$$dG \le -SdT + VdP + \sum_i \mu_i dX_i$$

## Gibbs phase rule - an introduction

tells us the number of phases that coexist at equilibrium.

also provides a method for determination of conditions of formation of a phase assemblage.

# of variables

# of components = $c$

# of phases = $\phi$

each phase can vary in composition,

so $c \cdot \phi$ variables and $T$ & $P$

can vary = $c\phi + 2$

# of constraints

for each phase you have stoichiometric constraints

$$\sum_{i=1}^{c} x_i = 1$$

there is one equation for each phase

for a total of $\phi$

## Gibbs phase rule cont'd

and we have conditions of equilibrium e.g. the chemical potentials of component $i$ in each phase is the same at equilibrium so, in phase A, B, C etc.

$$\mu_i^A = \mu_i^B = \mu_i^C \ldots$$

there are $\Phi - 1$ equalities, one for each component for a total of

$$c(\Phi - 1)$$

Gibbs phase rule $\underline{F}$ is the relation between the number of variables and the number of constraints

$$F = \#\text{ of variables} - \#\text{ of constraints}$$

$$c\Phi + 2 - [\Phi + c(\Phi - 1)]$$

$$= c + 2 - \Phi$$

leads to conditions...

$F = 0$ invariant

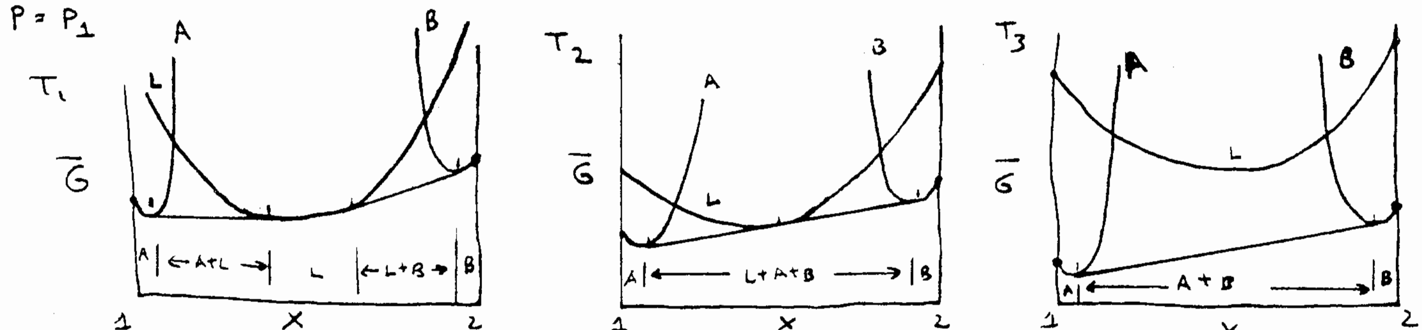
$F = 1$ univariant

$F = 2$ divariant

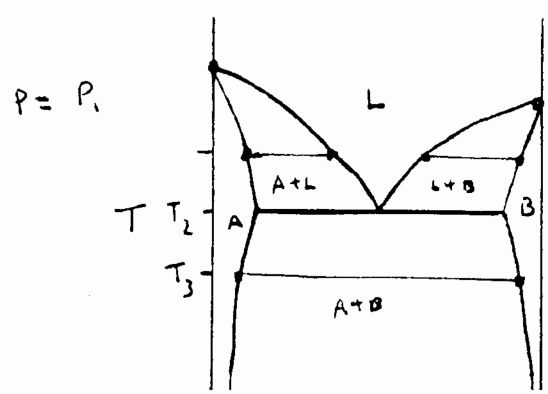
Recall the phase rule $F = c + 2 - \phi$ , or for a two component system $F = 4 - \phi$ .

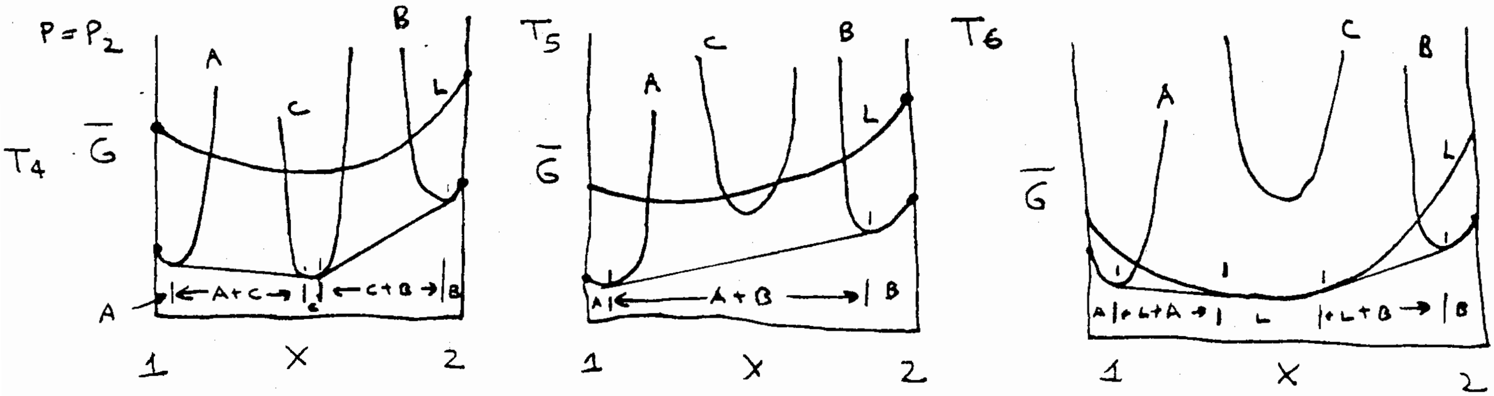
So, 4 phases coexist at an invariant point, 3 on a univariant curve and two phase coexistence is divariant. An invariant assemblage will on exist at a unique pressure and temperature. We will usually draw phase diagrams in two component systems using T - X as our coordinate axes. So, it would be very rare, in general, to find a 4-phase coexistence. A 3-phase, or univariant, equilibrium would be much more likey to occur if we consider the phase relations at a fixed pressure and variable temperature. So, we will generally see these 3-phase (univariant) lines on our T-X diagrams.

We will pick a pressure ($P_1$) and choose 3 arbitrary phases A, B and L in the system 1-2. We assume further that we know the relative positions of these G-curves and the way in which they move with variations in T. Our first G-X section is at $T_1$. Here all 3 phases are stable. The minimum free energy is give for single phases, or for mixtures of phases. A tangent line drawn to the lowest surface of the G-curve of adjacent phases demonstrates that for some parts of composition space, the lowest free energy is given by a mixture of two phases, rather than one phase with the bulk composition in that phase region.

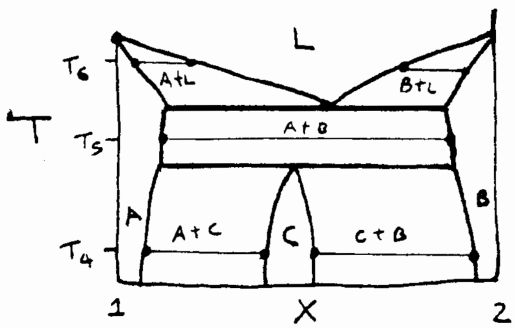



The next two G-X sections are at successively lower temperatures. The G-curve for L is moving to higher values of G relative to the G-curves for A and B. So, at $T_3$ L is no longer stable with respect to a mixture of A and B. At $T_2$ we have a special 3-phase coexistence where L+A+B all coexist. A T-X diagrams summarizes only the compositional information for each of these G-X sections, and looks like so:

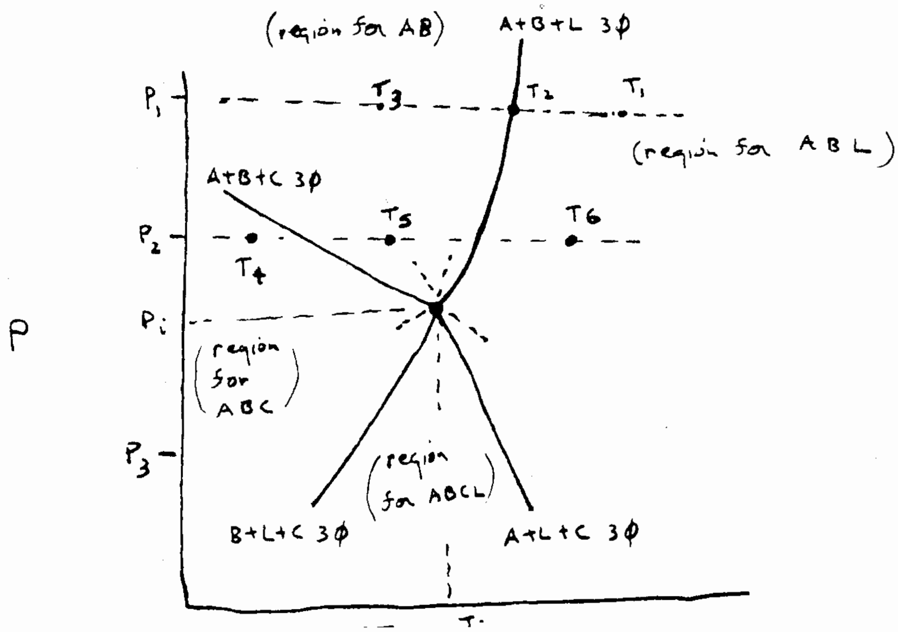





Now, let's change pressure to $P_2$ ( a lower pressure). Here, it turns out that there is another phase stable (C), in addition to L, A and B. This is all right, because we can have up to 4 phases coexisting in a two component system. Let us look at the changes in G-X relations among these 4 as we raise T. We draw G-X curves at successively higher temperatures $T_4$, $T_5$, and $T_6$. The T-X diagram for $P_2$ extracts only the compositional information of which phases coexist, and what their compositions are.

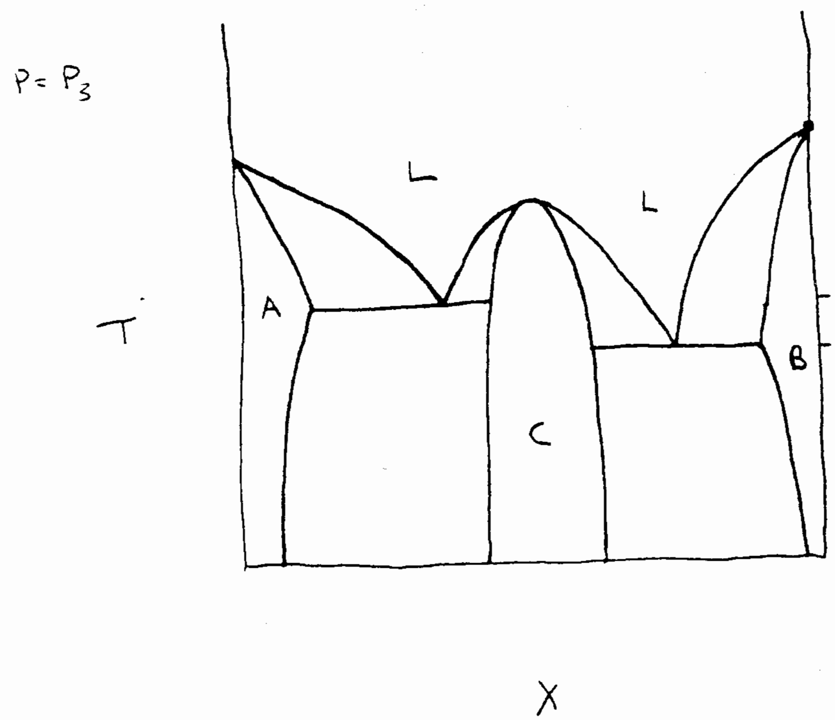



We can now project into P-T space, but we will lose some of the compositional information that we had in the T-X sections. The large regions in the T-P diagram are divariant regions, and the letters show the possible thermodynamically stable divariant (two phase) assemblages that can coexist in that region. Each divariant region is bounded by univariant curves ( these 3-phase coexistence lines which we saw in the T-X diagrams can occur at different temperatures with varying pressure. Finally, all the univariant lines meet at the invariant point, where all four phases coexist at a special $P_i$ and $T_i$.



In a two component system there will be 4 univainat lines (in general) around each invariant point, and they must be arranged around the point in such a way that the divariant region into which the metastable extensions of the univariant lines project do not violate the G-X stability criteria.

At $P_3$ a T-X diagram must look like ....




over this region of T-X space there are divariant assemblages for all 4 phases A+C, C+L and B+L.