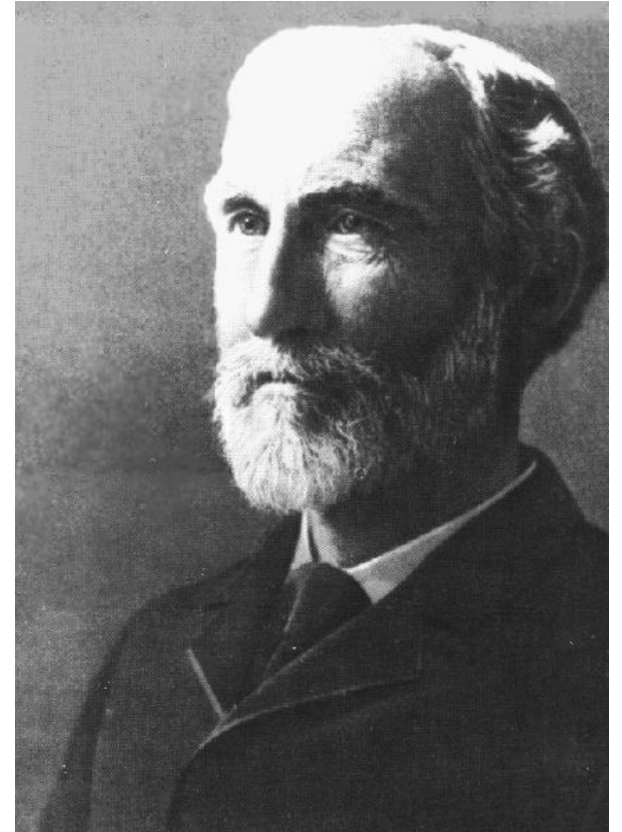


Lecture 8

Phase Equilibrium



Josiah Willard Gibbs 1839-1903

Discontinuity in the free energy, G versus T graph, phase transition.

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

$$\mu \text{ of phase A} = \mu \text{ of phase B}$$

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 $(dG/dT)_P$

Chemical Potential of each constituent must be the same everywhere. The simple way to write this for a one-component system, $d\mu = -SdT + \bar{V}dP$ (One component)

$$(\partial\mu/\partial T)_P = -S ; (\partial\mu/\partial P)_T = \bar{V}$$

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.

Phases of pure substances

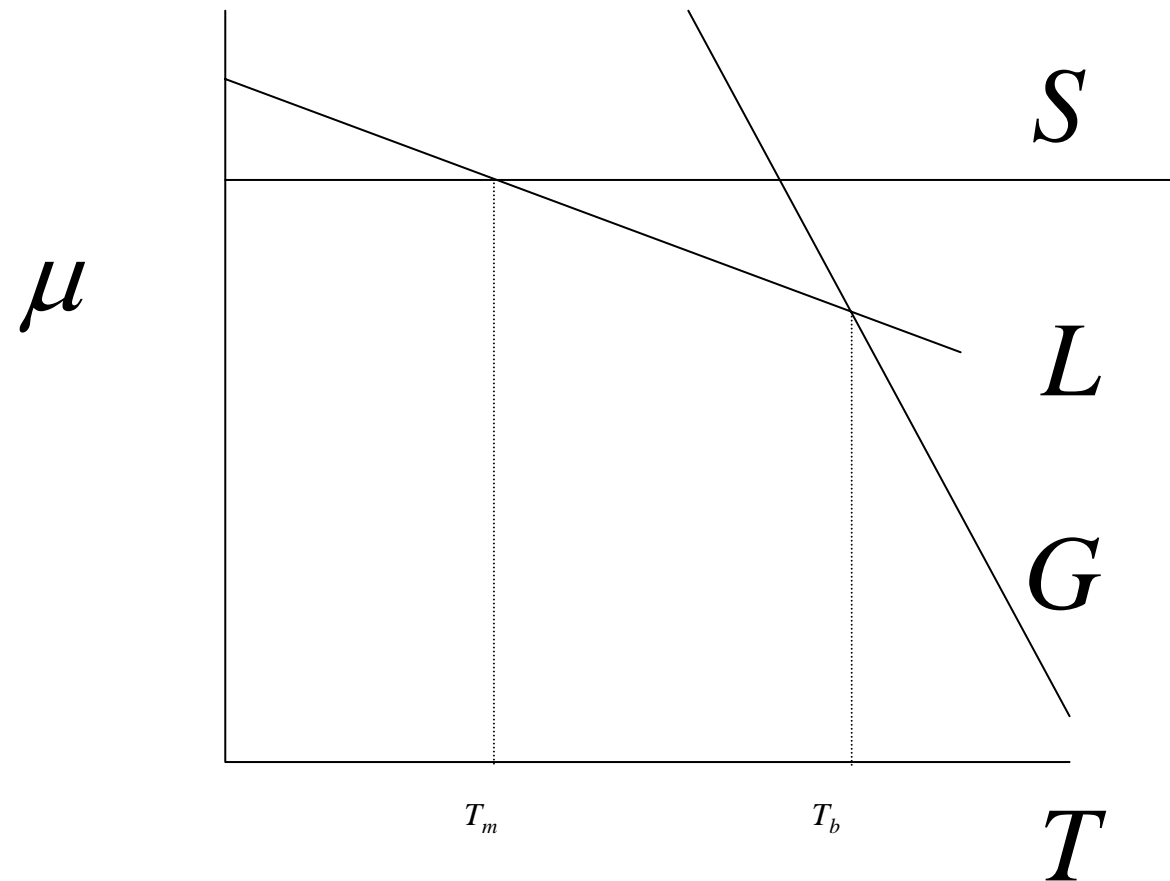
$$(\partial\mu_s/\partial T)_P = -S_{\text{solid}}$$

$$(\partial\mu_l/\partial T)_P = -S_{\text{liquid}}$$

$$(\partial\mu_v/\partial T)_P = -S_{\text{vapour}}$$

$$S_{\text{gas}} \gg S_{\text{liquid}} > S_{\text{solid}}$$

Slopes of μ Vs. T and μ Vs. P



Phase transitions occur when chemical potentials change discontinuously.

Why don't you see sublimation?

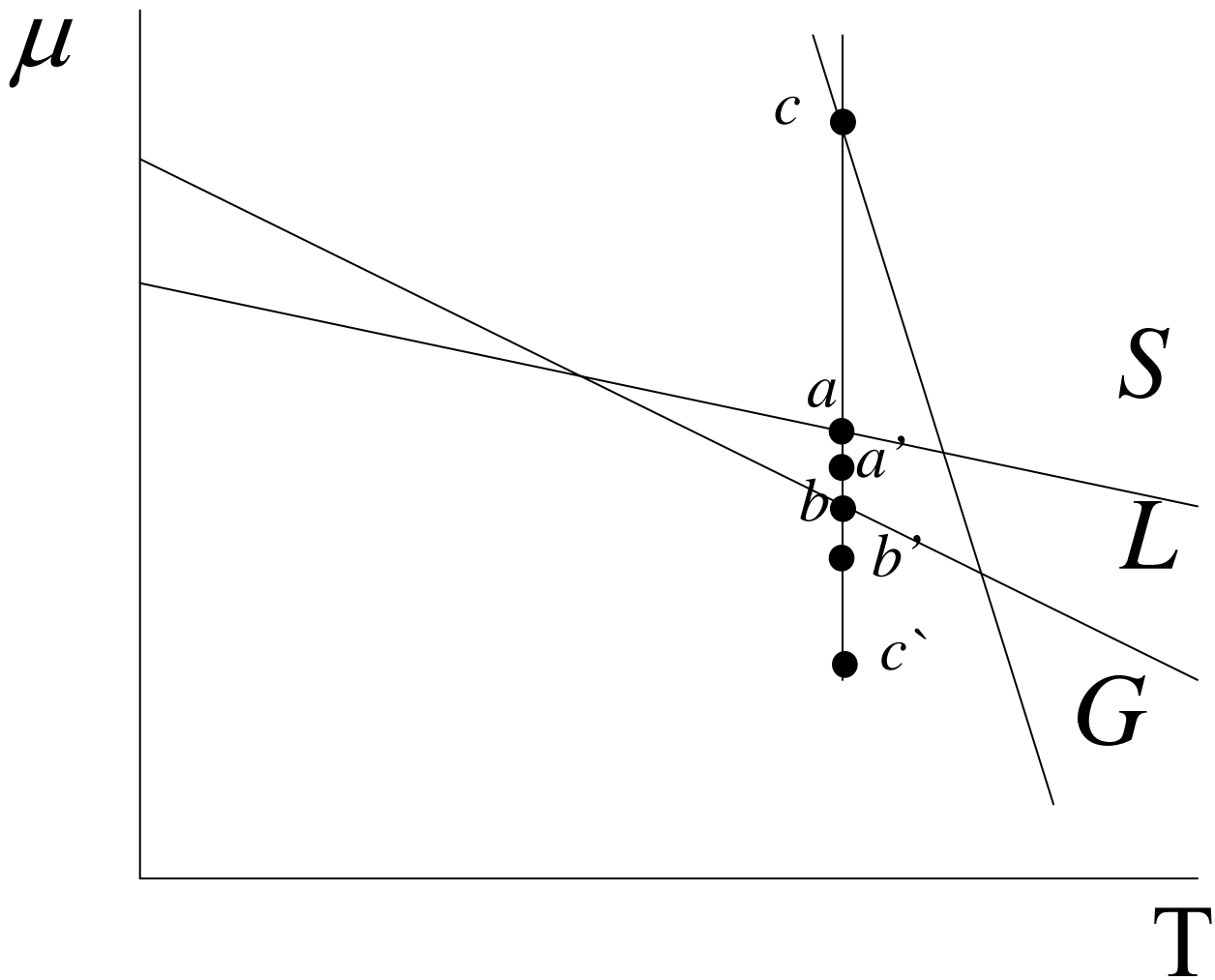
Pressure Dependence of μ Vs. T Curves

Change in pressure changes the free energy.

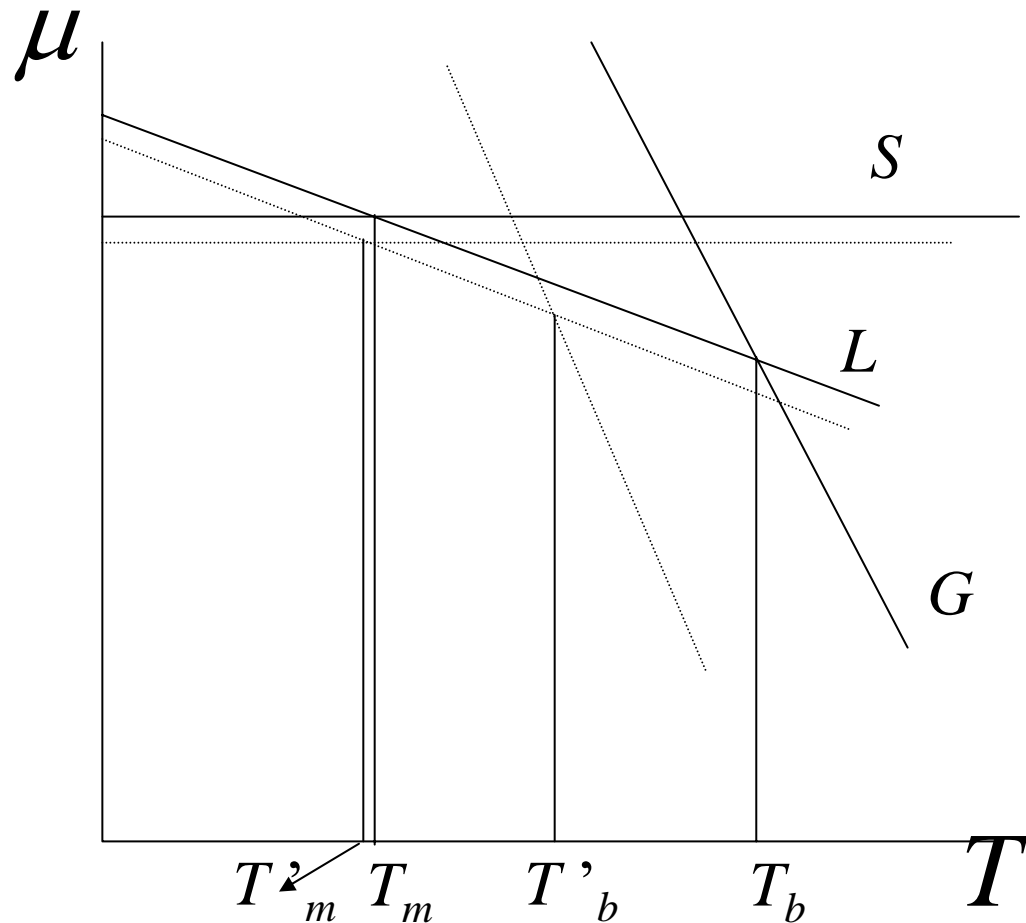
Since $(\partial\mu/\partial P)_T = V$, a decrease in pressure can only decrease the free energy as V is always positive (V is molar volume).

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.



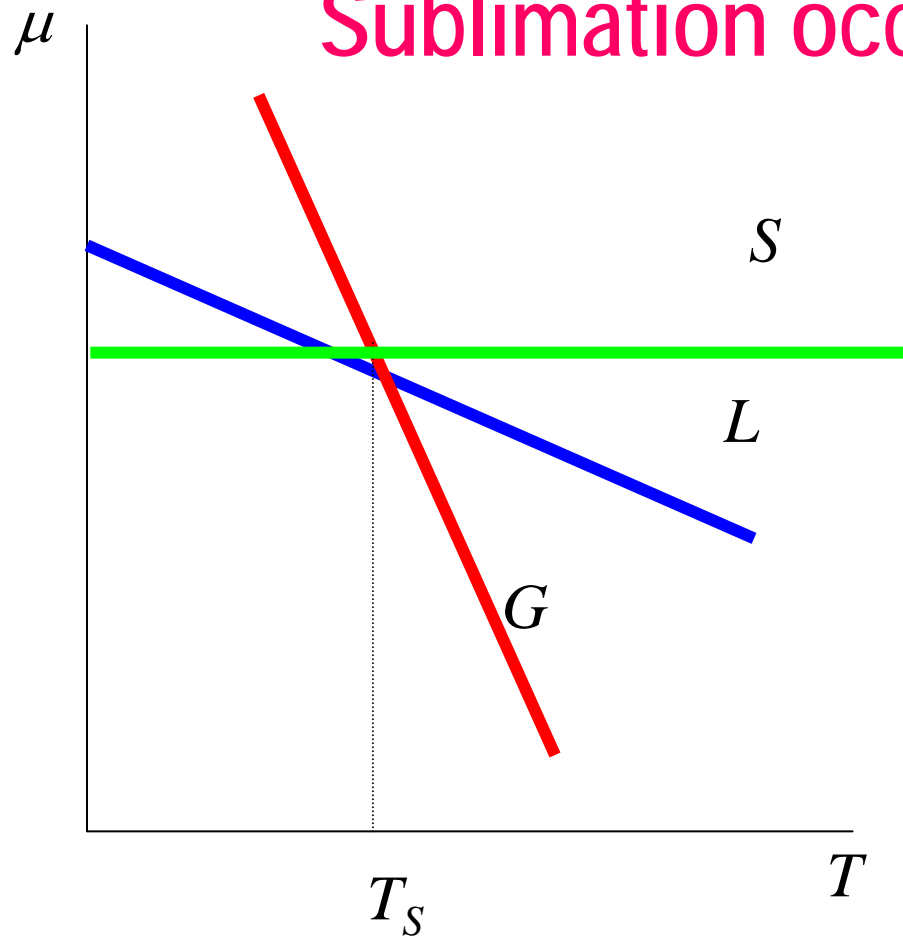
As a result of this shift the entire free energy curve shifts.
Let us plot the free energy at a different pressure.
The dotted lines are at a lower pressure.



As can be seen the boiling point and the melting point shift as a result of change in pressure. A special condition could arise as result of this shift. The boiling point may come lower than the melting point as shown in the figure below. This corresponds to the system evaporating below the melting happens, this is the sublimation.

As can be seen the system which sublimates can be made to melt and then boil depending on the pressure above it.

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

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

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

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

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

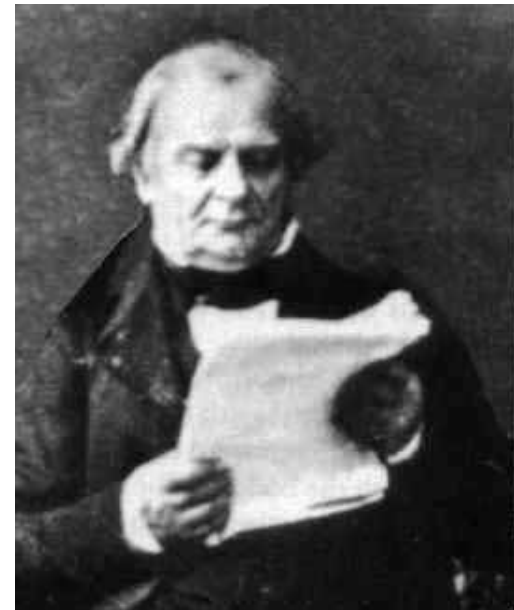
$$(S_{\beta} - S_{\alpha})dT = (V_{\beta} - V_{\alpha})dP$$

$\alpha \rightarrow \beta$ 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 $\Delta S_{fu} = 16 \text{ J/K/mol}$

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

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

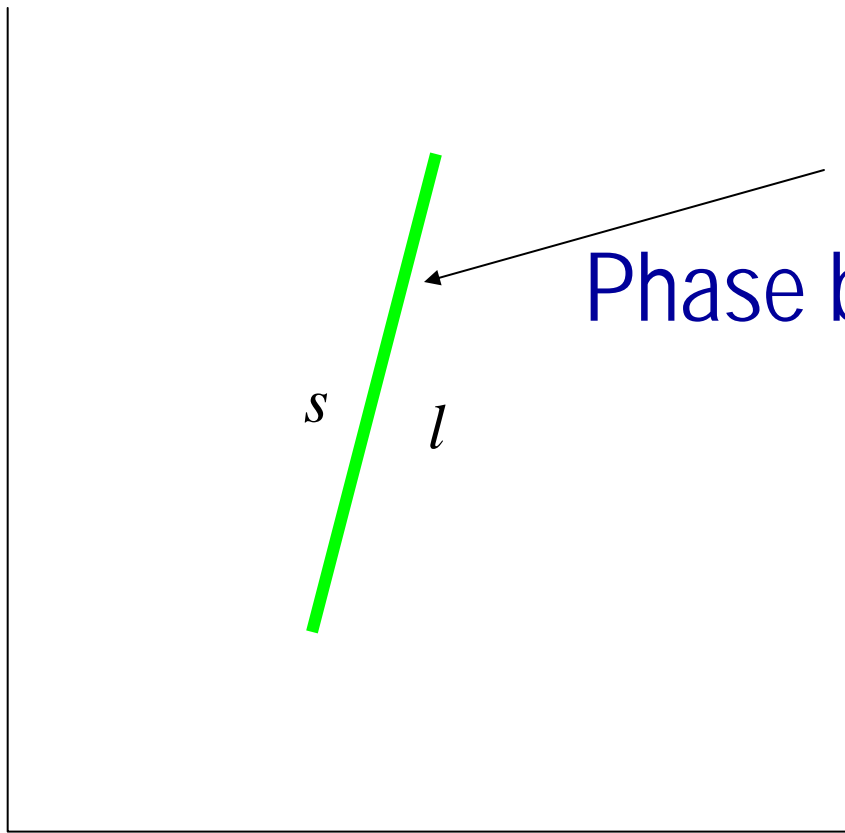
$= 40 \text{ atm/K}$

OR

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

dP/dT is positive for most substrates

P



Phase boundary

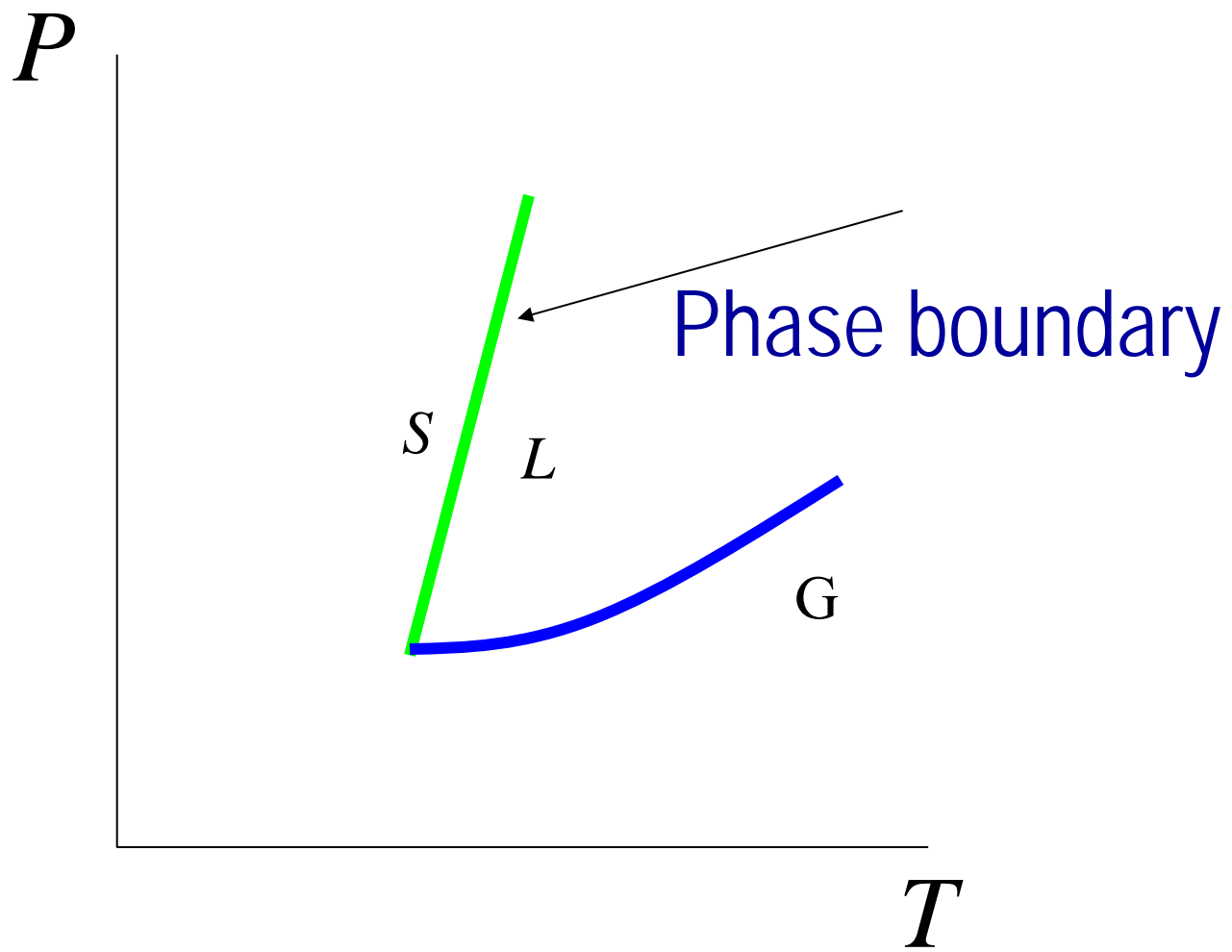
s

l

T

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.

