Physics 127b: Statistical Mechanics

Phase Transitions in Multicomponent Systems

The Gibbs Phase Rule

Consider a system with n components (different types of molecules) with r phases in equilibrium.

The state of each phase is defined by P, T and then $(n-1)$ concentration variables in each phase. The phase equilibrium at given P, T is defined by the equality of n chemical potentials between the r phases. Thus there are $n(r-1)$ constraints on $(n-1)r+2$ variables. This gives the *Gibbs phase rule* for the number of degrees of freedom f

$$f = 2 + n - r$$

A Simple Model of a Binary Mixture

Consider a condensed phase (liquid or solid). As an estimate of the coordination number (number of nearest neighbors) think of a cubic arrangement in d dimensions giving a coordination number $2d$. Suppose there are a total of N molecules, with fraction x_B of type B and $x_A = 1 - x_B$ of type A. In the mixture we assume a completely random arrangement of A and B. We just consider "bond" contributions to the internal energy U, given by ε_{AA} for $A-A$ nearest neighbors, ε_{BB} for $B-B$ nearest neighbors, and ε_{AB} for $A-B$ nearest neighbors. We neglect other contributions to the internal energy (or suppose them unchanged between phases, etc.). Simple counting gives the internal energy of the mixture

$$\begin{aligned} U &= Nd(x_A^2\varepsilon_{AA} + 2x_Ax_B\varepsilon_{AB} + x_B^2\varepsilon_{BB}) \\ &= Nd\{\varepsilon_{AA}(1-x_B) + \varepsilon_{BB}x_B + [\varepsilon_{AB} - (\varepsilon_{AA}+\varepsilon_{BB})/2]2x_B(1-x_B)\} \end{aligned}$$

The first two terms in the second expression are just the internal energy of the unmixed A and B, and so the second term, depending on $\varepsilon_{\text{mix}} = \varepsilon_{AB} - (\varepsilon_{AA}+\varepsilon_{BB})/2$ can be though of as the energy of mixing. An ideal mixture is one with $\varepsilon_{\text{mix}} = 0$.

There is also an entropy of mixing, which again considering a completely random arrangement of A and B atoms in the mixture is

$$S = -Nk[x_A \ln x_A + x_B \ln x_B].$$

Notice that this entropy of mixing is always positive, i.e. favors mixing, and the dependence on x_B has an infinite slope at the endpoints $x_B = 0, 1$. We will ignore any other contributions to the entropy.

To consider the question phase equilibria, it is easiest to look at $G(P, T, x_B) = U - TS + PV$, because in phase coexistence both phases have the same T and P, and this just leaves the dependence on x_B to investigate. In our simple model we will suppose the PV term is unimportant. The Gibbs potential of the mixture as a function of x_B for some fixed T and P is shown in Fig. 1.

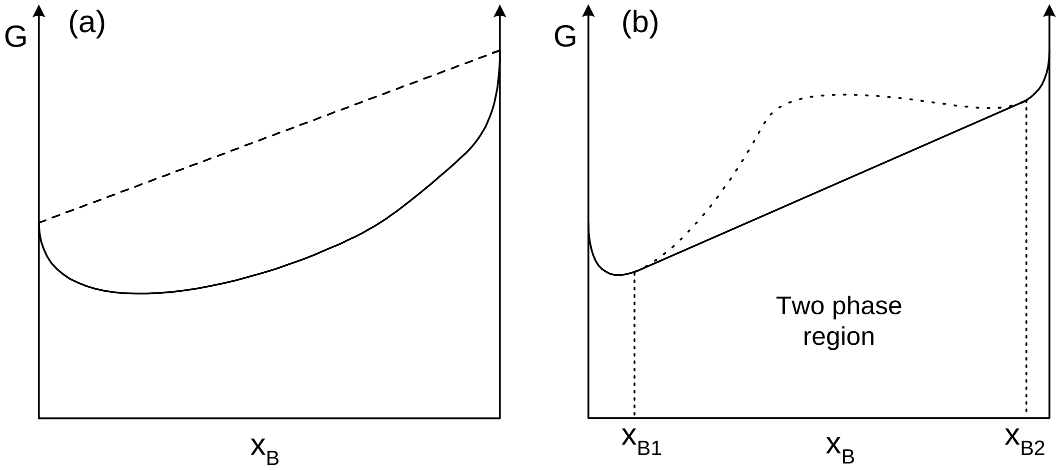

Figure 1: (a) $G(x_B)$ for an ideal mixture ($\varepsilon_{\text{mix}} = 0$) or one with $\varepsilon_{\text{mix}} < 0$. (b) $G(x_B)$ for ε_{mix} sufficiently positive and T sufficiently low that the entropy of mixing does not completely dominate. The dashed line in (a) is G for the unmixed state. In (b) convexity arguments show that we must replace the dotted portion of the curve by the common tangent.

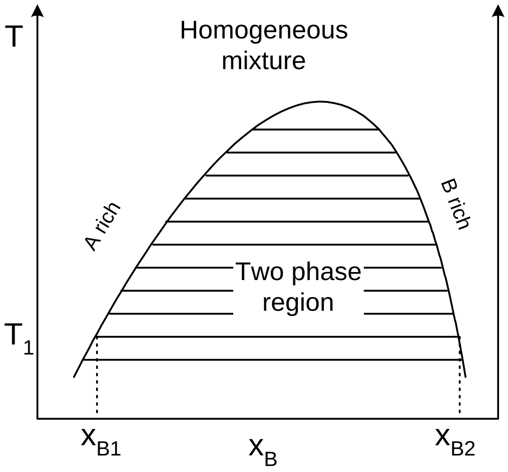

Figure 2: Phase diagram corresponding to Fig. 1b.

For an ideal mixture, $\varepsilon_{\text{mix}} = 0$, or one where the internal energy favors mixing $\varepsilon_{\text{mix}} < 0$ the situation is shown in panel (a). The Gibbs potential is a convex function of x_B as required, and the mixed state exists for any x_B, i.e. A and B are completely *miscible*.

On the other hand for ε_{mix} sufficiently positive, and if the temperature is not too high, the curve for G given by our expressions for U and S is *nonconvex* (the solid-dotted-solid curve). This is unstable to phase separation, and the dotted portion must be replaced by the common tangent. Note that the common tangent construction is *precisely* statement that the Gibbs potential is given by adding the Gibbs potential of the two phases as concentrations x_{B1} and x_{B2} present in the amounts to give the total amount of B equal to Nx_B. (Prove this for yourself!) The amount of these two phases is given by the *lever rule*: the fraction of phase x_{B2} for a system with B concentration x_B is $(x_{B2} - x_{B1})/(x_{B2} - x_{B1})$, etc. At higher temperatures the entropy will dominate, and the curve will again look as in panel (a). This gives is the phase diagram in the $T - x_B$ plane (at some fixed pressure) shown in Fig. 2. Below some temperature complete mixing is not possible for all x_B: for x_B in the shaded region, the system will phase separate into macroscopic regions of A rich and B rich solutions (e.g. at temperature T_1 the concentrations will be x_{B1} and x_{B2}). Again the lever rule tells us the amount of each solution for a given x_B.

Liquid-Gas Transition for Mixtures

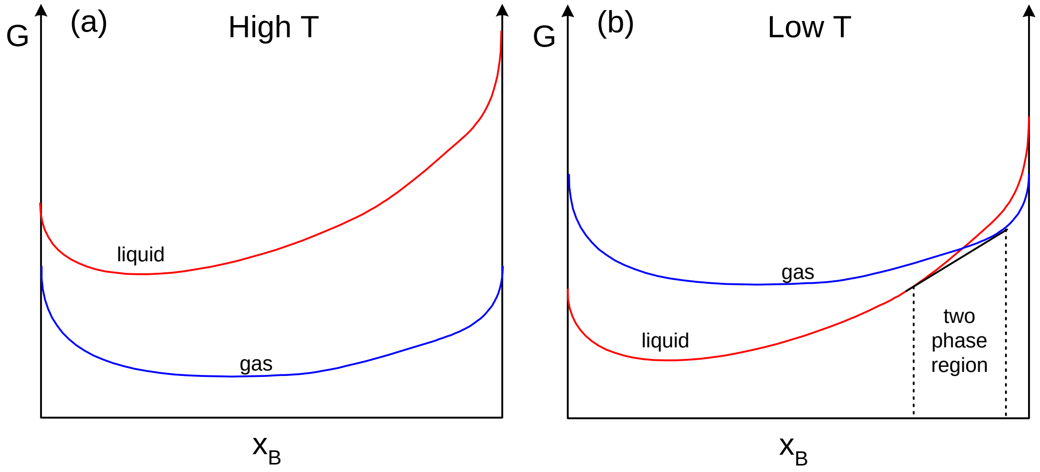

Figure 3: Gibbs potential plots for a simple liquid gas transition in a binary mixture.

As a very simple example of what can happen at the liquid gas transition in mixture, consider the Gibbs potential plots in Fig. 3. The Gibbs potential for the liquid is taken to be as in Fig. 1, and that for the gas the same but without the internal energy contribution. At high temperatures G for the gas is lower than G for the liquid for all x_B, and so the system is gaseous for all x_B. As T is lowered, G for the liquid becomes lower relative to the gas, until it intersects the gas curve at one endpoint (at a temperature corresponding to the higher of the boiling points of pure A or pure B—B in our example. The convex Gibbs potential curve is formed by the liquid curve at small x_B, the common tangent corresponding to a mixed phase region (A rich liquid in equilibrium with B rich gas), and then the gas curve at large x_B.

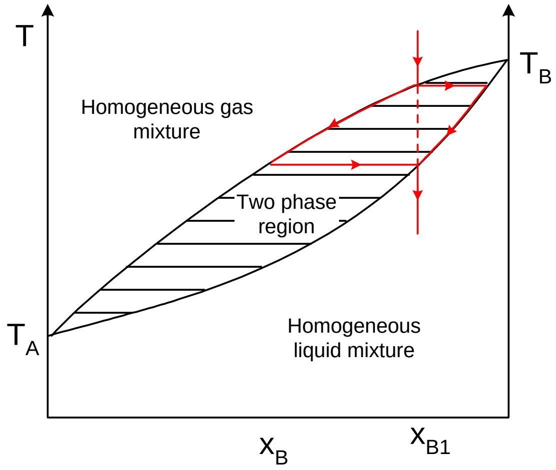

Figure 4: Phase diagram for the liquid gas transition in an ideal mixture.

The phase diagram is shown in Fig. 4. Note that if gas at some concentration (e.g. x_{B1}) is cooled, there is a range of temperatures over which liquid and gas are in equilibrium (with the gas being more A rich and the liquid more B rich for the example shown). For a one component system on the other hand, the liquid-gas transition occurs at a unique temperature at a given P. This difference is an example of the Gibbs phase rule. This is only the simplest of the various phase diagrams that can be found.

Eutectics

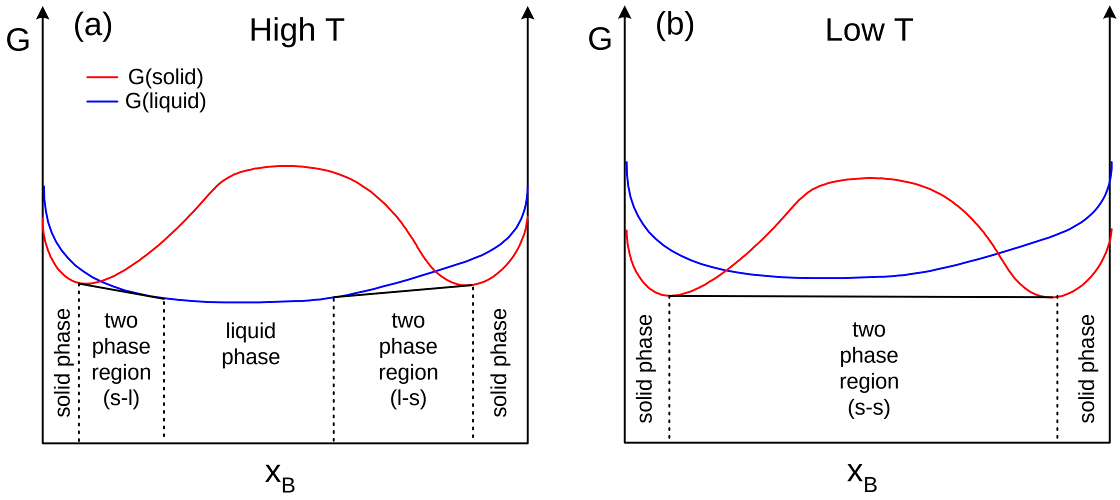

Figure 5: Phase diagram for the case with a large energy cost for mixing in the low temperature phase.

If the Gibbs potential of the low temperature phase is "humped" as in Fig. 1b the phase diagram is more complicated. This often occurs for the solid phase at a liquid-solid transition in a mixture, since if A and B have different crystal structure there will be a large energy cost for the solution of one in the other, and I've labelled the figure for this case. At the temperature corresponding to panel (a) there are two common tangent constructions giving two ranges of x_B for phase coexistence (both solid-liquid). In (b), at a lower temperature, there is a single range of x_B giving phase coexistence between two solid phases with different concentrations.

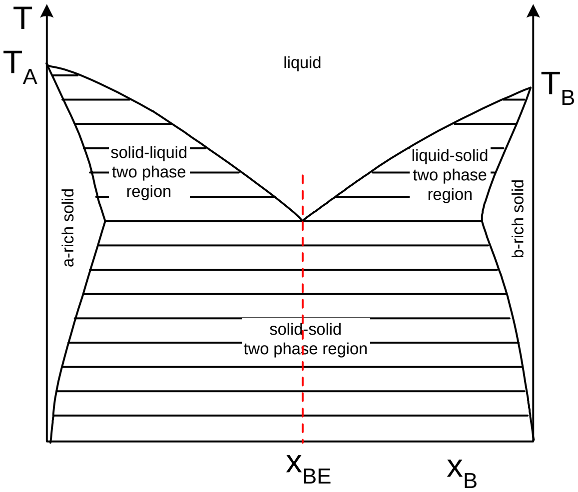

Figure 6: Eutectic Phase diagram

The phase diagram in this case is shown in Fig. 6. As usual shaded regions are two phase coexistence regions, with the concentrations of the two phases given by the ends of the tie lines. For most concentrations, if the liquid is cooled, either A-rich or B-rich solid will start forming, in equilibrium with the liquid, over a range of temperatures. There is one particular concentration x_{BE} known as the Eutectic concentration for which solidification occurs at a single temperature–the temperature at which two solid phases and a single liquid phase are in equilibrium (cf. the Gibbs phase rule).

Again, there are many other possibilities for phase diagrams, particularly for liquid-solid transitions, since many alloy states are found—concentrations (usually stoichiometric rations) at which particular chemical compounds form. The iron-carbon phase diagram is notoriously complicated, for example.