Lecture 30

Phase Diagrams

Last Time

Common Tangent Construction

Construction of Phase Diagrams from Gibbs Free Energy Curves

If the temperature in Figure 28-5 is decreased a little further:

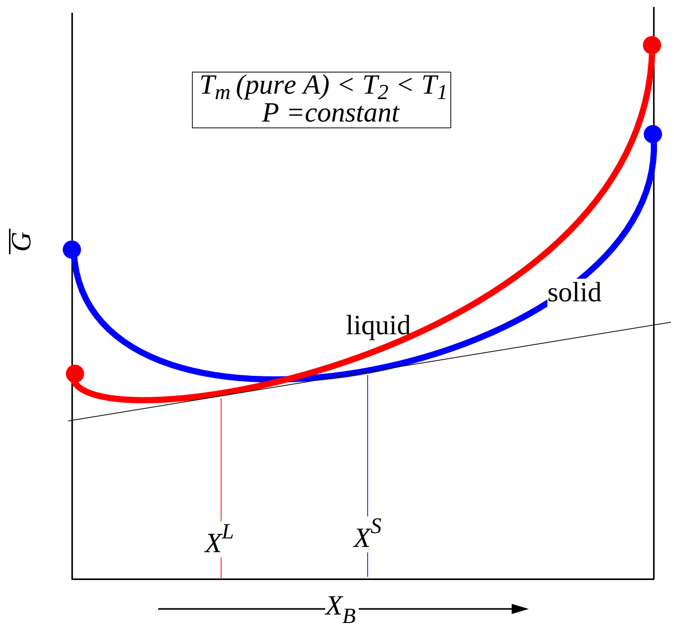

Figure 30-1: Figure 28-5 drawn at an even lower temperature than Figure 28-3.

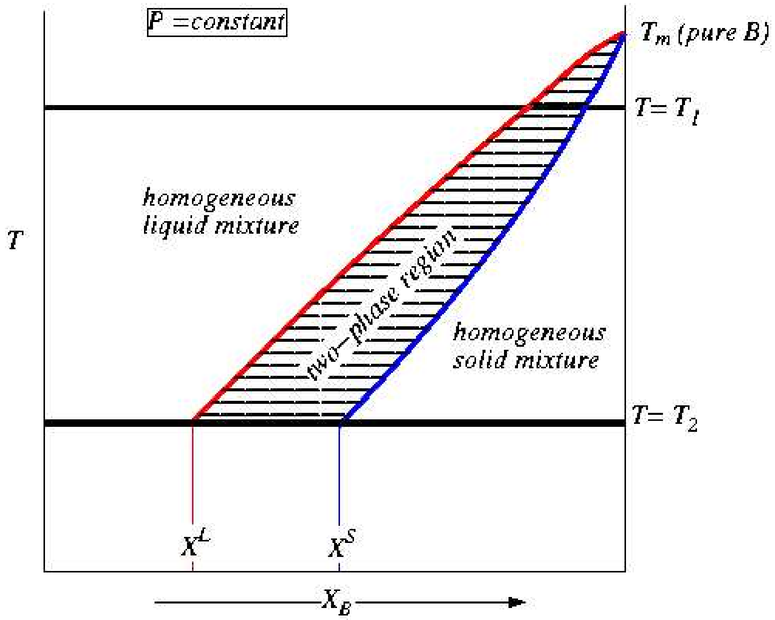

Figure 30-2: Plot of the equilibrium compositions as the temperature is decreased.

Lowering it to the melting point of pure A

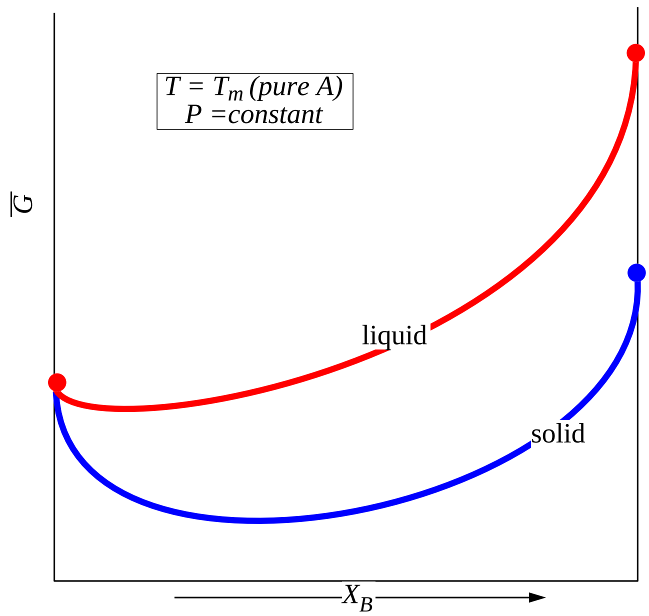

Figure 30-3: Figure 28-5 at the melting point of pure A.

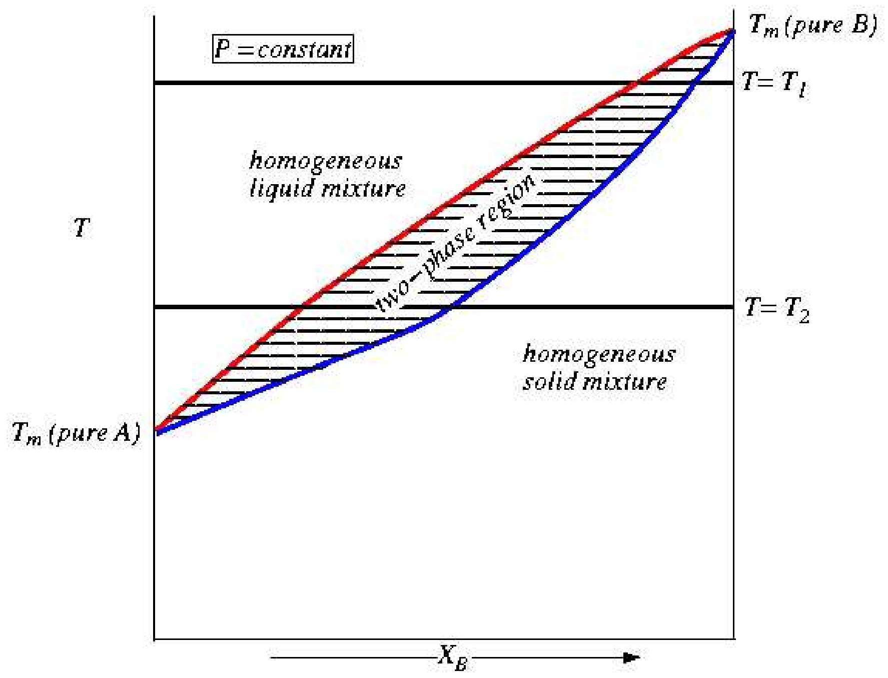

Figure 30-4: A binary alloy phase diagram—derived from Figures 28-4 through 30-3.

A Menagerie of Binary Phase Diagrams

The phase diagram in Figure 30-4 is the simplest possible two-component phase diagram at constant pressure.

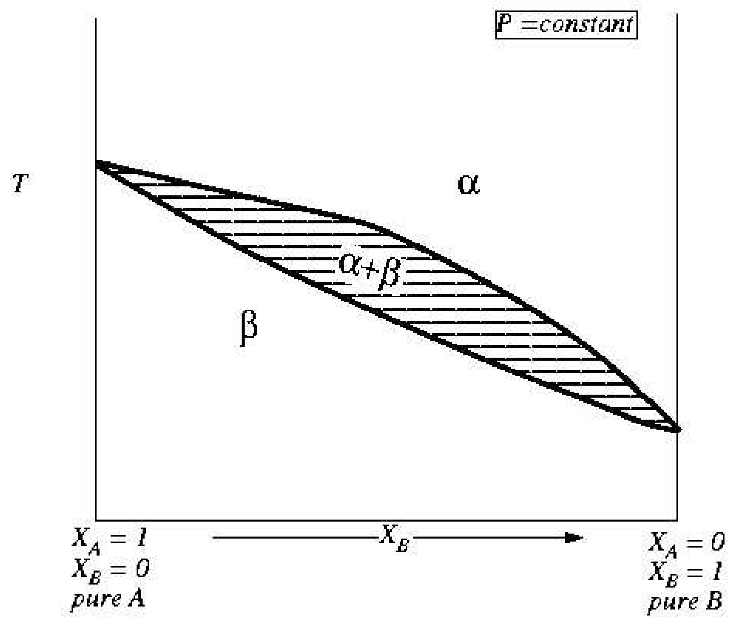

Figure 30-5: The so-called "lens" phase diagram. The upper line is the limit of $f^{\text{solid}} \rightarrow 1$ and is called called the solidus curve. The lower line is called the liquidus curve.

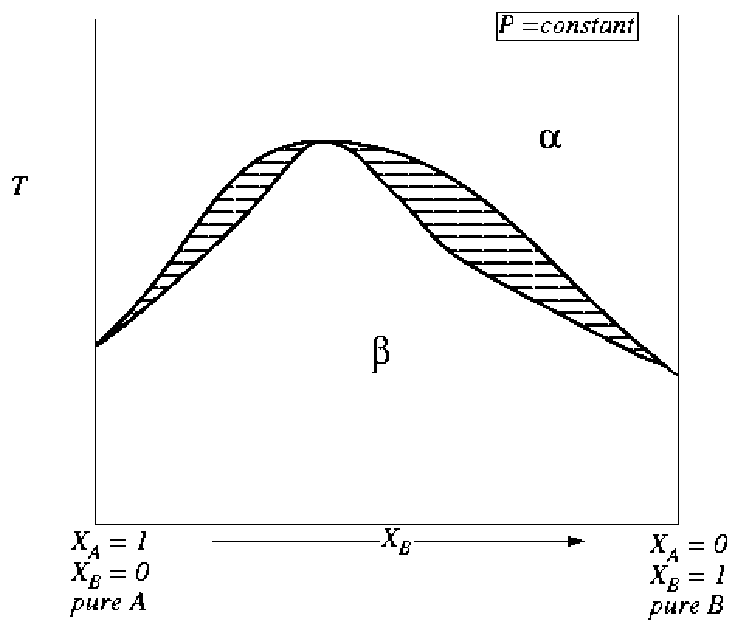

Figure 30-6: A variation on the lens phase diagram.

Consider how the Gibbs phase rule relates to the above phase diagrams.
The Gibbs phase rule is: $D = C + 2 - f$
However, P is constant so we lose one degree of freedom: $D = C + 1 - f$
In the two phase region—$D = 2 + 1 - 2 = 1$—so there is one degree of freedom.

Question: What is the degree of freedom? What does it mean?

- If temperature is changed at fixed $\langle X_\circ \rangle$, then the change in volume fraction of phases is determined. In other words there is a relation between dT and df^{solid}.
- If $\langle X_\circ \rangle$ is changed with fixed phase fractions then ΔT is determined by the change.

Consider another two-component phase diagram and see if it violates the Gibbs phase rule.

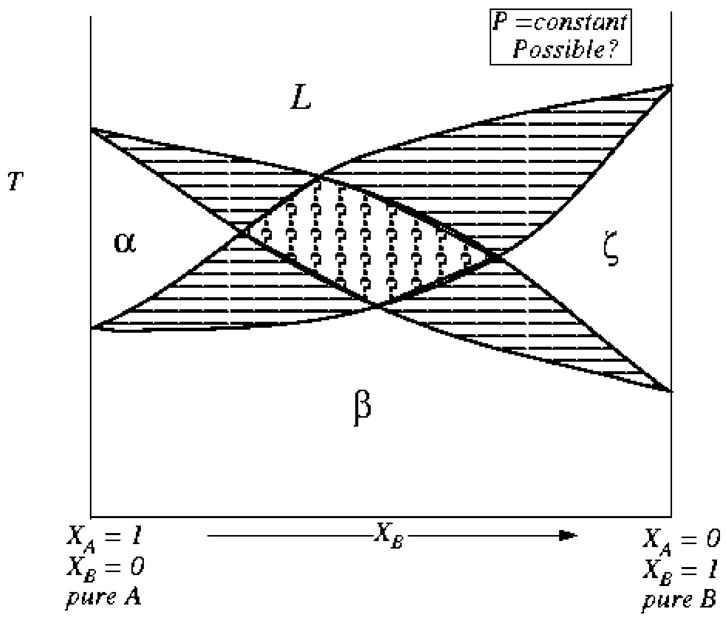

Figure 30-7: Is this a possible phase diagram?

Consider the three-phase region: $D = C + 1 - f = 0$

Because there are no degrees of freedom, the three-phase region must shrink to a point in a two component system. This places restrictions on the topology of binary phase diagrams.

The diagrams below illustrate how such an invariant point (i.e., three phase equilibria in a two component system) arises:

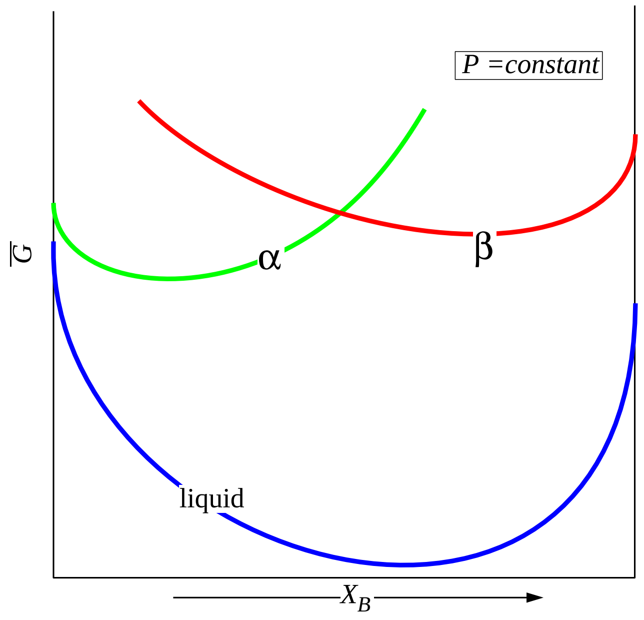

Figure 30-8: Liquid is stable at all compositions at this temperature.

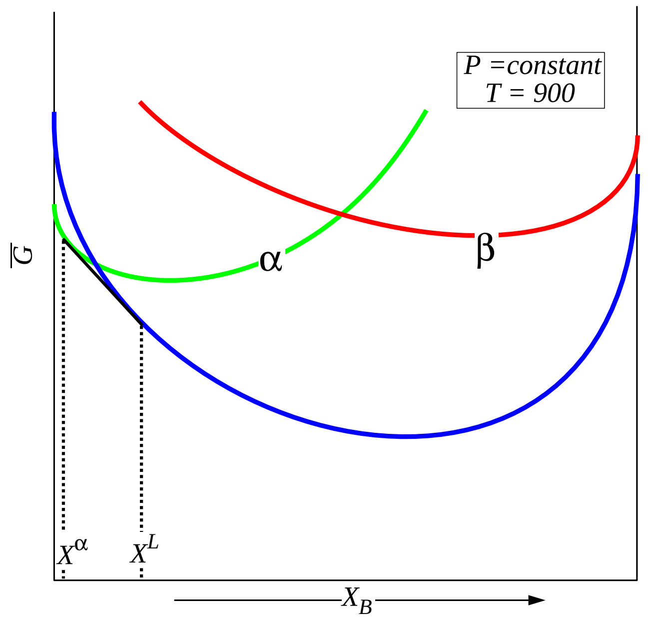

Figure 30-9: One of the solid phases becomes stable.

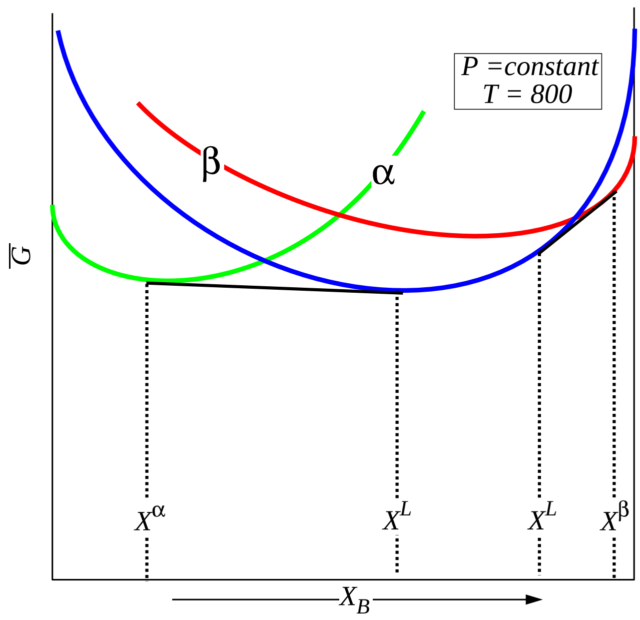

Figure 30-10: The second solid phase becomes stable as well, but not at the same compositions as the first.

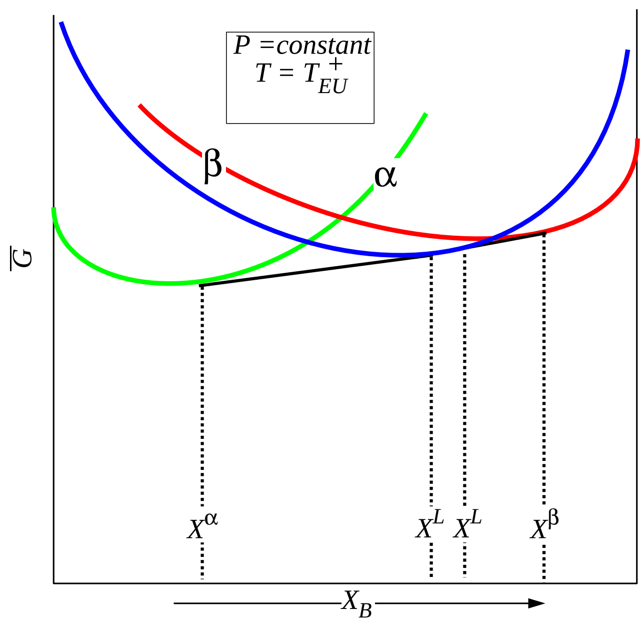

Figure 30-11: At one unique temperature (the *Eutectic*) the two phase regions converge–this is the invariant point.

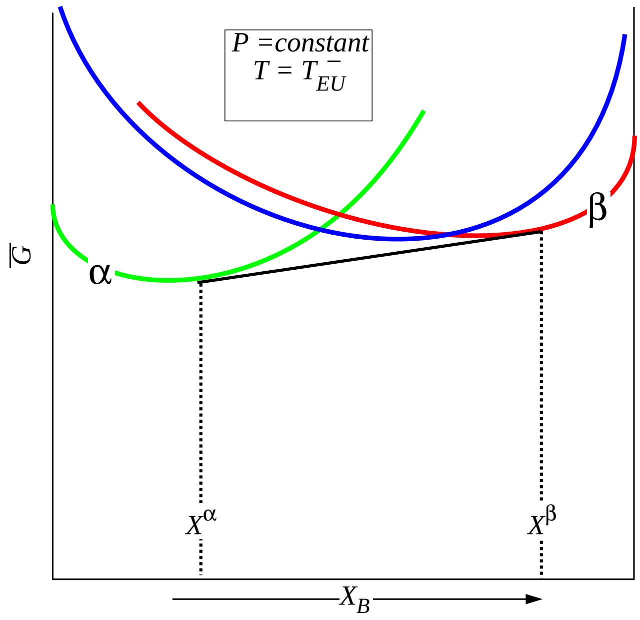

Figure 30-12: Below the eutectic, the two solid phases are separated by a two-phase region.

This yields the following phase diagram

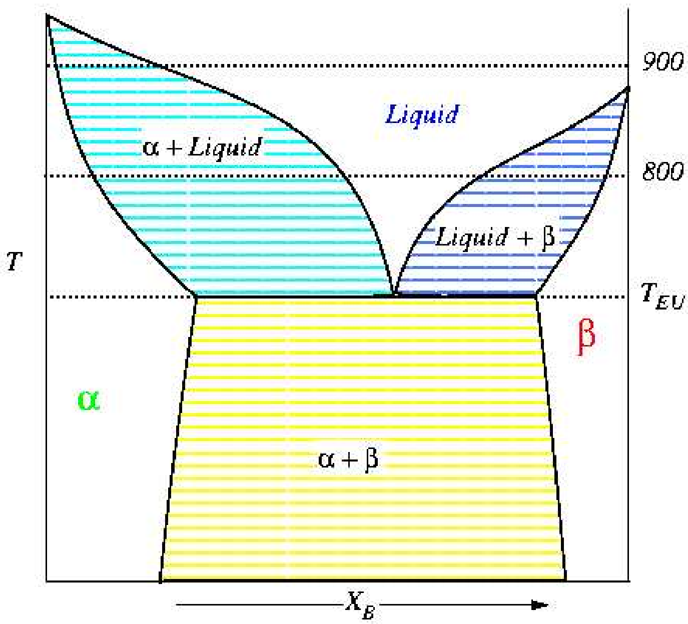

Figure 30-13: The free curves from Figures 30-8 through 30-12, result in a *eutectic phase diagram.*

Classifying the Invariant Points: Drawing Phase Diagrams

There are two fundamental ways that invariant points can arise:[29]

1. When *two* two-phase regions join at a temperature and become *one* two-phase region:

   Eutectic $(\alpha + \text{liquid}) + (\text{liquid} + \beta) \rightleftharpoons (\alpha + \beta)$

   Eutectoid $(\alpha + \gamma) + (\gamma + \beta) \rightleftharpoons (\alpha + \beta)$

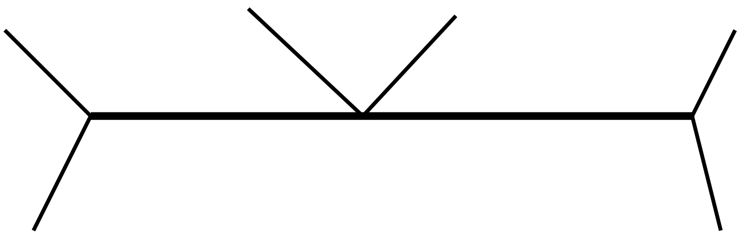

Figure 30-14: Eutectic-type (EV-TYPE at MASSACHVSETTS INSTITVTE OF TECHNOLOGY) invariant points.

2. When *one* two-phase region splits into *two* two-phase regions:

   Peritectic $(\alpha + \text{liquid}) \rightleftharpoons (\text{liquid} + \beta) + (\alpha + \beta)$

   Peritectoid $(\alpha + \gamma) \rightleftharpoons (\gamma + \beta) + (\alpha + \beta)$

[29]There is a third type of invariant point that we will learn about later.

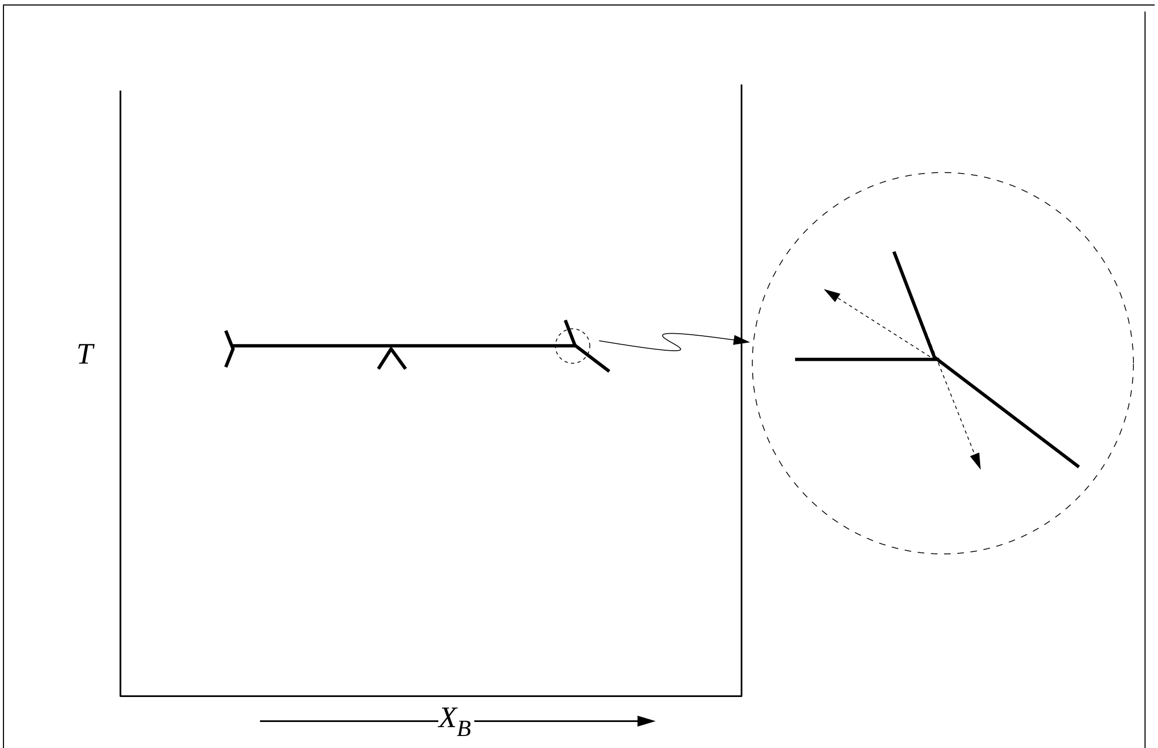

Figure 30-15: **P**eritic-type invariant points.

The invariant points determine the topology of the phase diagram:

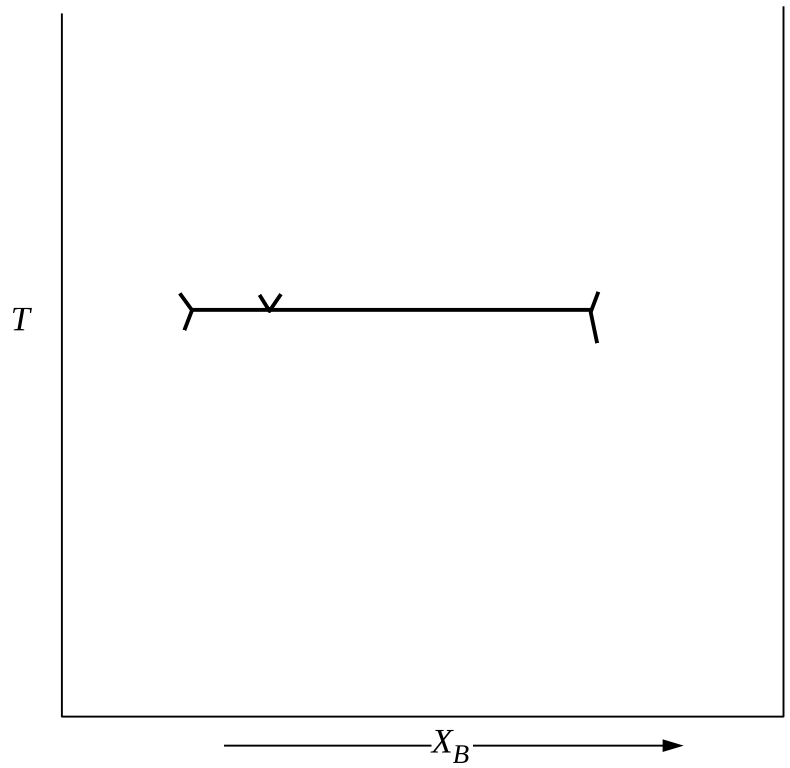

Figure 30-16: Construct the rest of the Eutectic-type phase diagram by connecting the lines to the appropriate melting points.

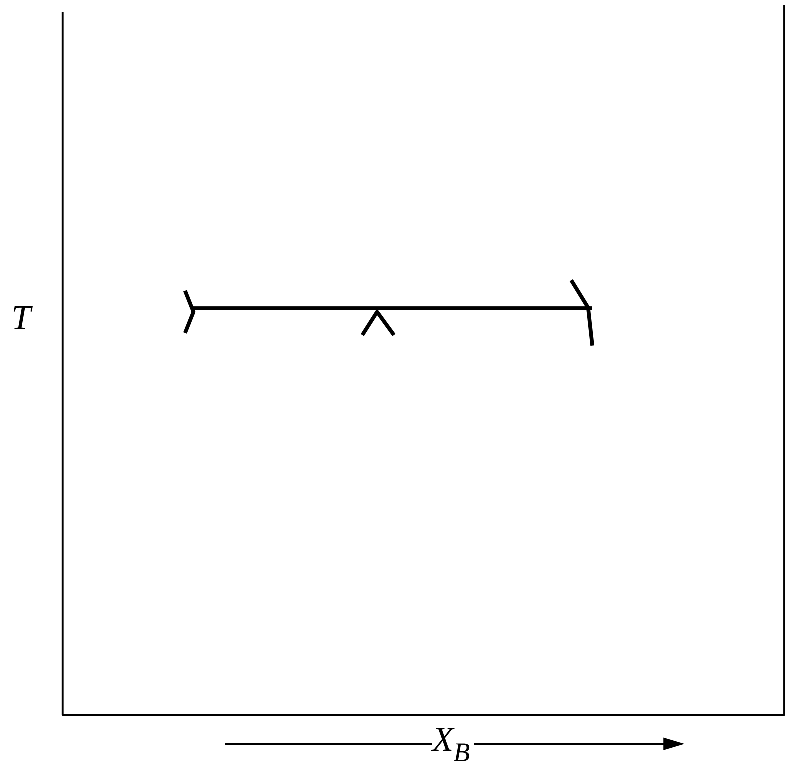

Figure 30-17: Construct the rest of Peritectic-type phase diagram, on the left a rule for all phase diagrams is illustrated—the "lines" must metastably "stick" into the opposite two phase region.

These diagrams can be combined and drawn:

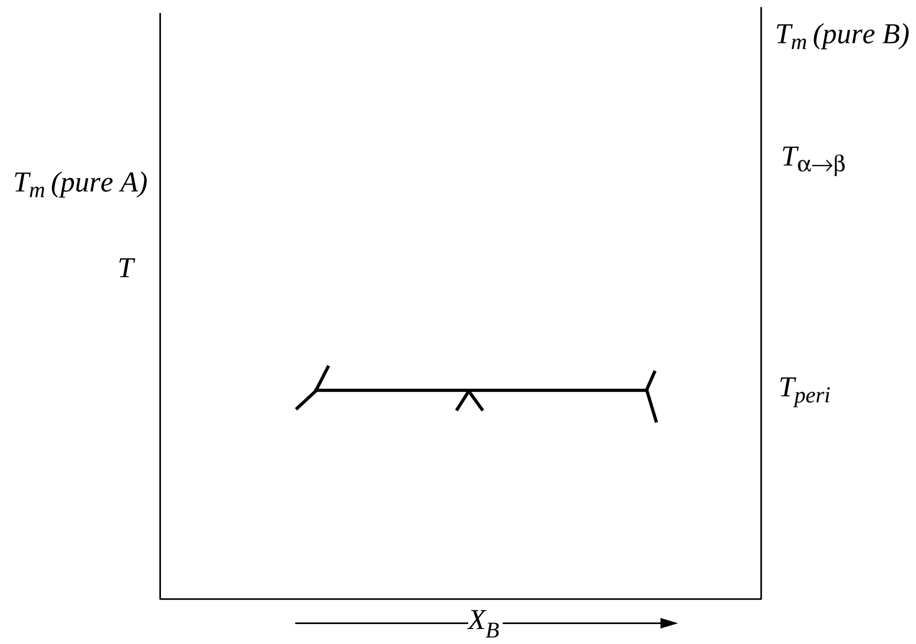

Figure 30-18: Construct the lens over peritectoid phase diagram.

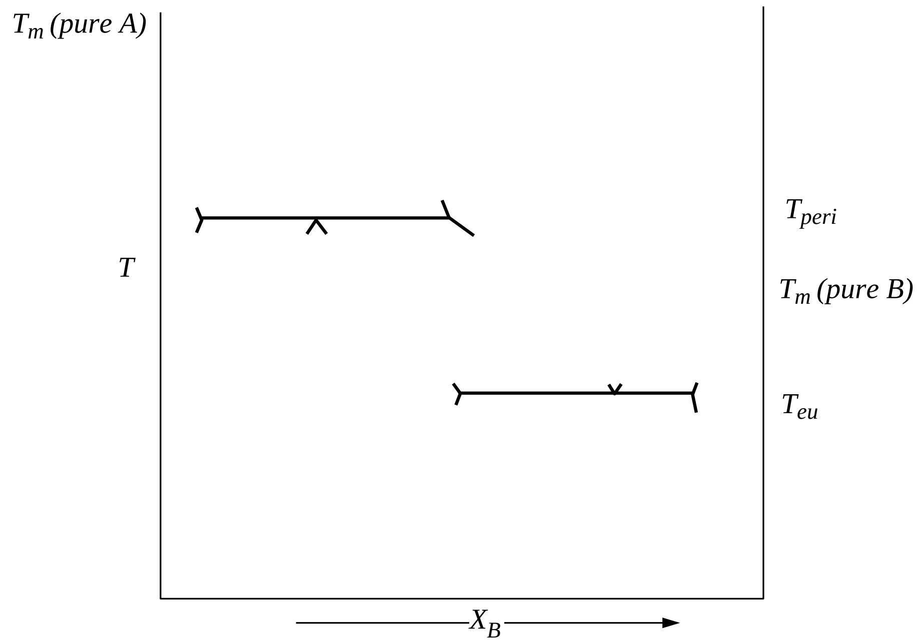

Figure 30-19: Construct the peritectic over eutectic phase diagram.

In all cases, you should be able to predict how the phase fractions and equilibrium compositions change as you reduce the temperature at equilibrium.