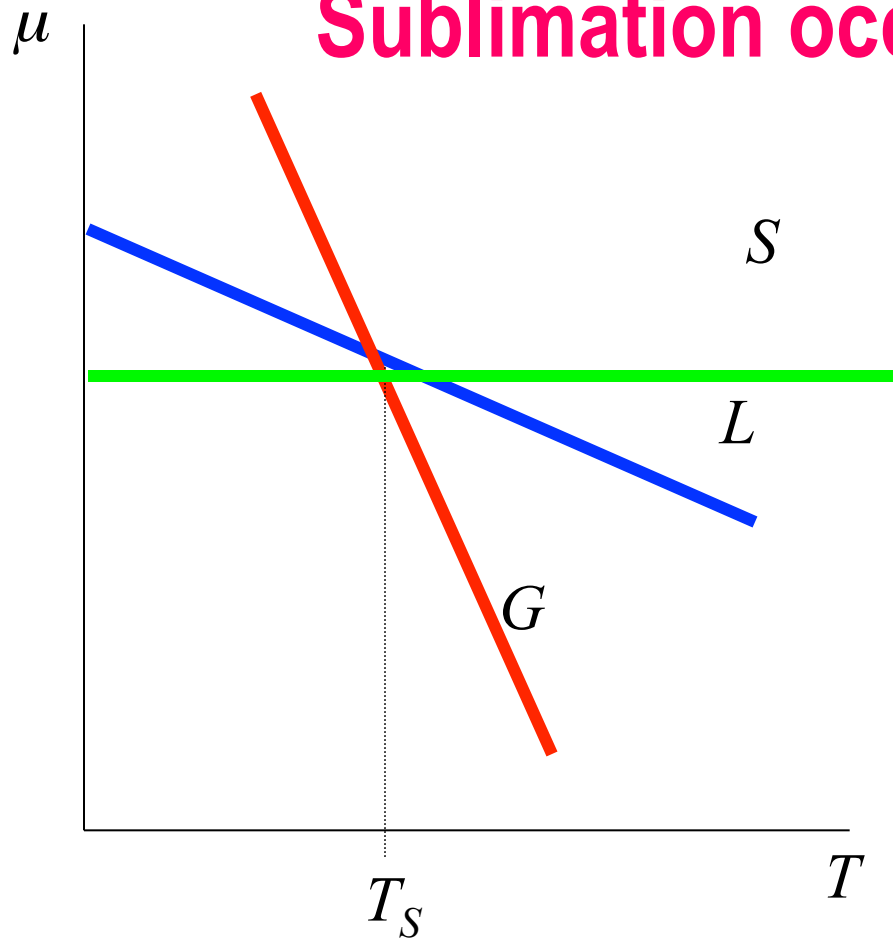
The change in values for S, L and G are from a to a' , b to b' and c to c' , respectively.



As a result of this shift the entire free energy curve shifts.
Let us plot the free energy at a different pressure.
The dotted lines are at a lower pressure.



Sublimation occurs



Clapeyron Equation

Let us consider a phase transition between phases, α and β .

Let us also assume that β is the product phase. At equilibrium,

$$\mu_{\alpha}(T, P) = \mu_{\beta}(T, P)$$

If μ_{α} and μ_{β} can be written in terms of T and P.

This equation can be solved for T and P if know the complete form of the analytical expression.

Even if we don't know, we can get an expression for derivatives

$$\mu_{\alpha}(T, P) + d\mu_{\alpha} = \mu_{\beta}(T, P) + d\mu_{\beta}$$

$$\text{But } \mu_{\alpha}(T, P) = \mu_{\beta}(T, P)$$

$$d\mu_{\alpha} = d\mu_{\beta}$$

$$-S_{\alpha}dT + V_{\alpha}dP = -S_{\beta}dT + V_{\beta}dP$$

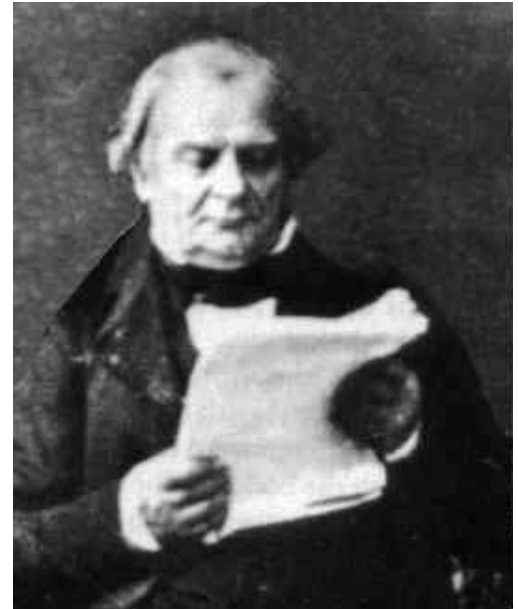
$$(S_{\beta} - S_{\alpha})dT = (V_{\beta} - V_{\alpha})dP$$

$\alpha \rightarrow \beta$ is the phase transition

$$dT/dP = \Delta V/\Delta S \text{ or } dP/dT = \Delta S/\Delta V$$

Either of this is the Clapeyron equation

The important advantage of this equation is that equilibria between two phases can be discussed quantitatively.



Solid – Liquid

$\Delta S = \Delta S_{\text{fusion}} = S_{\text{liq}} - S_{\text{sol}}$ Positive for all transitions.

$\Delta V = \Delta V_{\text{fusion}} = V_{\text{liq}} - V_{\text{sol}}$ Positive for most and negative for some

$\Delta S_f = 8 - 25 \text{ J/K/mol}$ (typically)

$\Delta V_{fu} = \pm 1 \text{ to } 10 \text{ cm}^3/\text{mol}$ (typically)

Assume $\Delta S_{fu} = 16 \text{ J/K/mol}$

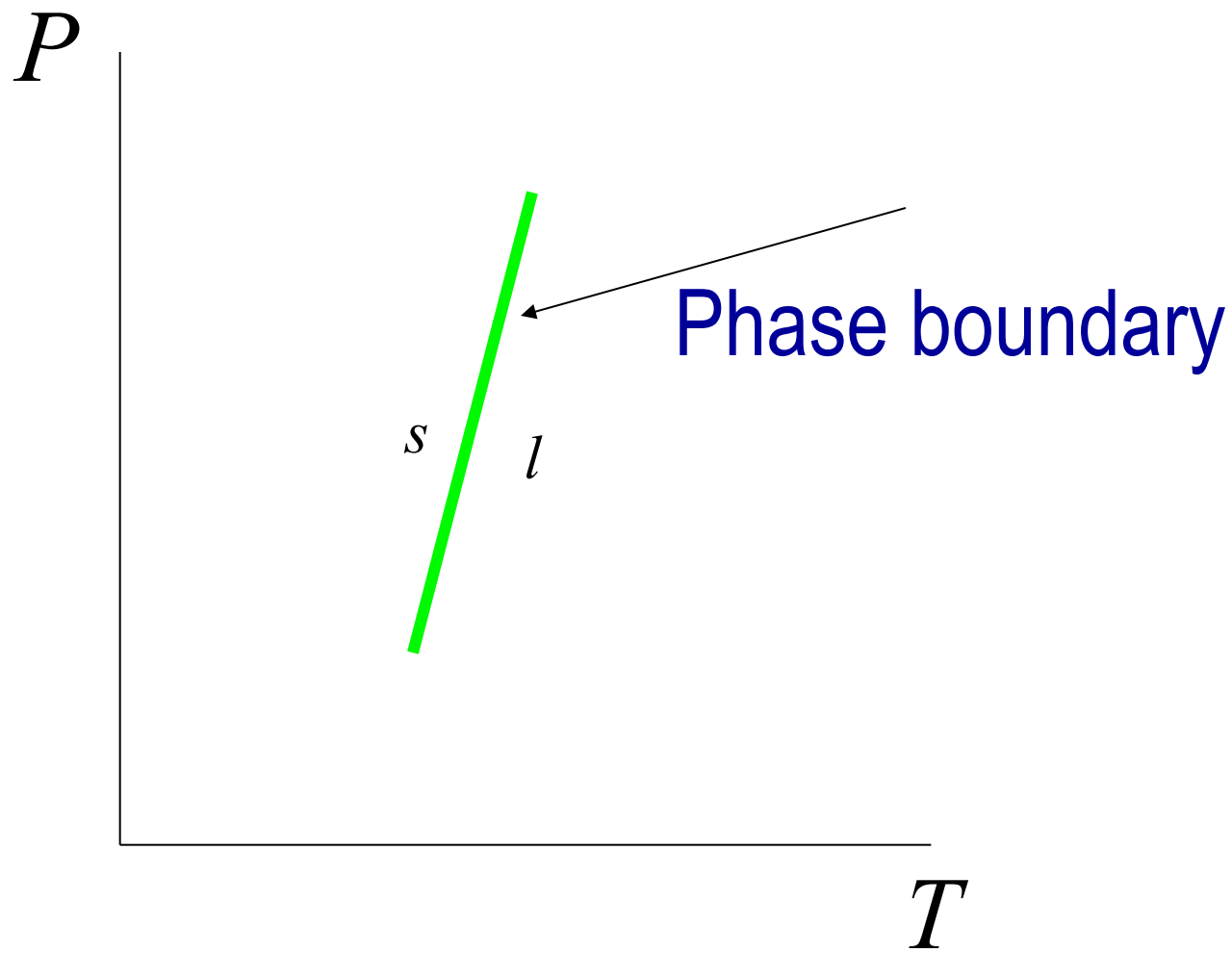
$\Delta V_{fu} = \pm 4 \text{ cm}^3/\text{mol}$

$dP/dT = ((16 \text{ J/K/mol}) / \pm 4 (10^{-6})\text{m}^3/\text{mol}) = \pm 4 (10^6)\text{Pa/K}$
 $= 40 \text{ atm/K}$

OR

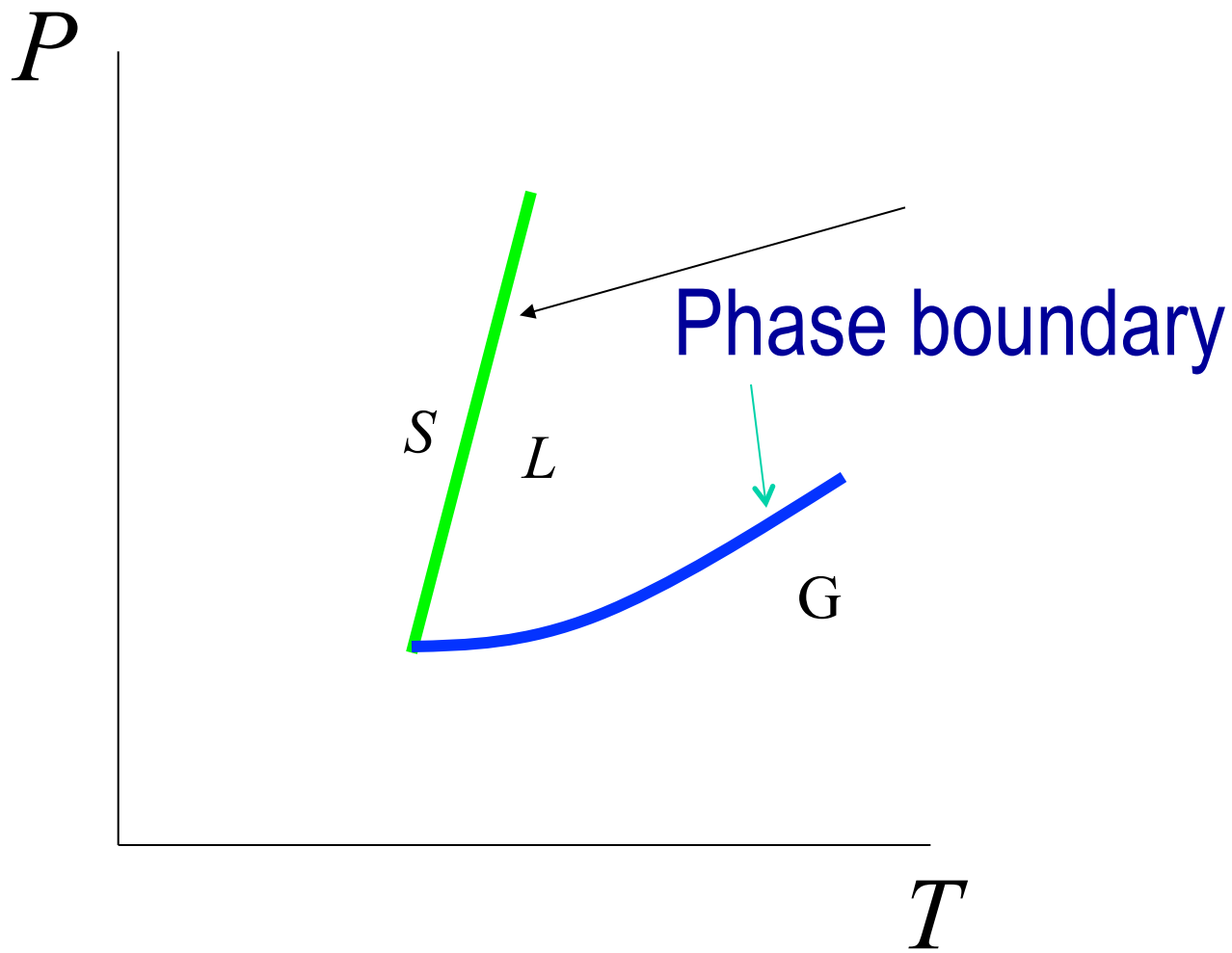
$dT/dP = \pm 0.02 \text{ K/atm}$

dP/dT is positive for most substrates



Liquid - Gas

$$\begin{aligned}\Delta S &= S_{\text{gas}} - S_{\text{liq}} = \Delta H_{\text{vap}}/T \text{ Positive} \\ \Delta V &= V_{\text{gas}} - V_{\text{liq}} \text{ Positive} \\ dP/dT &= \Delta S/\Delta V \text{ Positive}\end{aligned}$$



Solid-Gas

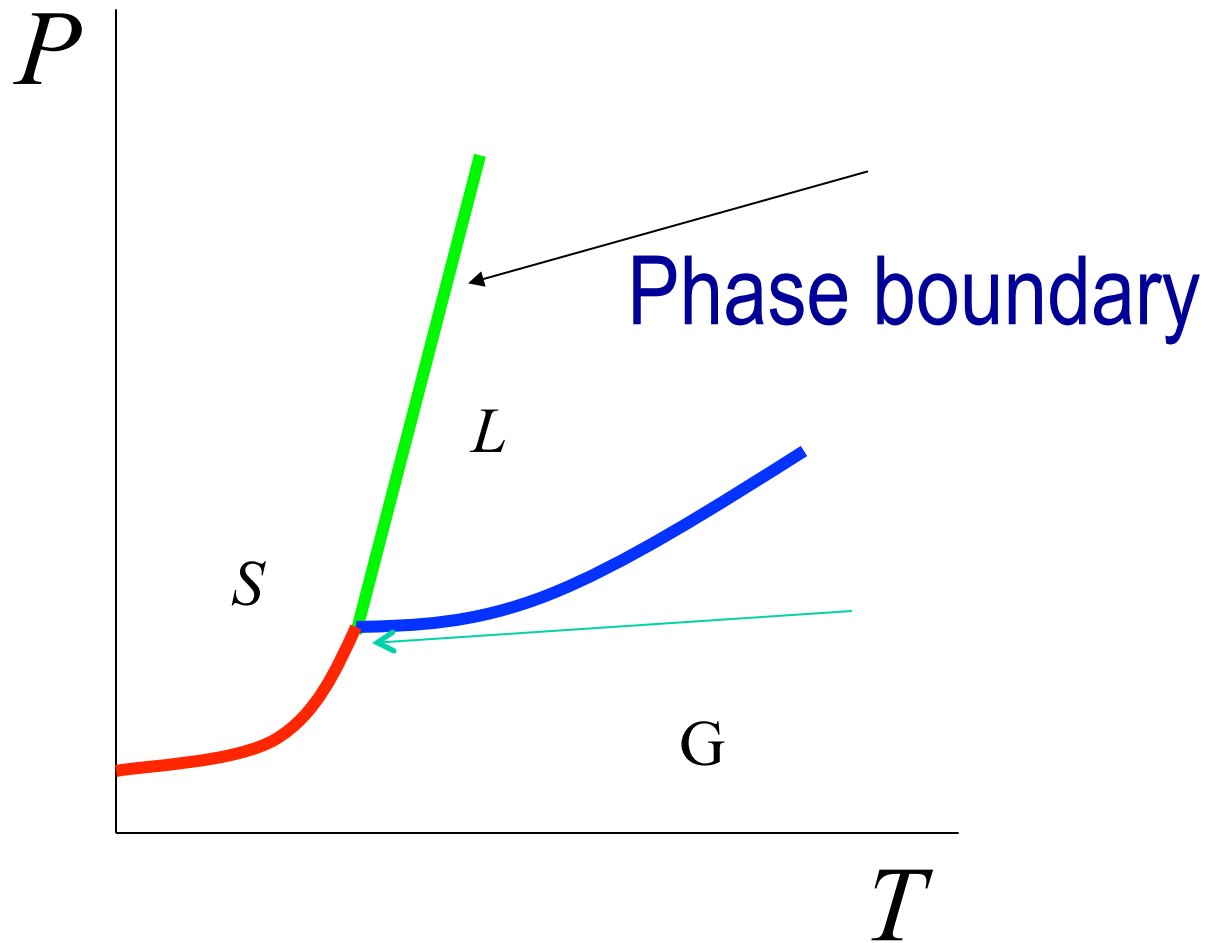
$$\Delta S = S_{\text{gas}} - S_{\text{solid}} = \Delta H_{\text{sublimation}}/T \quad \text{Positive}$$

$$\Delta V = V_{\text{gas}} - V_{\text{solid}} \quad \text{Positive}$$

$$dP/dT = \Delta S/\Delta V \quad \text{Positive}$$

Since ΔS is more than the gas-liquid case and ΔV is similar to that of gas-liquid, dP/dT will be more for this phase transition.

Thus a phase diagram can be constructed for a one component system. Note that the condition of equilibrium implies that there is a temperature and pressure condition where all these phases have to coexist, this is called the triple point.



Phase diagrams of simple systems

Stability of phases - free energy condition

In the following diagram for all temperatures below T_B the liquid is stable and for all temperatures below T_M the solid is stable. For all temperatures above T_B , gas is stable.

Is a G vs. T diagram enough?

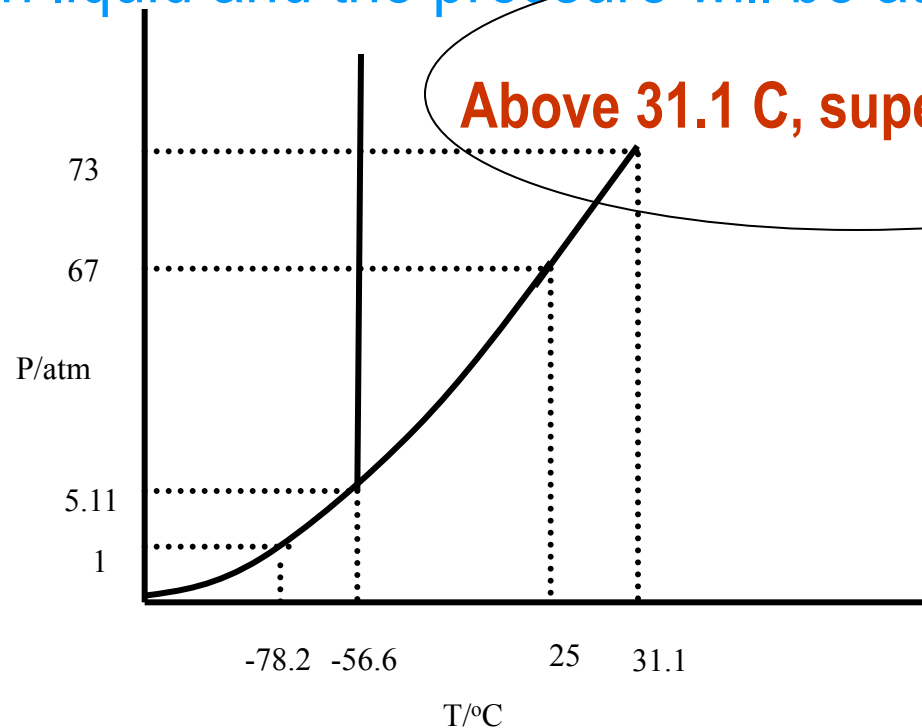
Phase diagram represents state of the system.

Any point in the phase diagram tells about the system completely. The phase diagram is far more informative than the simple free energy vs. temperature diagram.

Carbon dioxide

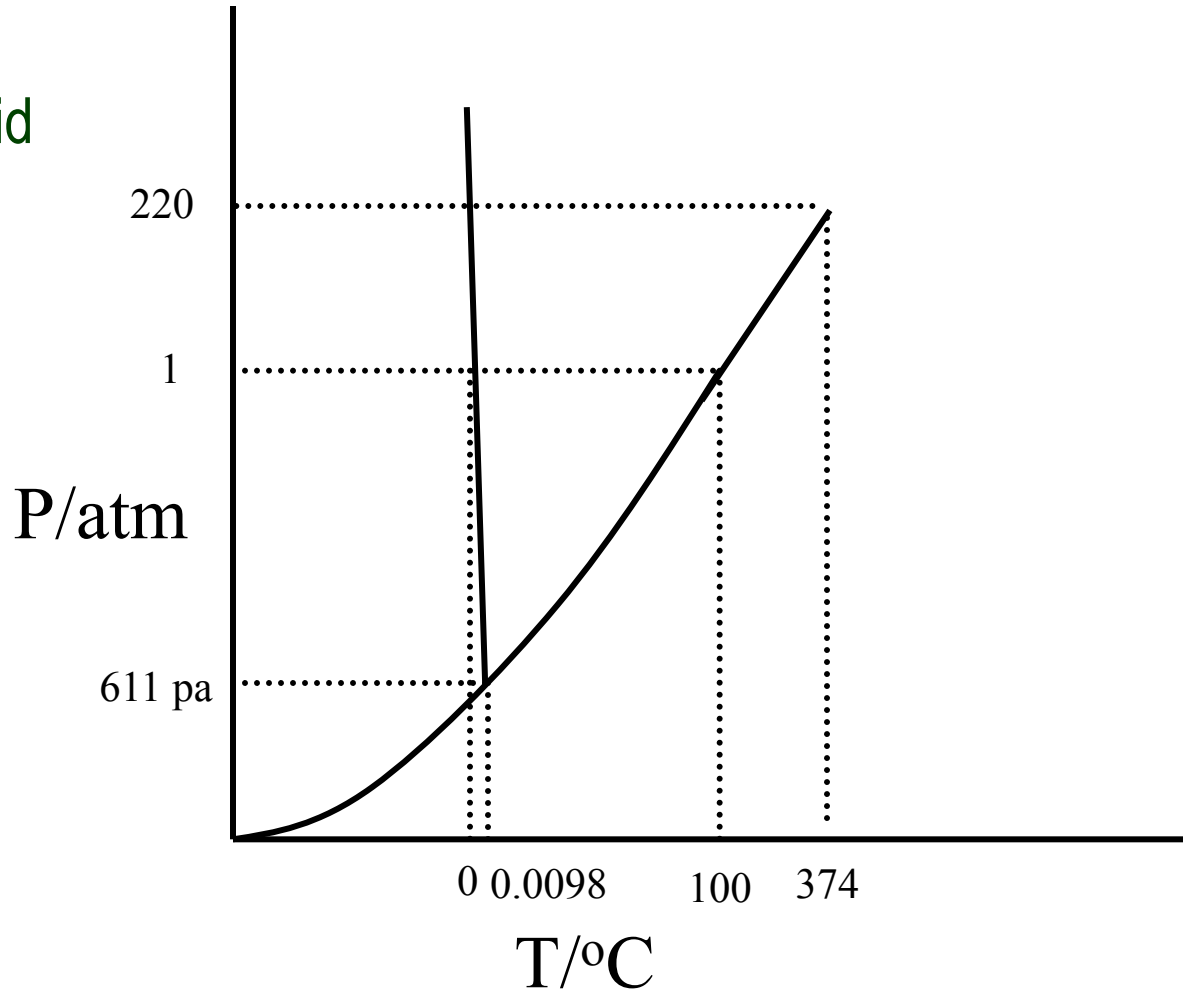
$$V_{\text{liq}} > V_{\text{solid}}$$

Dry ice – No stable liquid phase at 1 atm and therefore, the ice evaporates directly and thus dry. In a CO₂ cylinder, the critical point is above RT and in CO₂ cylinders at 25 C, gas will be in equilibrium with liquid and the pressure will be at 67 atm.

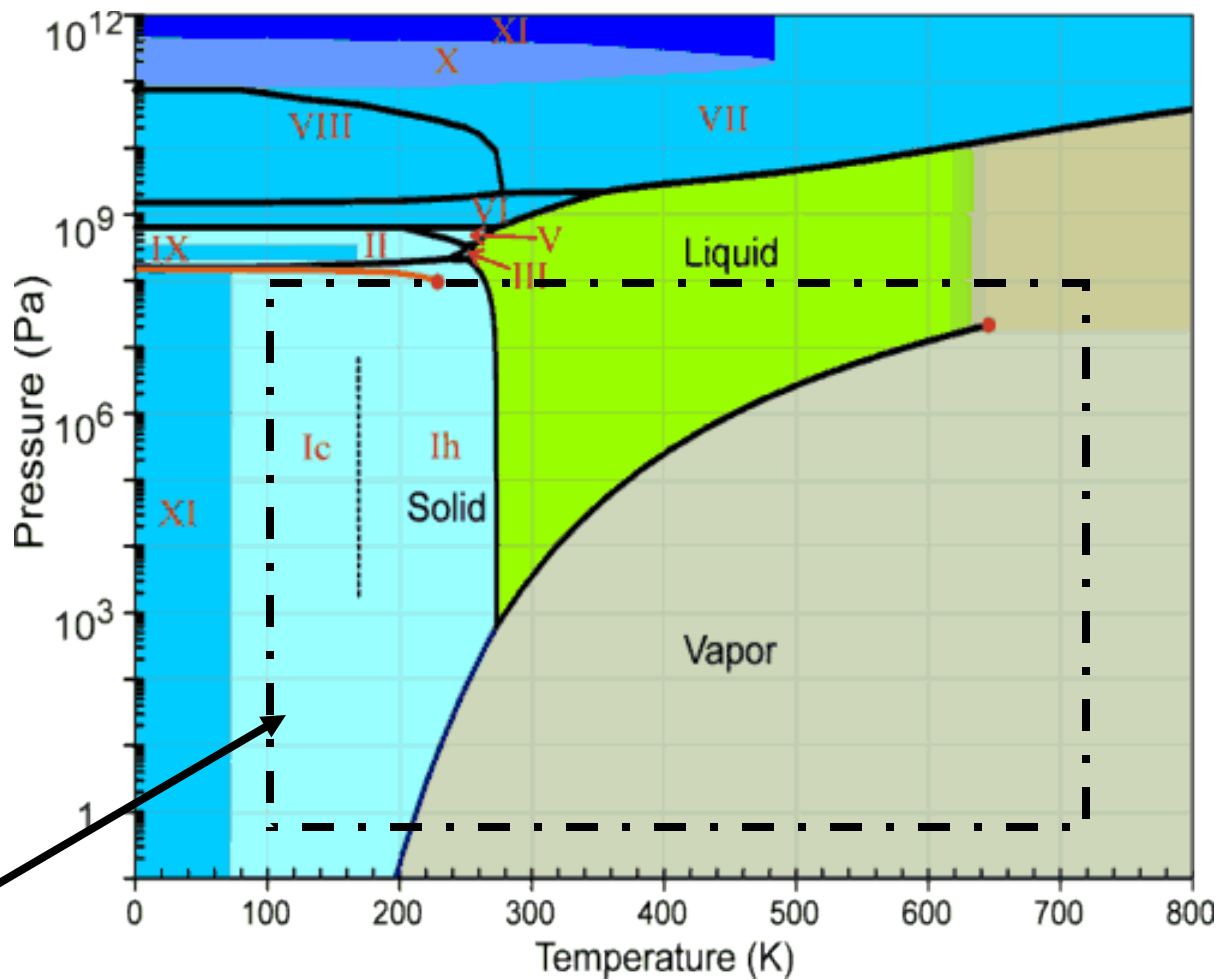


Water

$$V_{\text{liq}} < V_{\text{solid}}$$



The region you saw earlier



Phase Diagram of Ice

Ehrenfest classification of phase transitions

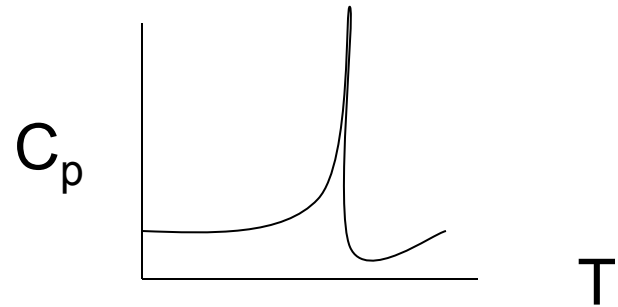
A \rightarrow B transition

$$(\partial\mu_B/\partial T)_P - (\partial\mu_A/\partial T)_P = -S_B + S_A = -\Delta S = -\Delta H/T$$

$$(\partial\mu_B/\partial P)_T - (\partial\mu_A/\partial P)_T = V_B - V_A = \Delta V$$

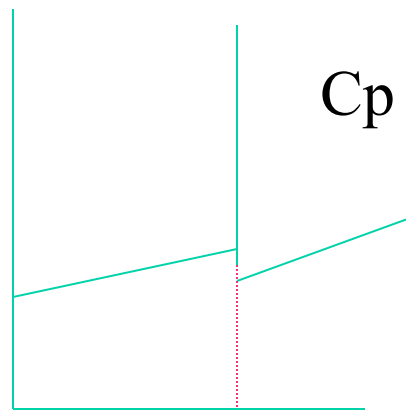
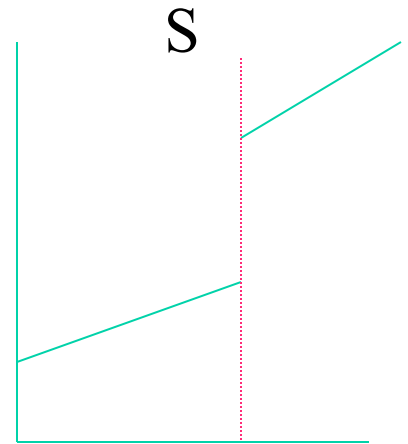
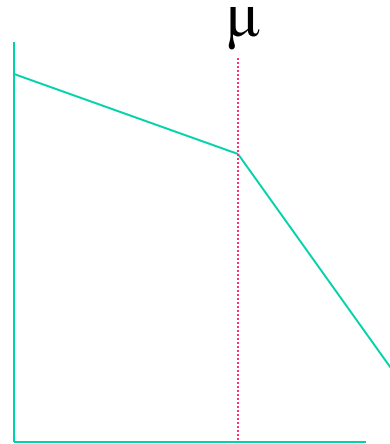
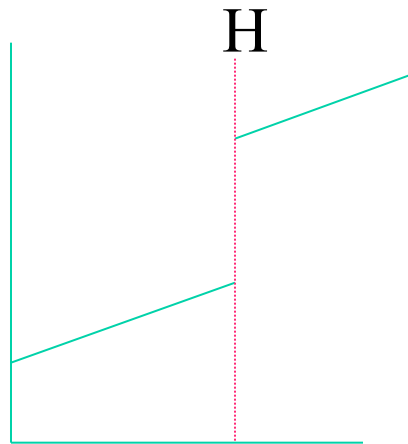
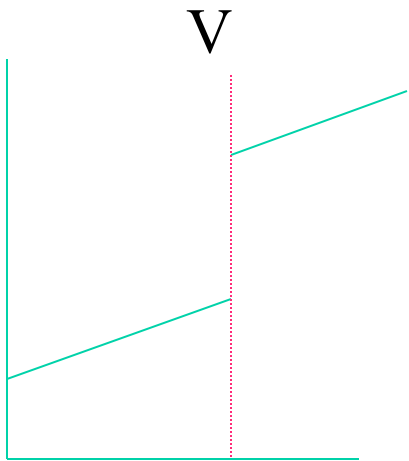
ΔS and ΔV are non-zero and slope of chemical potential changes at phase transitions such as melting. Discontinuity at phase transition. First derivatives of chemical potential with respect to P and T are discontinuous.

First order transitions.



Slope of H vs. T plot is C_p . H changes by a distinct quantity with infinitesimal change in T . Thus C_p is infinite at the transition. λ transition.

Second order transitions – no discontinuous change in S and V .



First order transitions

Temperature

Phase rule

Coexistence of two phases, condition:

$$\mu_{\alpha}(T,P) = \mu_{\beta}(T,P)$$

The two intensive variables are related.

Only one true variable - univariant

Three phases,

$$\mu_{\alpha}(T,P) = \mu_{\beta}(T,P)$$

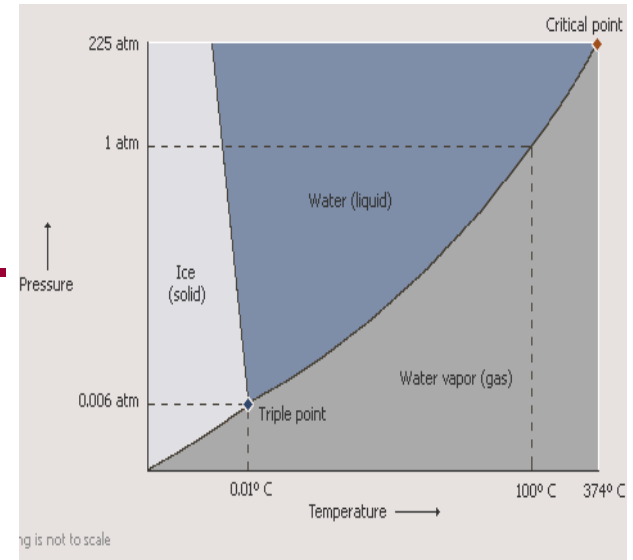
$$\mu_{\beta}(T,P) = \mu_{\gamma}(T,P)$$

There are two relations and therefore the system is invariant

This is the case of a pure one component system.

So for one component, number of variables,

$F = 3 - P$, is the **Phase Rule**.



How about a general rule?

There are several components and several relations between components. At equilibrium, there are relations between chemical potentials.

How many variables to be known?

1. PC - Composition variables for P phases

(In each phase, mole fraction of each component has to be specified. C mole fractions for one phase, PC for P phases.) **Component/constituent**

2. 2 – Variables corresponding to T and P

Total variables to be known = PC + 2

We have also some relations existing.

1. P - P relations of mole fractions

Why: Each phase, there is a relation, $x_1 + x_2 + x_3 + \dots + x_C = 1$

P phases, P equations

2. C(P-1) - C(P - 1) equations of μ 's.

Why: For each component, there are a set of equations:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots = \mu_i^P$$

(there are P-1 relations in each set, C(P-1) for C components)

Finally the number of variables,

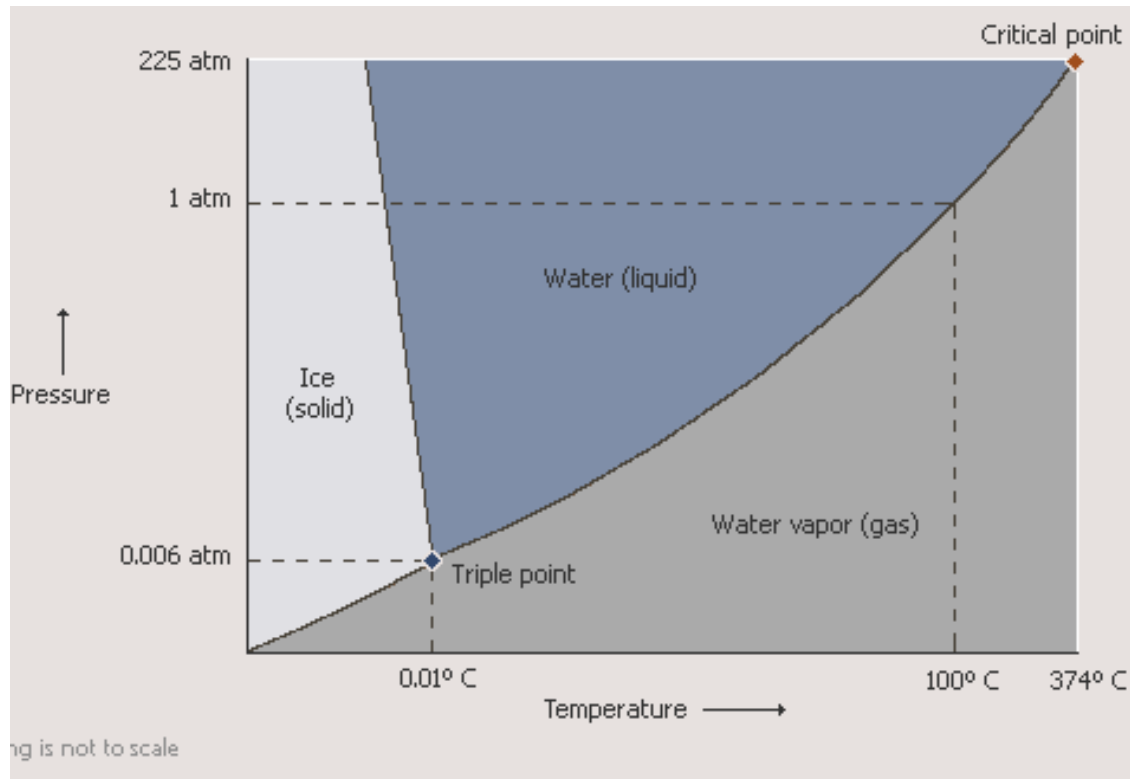
$$F = PC + 2 - P - C(P - 1)$$

or

$$F = C - P + 2$$

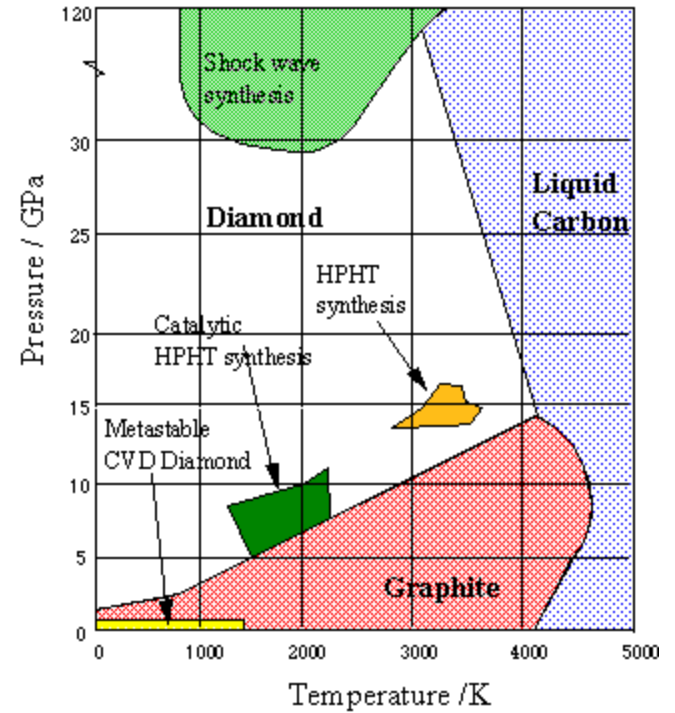
Degree of freedom

This is the Gibbs phase rule. Can we find out F for a given system?



- the solid-liquid equilibrium is tilted to the left-has a negative slope
- melting point of ice decreases with increase of pressure-ice occupies a greater volume compared to water
- there is a triple point-a temperature and pressure at which all three phases of water co-exist
- it is an invariant $F=0$ as $C=1$, and $P=3$
- the liquid-vapor curve terminates at the critical point, beyond this there is only vapor phase

Phase diagram of carbon



Solid-liquid equilibria; the simple eutectic diagram

Greek, Eutektos – easily melting
Eu – good, well + tekein – to melt

Motivation:

A two component system is the simplest of multicomponent systems.

A **condensed phase rule** is the one used to represent the phase diagram of a condensed system, either liquid or solid. In such a case, for two or more components, the phase diagram becomes **multidimensional**.

Look at, $F = C - P + 2$, for one phase, $2 - 1 + 2 = 3$ and the phase diagram will have three dimensions. This is difficult to represent. For larger number of components, the situation becomes complicated.

What is a component in case of equilibria?

Simplification:

One way to reduce complexity is to disregard the vapour phase in all discussions. In fact the error involved in this is not large.

Another way is to fix one of the variables, say pressure and discuss the phase diagram at constant pressure. This option is satisfactory as most of the phase changes of importance occur at atmospheric pressure. This phase rule, which is the condensed phase rule can be represented as $F' = C - P + 1$, when pressure is constant.

When a mixture of A and B is cooled, solid will separate at a the freezing point which will vary with composition. This variation can be represented by the equation,

$$\ln x_A = - \Delta H_{\text{fus,A}} / R (1/T - 1/T_{0A}),$$

Where x refers to the mole fraction and rest of the quantities have their usual meaning. T_{0A} is the pure A melting point.

This variation is depicted below.

The region above the line is the liquid phase and below is the solid phase.

The curve is called the **liquidus** curve.

At a point represented by **a**, the liquid of composition **b** is in equilibrium with solid **A** of composition **c** (in this case the solid is pure A).

The ratio of amount of liquid to solid is equal to the ratio of the lengths ac/ab .

This curve does not represent the situation over the entire region of composition. At larger mole fractions of B, solid B separates out.

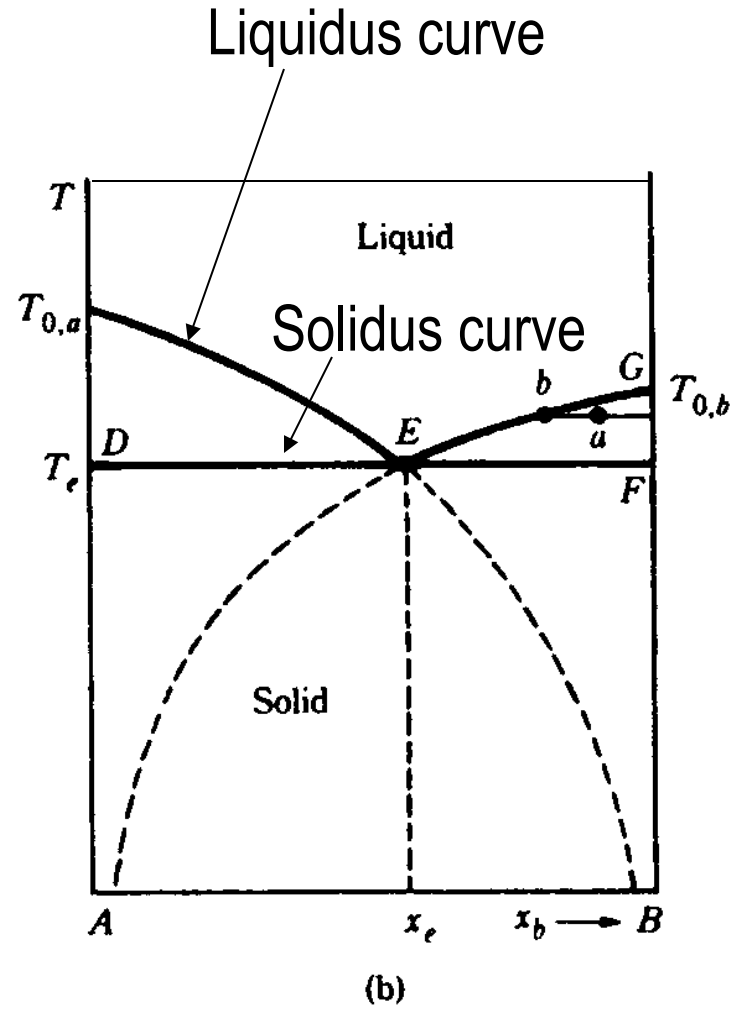
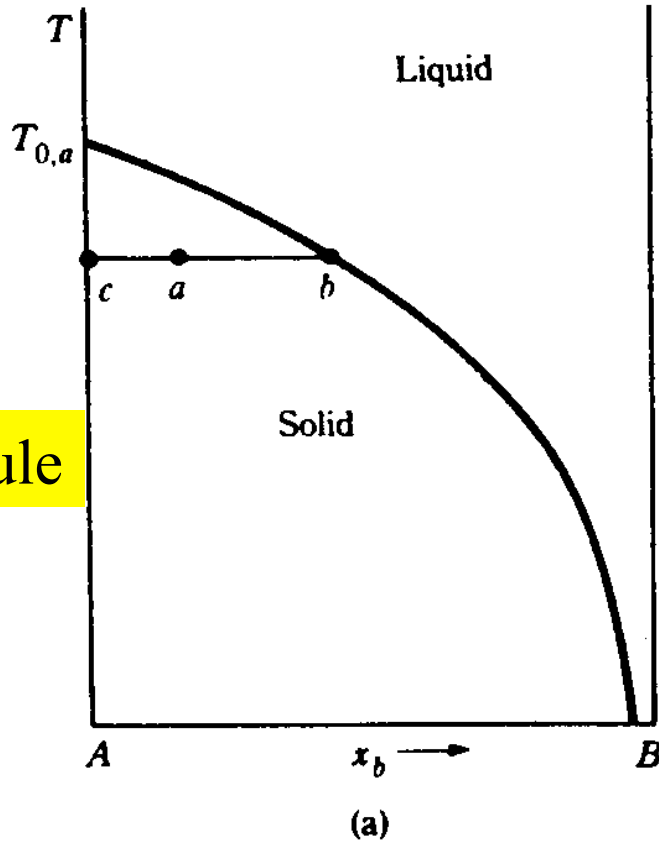
If the solution is ideal, the same law holds good for the pure substance, B. In this case,

$$\ln x_B = - \Delta H_{\text{fus,B}} / R (1/T - 1/T_{0B}),$$

At temperature T_e both the curves meet and this is the minimum in temperature that can be reached by the system with solid A, B and solution in equilibrium. **This temperature is called the eutectic temperature.** At this point, $F' = 3 - P = 3 - 3 = 0$, the system is **invariant** at this temperature. If heat is removed from the system, the three **phases will be in equilibrium**. The relative amounts of phases will change depending on the heat flow into the system.

The total phase diagram is represented in the diagram (b). The line DEF is the **solidus** curve. Below this line only solid A and B exist. The ideal system depicted in (a) is also shown.

Lever rule



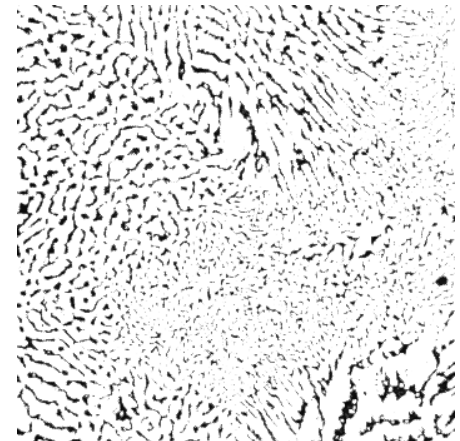
Solid-liquid equilibrium in a two component system.

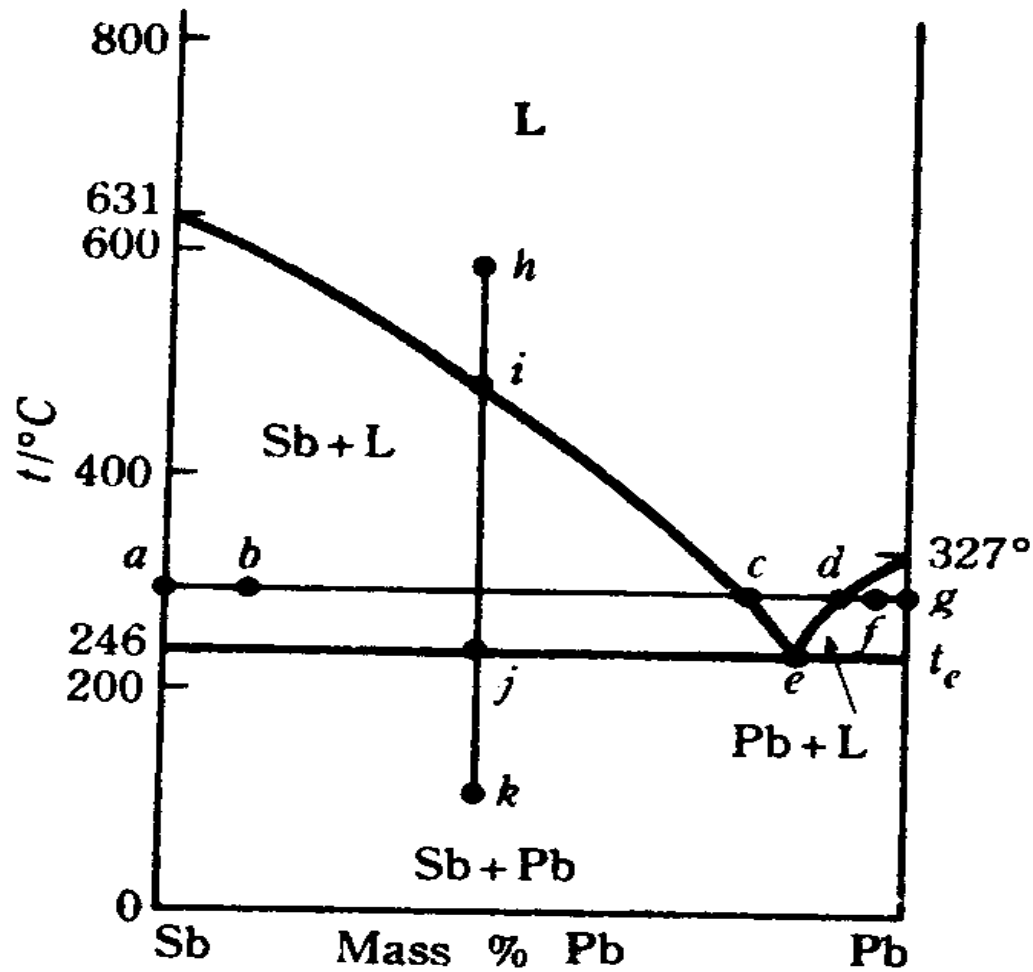
The lead-antimony system is a simple eutectic system. This is shown below as an example. The various temperatures are shown in the graph. The line *hijk* is called an **isopleth**, representing constant composition. This represents the changes in the system as the temperature is varied.

It was thought that at this temperature what is melted is a compound. But microscopic analysis showed that these are isolated crystals of A and B in the system.

In systems such as lead-antimony which form alloys, the grains of A and B are much smaller, yet the two phases remain. In aqueous systems, this eutectic mixture is called a cryohydrate and the eutectic point is called the **cryohydric point**.

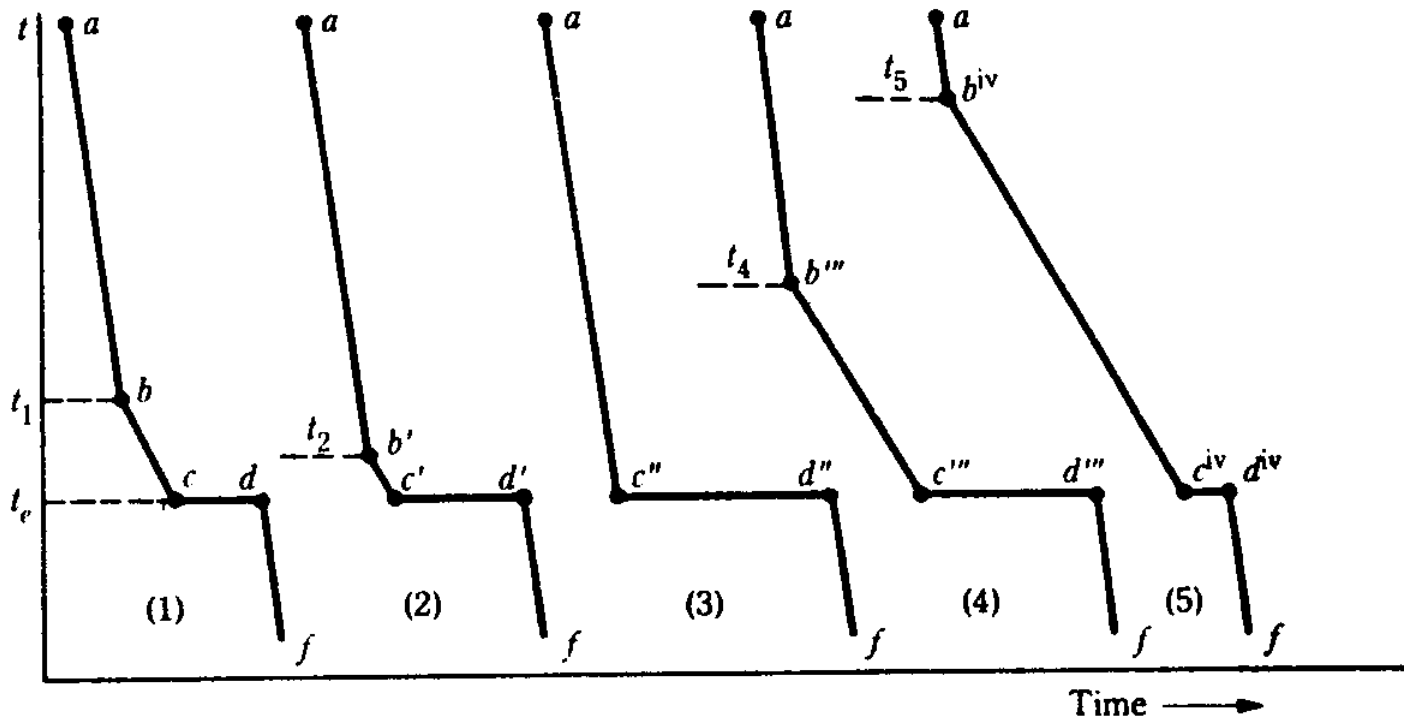
Micrograph of eutectic Pb-Sn alloy showing a fine mixture of Pb-rich and Sn-rich phases





Lead-antimony system

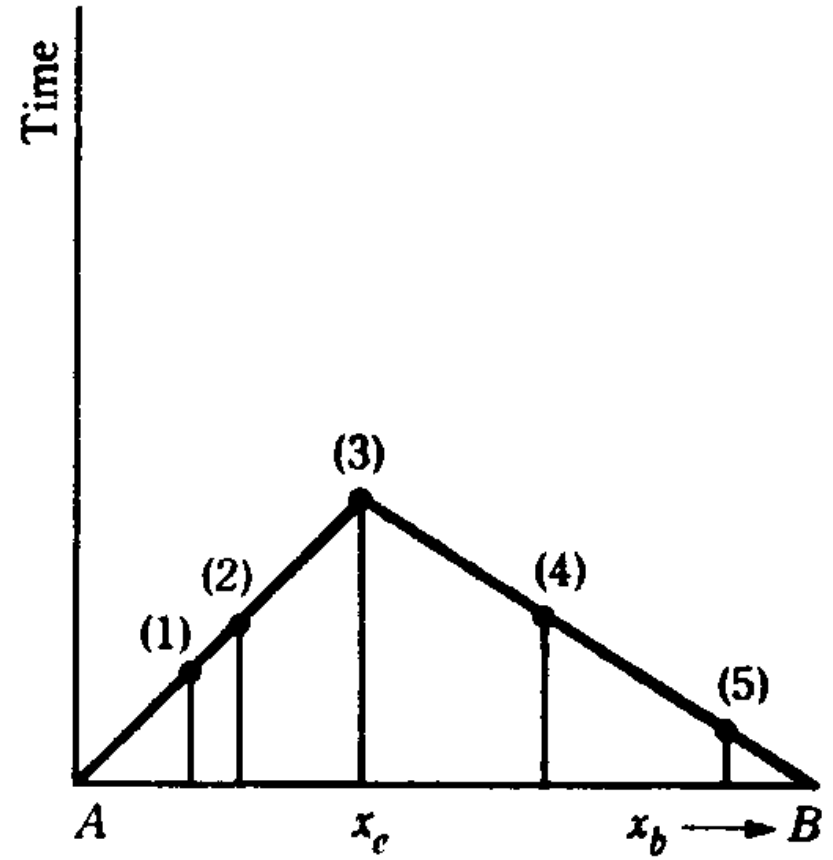
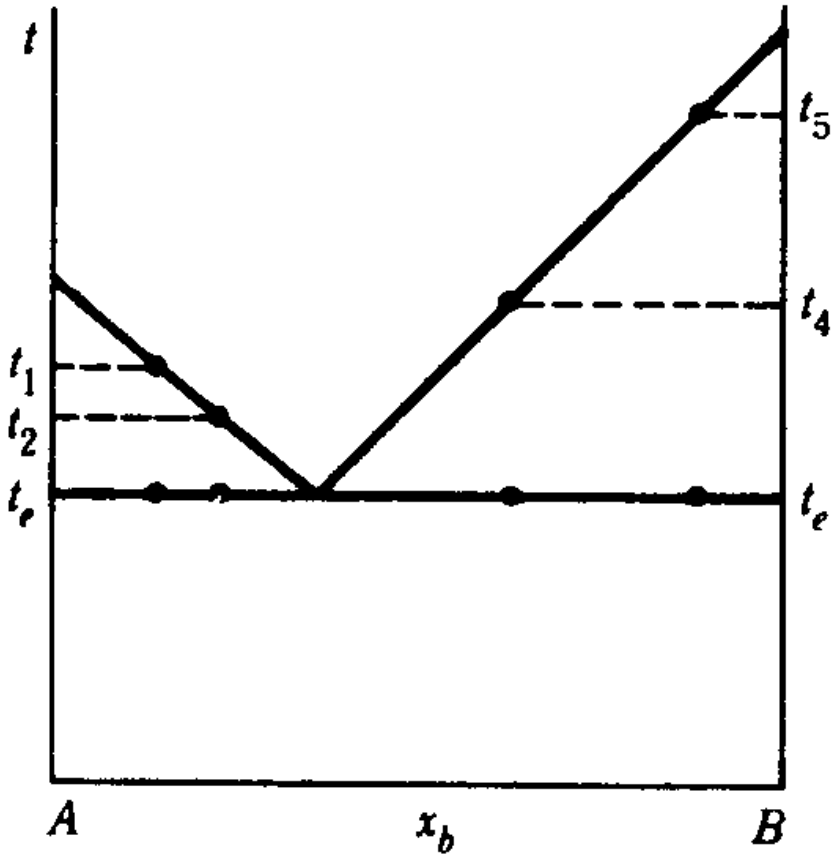
The phase diagram can be studied using **cooling curves**. A series of compositions are taken at a temperature above the melting points of A and B. The mixture is allowed to cool. The temperature is noted as a function of time. The cooling curve is plotted as given below.



Cooling curves

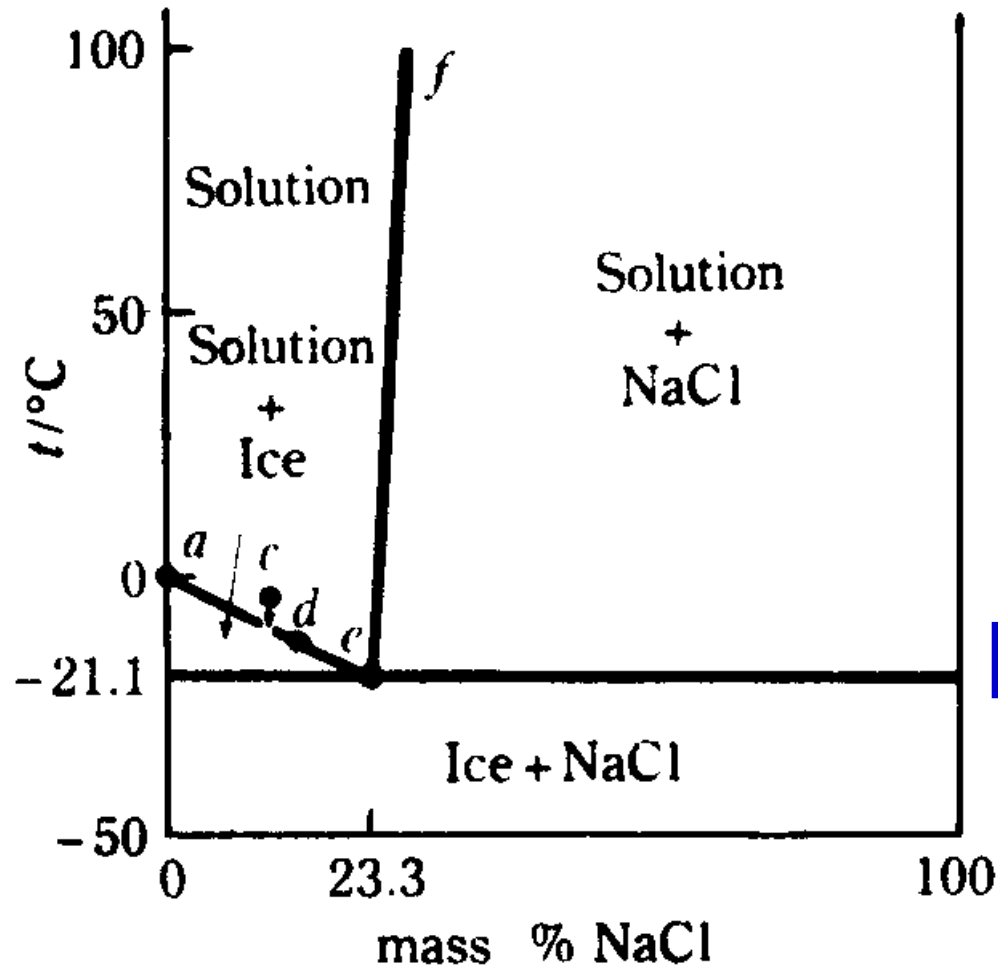
The two points at which the slope changes correspond to the melting point of the mixture and the eutectic point. In composition marked (3) no melting point is noted only the eutectic point is observable.

The horizontal plateau is called the **eutectic halt**. This increases as the composition is closer to eutectic composition. The phase diagram can be drawn by using either of the data. The eutectic point can be found out by plotting the **eutectic halt as a function of composition**.



Eutectic halt as a function of composition

The freezing mixture

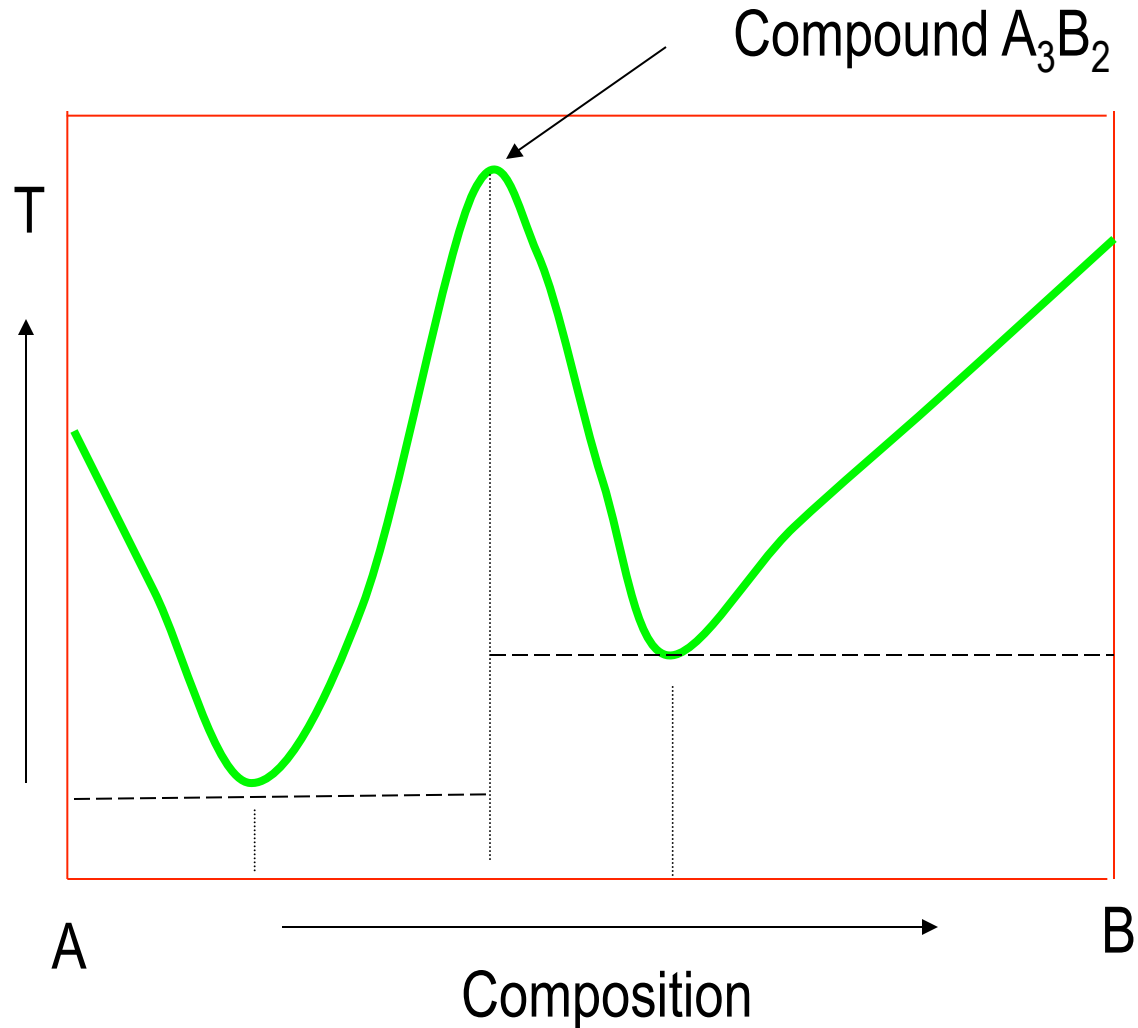


NaCl/water system

The eutectic compositions for several freezing mixtures are given below.

Salt	Eutectic temperature C	Mass percent anhydrous salt in eutectic
Sodium chloride	-21.1	23.3
Sodium bromide	-28.0	40.3
Sodium sulfate	-1.1	3.84
Potassium chloride	-10.7	19.7
Ammonium chloride	-15.4	19.7

Eutectic system with compound formation



Integration of Clapeyron equation

$$dP/dT = \Delta S_{\text{liq}}/\Delta V_{\text{fus}} \leftarrow \text{CLAPEYRON EQUATION (Melting)}$$

$$\int_{P_1}^{P_2} dP = \int_{T_M}^{T_{M'}} [\Delta H_{\text{fu}}/\Delta V_{\text{fu}}] dT/T$$

ΔH and ΔV are nearly independent of temperature

$$P_2 - P_1 = [\Delta H_{\text{fu}}/\Delta V_{\text{fu}}] \ln T_{M'}/T_M$$

$T_{M'} - T_M$ is quite small.

$$\ln T_{M'}/T_M = \ln [(T_M + T_{M'} - T_M)/T_M] = \ln [1 + (T_{M'} - T_M)/T_M]$$

$$\approx (T_{M'} - T_M)/T_M \quad \ln(1+x) = x - 1/2 x^2 + 1/3 x^3 \dots \text{ and if } x \ll 1, \approx x$$

$$\Delta P = \Delta H_{\text{fu}}/\Delta V_{\text{fu}} \Delta T/T_M$$

SOLID – GAS OR LIQUID – GAS EQUILIBRIUM

$$dP/dT = \Delta S/\Delta V = \Delta H/T(V_g - V_{s/l}) = \Delta H/T(RT/P) \quad \text{We know, } V_g = RT/P$$

$$V_g \gg V_{s/l}$$

$$d \ln P/dT = \Delta H/RT^2 \quad dx/x = d \ln x$$

$$\int_{P_0}^P d \ln P = \int_{T_0}^T \Delta H/RT^2 dT$$

$$\ln P/P_0 = -\Delta H/R (1/T - 1/T_0)$$

$$= -\Delta H/RT + \Delta H/RT_0$$

$P_0 = 1 \text{ atm}$ $T_0 = T$, the normal boiling point

Standard boiling point – 1 bar

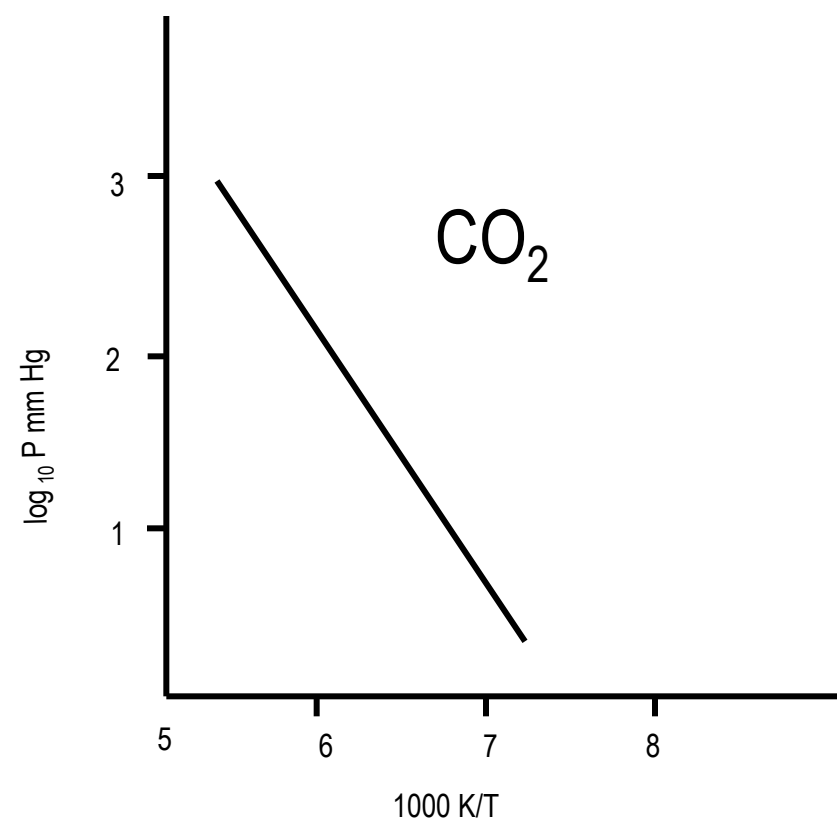
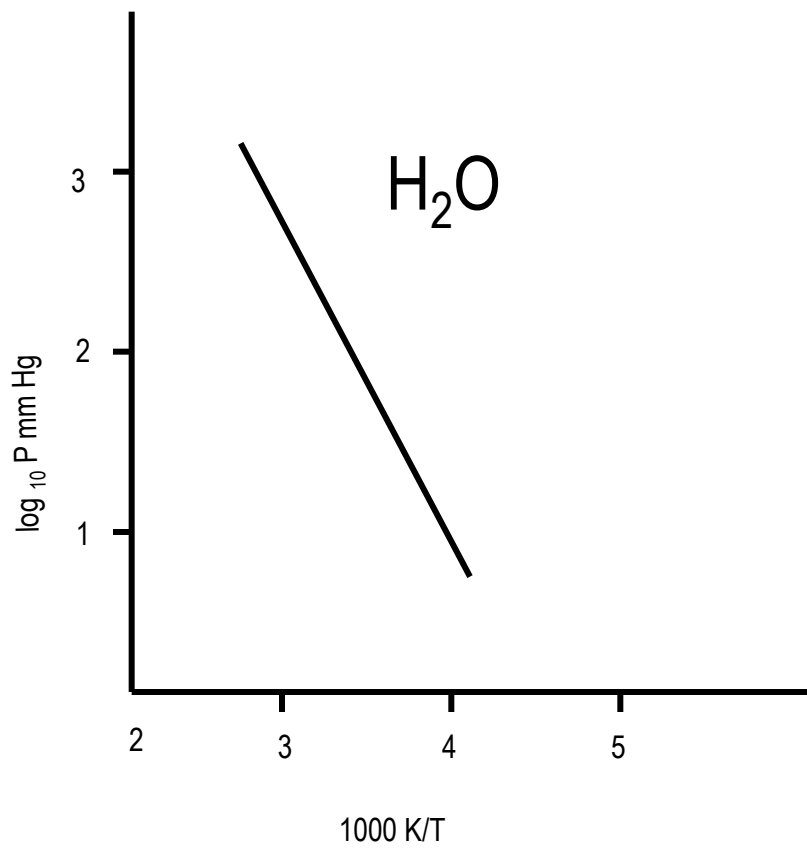
$$\ln P = \Delta H/RT_0 - \Delta H/RT$$

$$\log_{10} P = \Delta H/2.303RT_0 - \Delta H/2.303RT$$

Plot $\ln P$ or $\log_{10} P$ vs. $1/T$, Slope $-\Delta H/R$ or $-\Delta H/2.303R$, Intercept $\Delta H/RT_0$ or $\Delta H/2.303RT_0$.

This equation is the same as, $\log_{10} P = A + BT$

A and B are tabulated for substances



The Nernst heat theorem:

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Another way:

$$G = H - TS \qquad \lim_{T \rightarrow 0} \Delta G = \Delta H$$

Experiments support this.

However, we know that $-\Delta S$ is the slope of the ΔG vs. T graph.

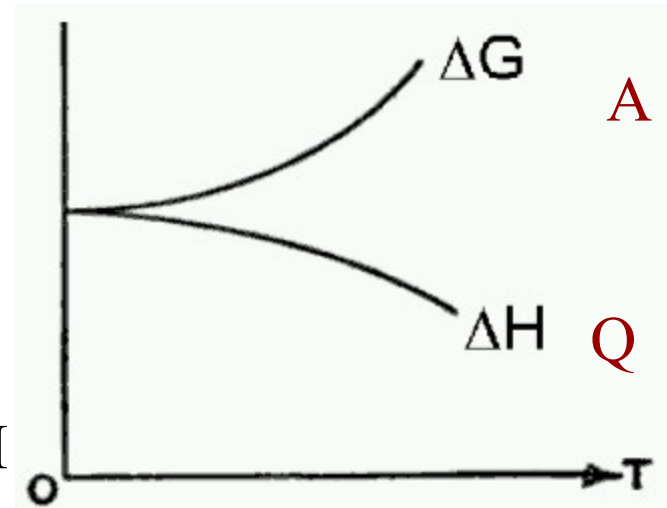
Slope goes to the horizontal limit of 0 as $T \rightarrow 0$

Implication is that $\Delta S \rightarrow 0$.

Max Planck used it to give the third law of thermodynamics:

Entropy of all pure, perfectly crystalline homogeneous materials is 0 at absolute zero.

This gives third law entropies.



Chemical equilibrium

$$\int dG = \int V dP$$

Calculate the free energy of XX

$$G - G_0 = \int_{P_0}^P V dP$$

$$G = G_0(T) + RT \ln P/P_0 \text{ for ideal gases}$$

and

$$G = G_0(T) + V (P - P_0) \text{ for solids and liquids}$$

$$\mu = \mu_0 + RT \ln P \text{ (for one mole)}$$

Equilibrium constant and ΔG

$\mu_i = \mu_{i0} + RT \ln P_i$ i is a component gas, for one mole

Consider the reaction (for an ideal gas), $aA + bB \rightarrow cC + dD$ (1)

ΔG of the reaction can be given in terms of equation (1)

Assume, $\Delta G^\circ = c \mu_{C0} + d \mu_{D0} - (a \mu_{A0} + b \mu_{B0})$

So, $\Delta G = \Delta G^\circ + RT \ln [P_C^c P_D^d / P_A^a P_B^b]$ or

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = RT \ln Q/K$$

$[P_C^c P_D^d / P_A^a P_B^b]_e = K$, equilibrium constant

At equilibrium, $0 = \Delta G^\circ + RT \ln [P_C^c P_D^d / P_A^a P_B^b]$

$$\Delta G^\circ = - RT \ln [P_C^c P_D^d / P_A^a P_B^b] = - RT \ln K$$

Effect of Temperature on Chemical Equilibrium

The equilibrium constant of a chemical reaction is constant at a given temperature, but varies considerably with changes in temperature.

A quantitative relation can be found with van't Hoff equation.

$$\Delta G^\circ = - RT \ln K$$

or

$$\ln K_a = - \Delta G^\circ / RT$$

On differentiating equation with respect to T at constant pressure we get, **why constant P?**

$$d \ln K/dT = - 1/R[d(\Delta G^\circ/T)/dT]_P$$

{As $[d(\Delta G^\circ/T)/dT]_P = - \Delta H^\circ/T^2$ } **→ G-H equation**

$$d \ln K/dT = -1/R (-\Delta H^\circ/T^2)$$

or

$$d \ln K/dT = \Delta H^\circ/RT^2$$

For gaseous reactions, $K_a = K_p$ and hence equation becomes,

$$d \ln K_p/dT = \Delta H^\circ/RT^2$$

In the case of solutions, K has to be in terms of activities.

This result represents the variation of equilibrium constant with temperature and is generally known as the **van't Hoff equation**.

In order to integrate the equation, ΔH° must be known as a function of temperature. Assuming ΔH° to be constant over a small range of temperatures integration of equation yields:

$$\int_{K_{P1}}^{K_{P2}} d \ln K_p = \int \Delta H^\circ / RT^2 dT$$

$$[\ln K_p] = \Delta H^\circ / R [-1/T]$$

$$\begin{aligned} \ln K_{P2} / K_{P1} &= \Delta H^\circ / R [-1/T_2 + 1/T_1] \\ &= \Delta H^\circ / R [T_2 - T_1 / T_1 T_2] \end{aligned}$$

$$\log K_{P2} / K_{P1} = \Delta H^\circ / (2.303R) [T_2 - T_1 / T_1 T_2]$$

Equation helps in calculating K_{p_2} at T_2 provided the enthalpy of the reaction at constant pressure ΔH° , K_{p_1} and T_1 are known.

Alternatively,

ΔH° can be determined if K_p is known at two temperatures.

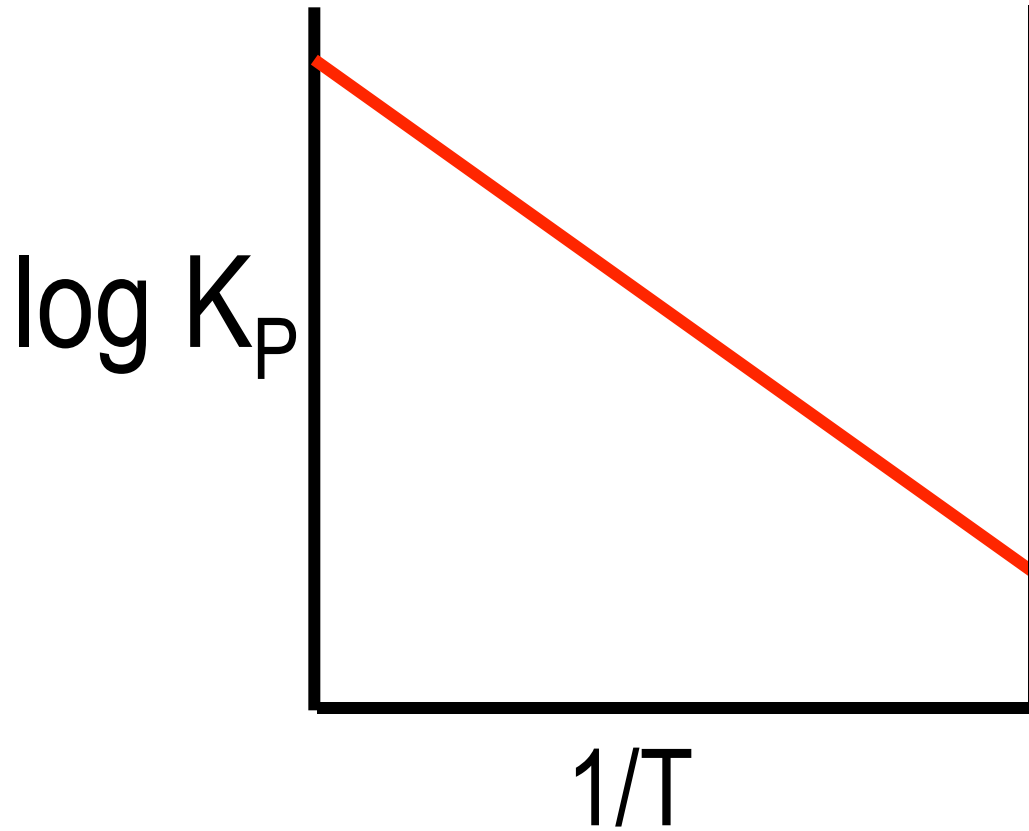
Integrating equation without using limits, we get

$$\int d \ln K_p = \int \frac{\Delta H^\circ}{RT^2} dT$$

$$\ln K_p = - \frac{\Delta H^\circ}{RT} + \text{constant}$$

Or

$$\log_{10} K_p = - \frac{\Delta H^\circ}{2.303 RT} + \text{constant}$$



Plot of $\log K_p$ against $1/T$

Ideal solutions, Raoult's law

$$P_A = X_A P_A^\circ$$

$$\mu_A = \mu_A^\circ + RT \ln P_A/P_A^\circ$$

$$\mu_A = \mu_A^\circ + RT \ln X_A$$

For non-ideal solutions,

$$\mu_A = \mu_A^\circ + RT \ln a_A$$

a_A is activity of A, an effective mole fraction

$a_A = P_A/P_A^\circ$, it can be measured by measuring vapour pressures.

Activity of a solvent approaches mole fraction when concentration of solute approaches zero.

Activity is often expressed as $a_A = \gamma_A X_A$

γ is the activity coefficient, $\gamma \rightarrow 1$ as $x_A \rightarrow 1$

How about solutes?

Henry's law (ideal)

$$P_B = K_B X_B$$

$$\mu_B = \mu_B^\circ + RT \ln X_B$$

Real solutions,

$$\mu_B = \mu_B^\circ + RT \ln a_B$$

Entropy change during phase transition:

$$\Delta_{trs.} S = \frac{q_{rev}}{T_{trs}} = \frac{\Delta_{trs} H}{T_{trs}} \quad (\text{phase transition at fixed pressure and fixed temperature})$$

Trouton's Rule:

The entropy of vaporization of all normal liquids at their boiling points has an almost constant values of $\sim 21 \text{ cal K}^{-1} \text{ mol}^{-1} \equiv 87.9 \text{ JK}^{-1} \text{ mol}^{-1}$.

Standard entropy of vapourisation is the same for all liquids $\sim 85 \text{ JK}^{-1} \text{ mol}^{-1}$.

Absolute entropy of a gas at temperature (T):

$$S(T') = \int_0^{T_{fus}} \frac{C_P^S(T) dT}{T} + \frac{\Delta_{fus} H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^l(T) dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^{T'} \frac{C_P^g(T) dT}{T}$$

Additional reading

Partial molar quantities

Properties such as, U , H , S , G , A , etc. depend upon the number of moles, n , in addition to P , V and T .

$$U = f(P, V, T, n_1, n_2, \dots, n_i)$$

n_1, n_2, \dots, n_i represent the number of moles of each constituent in volume, V .

$$U = f(P, T, n_1, \dots, n_i)$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_{T, n_1, \dots, n_i} dP + \left(\frac{\partial U}{\partial T}\right)_{P, n_1, \dots, n_i} dT + \left(\frac{\partial U}{\partial n_i}\right)_{P, T, n_1, \dots, n_i} dn_i$$

$\left(\frac{\partial U}{\partial n_i}\right)_{P, T, n_1, \dots, n_{i-1}}$ is the **partial molar internal energy** \bar{U}_i .

Similarly S_i , H_i , etc can be defined. $\partial U / \partial n_i$ refers to the change in U with the addition of one mole of the i^{th} component keeping all the other variables constant. Thus the system should be dilute such that the addition of a mole of one constituent does not change the concentration appropriately.

The quantity,

$(\partial G/\partial n_i)_{P, T, n_1, \dots} = \mu_i$ is called the chemical potential.

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$(dG)_{T, P} = \sum_i \mu_i dn_i$$

$$G_{T, P} = \mu_1 n_1 + \mu_2 n_2 + \dots$$

Partial molar free energy is the contribution per mole of that constituent to the free energy of the system.

For a one component system, $\mu = G/n$, partial molar free energy is the chemical potential for a pure substance.