Lecture 18

Describing the State of an Alloy

Last Time

Virtual Variations

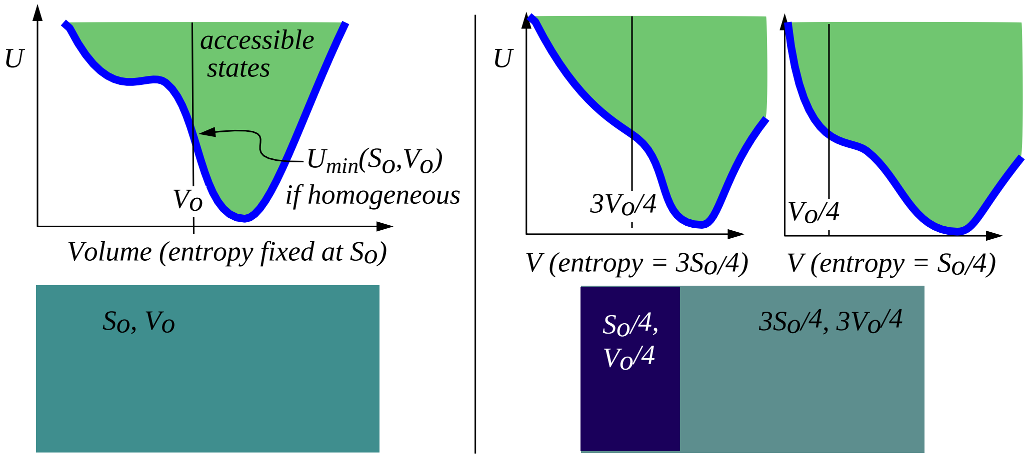

Figure 18-1: Example of one particular choice of a virtual variation of a system. The originally homogeneous system is compared to two other systems of different size.

Question: Because they are extensive, shouldn't the internal energy in Figure 18-1 scale linearly with the volume?

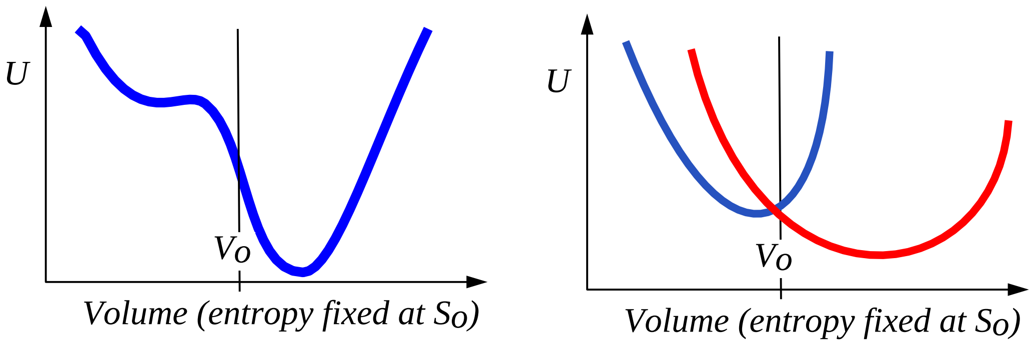

Figure 18-2: Example of why it is not sufficient to consider variations like $\Delta U = U_o + U'\Delta V + U''\Delta V^2/2 + \ldots$

Equilibrium: $(\delta S)_{\delta U=0\,,\,\delta V=0} \leq 0$

Equilibrium: $(\delta U)_{\delta S=0\,,\,\delta V=0} \geq 0$

P and T are Uniform when Volume and Energy can be Exchanged

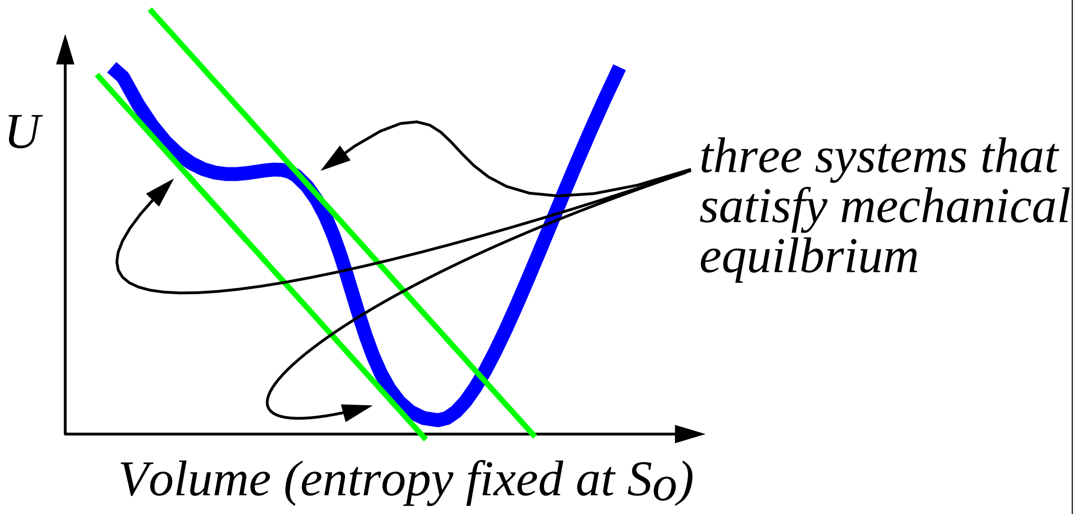

Figure 18-3: Three separate systems that are in mechanical equilbrium, but not necessarily thermal equilibrium.

Equilibrium for Systems with Internal Degrees of Freedom

The expressions of equilibrium that have been derived are not terribly profound or useful so far. Another condition of equilibrium that is *very* useful will be derived below and this is one that you will use over and over again as professional scientists.

Recall that when considering other types of work:

$$dU = TdS - PdV + \sum_i F_i dx_i \tag{18-1}$$

where F_i were the various forces acting on the system and the x_i were the extensive variables that changed according to those forces. We consider the V and the x_i to be the degrees of freedom associated with the system.

Composition Variation and Phase Fractions

We now consider a very important system that has internal degrees of freedom: a system composed of variable chemical elements and various phases. In other words, the internal degrees of freedom are the compositions of the various regions that compose our system.

This topic often confuses students, so I will go over the terms very carefully, first a few definitions:

phase A part of a system that can be indentified as "different" from another part of the system. A phase is always separated from another phase by an identifiable interface. Examples of phases are a solution of iron and carbon in an FCC structure and a solution of iron and carbon in a BCC structure.

composition The fractions of the various chemical components that comprise a system.

phase fraction of α The fraction of a system that is the α-phase.

composition of phase α The composition of the subsystem composed of α-phase alone.

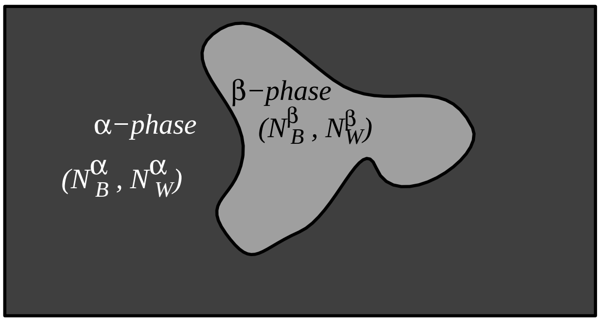

Figure 18-4: A system in equilibrium with its surroundings and composed of two phases α and β, each having a different chemical composition. This illustration is for two phases and two independent components but it may be extrapolated to to as many phases and components as required. Later, a relation between the number of phases f and the number of components C that can exist at equilibrium will be derived.

N_B and N_W represent numbers of B- and $W-$type molecules. The number of moles in phases α and in phase β can be varied.

The following notation should be studied carefully.

Notation	
N_B^α	Number of B atoms (or molecules) in α-phase
N_W^α	Number of W atom in α-phase
N_B^β	Number of B atom in β-phase
N_W^β	Number of W atom in β-phase

Therefore the total numbers of B molecules (or atoms) and W molecules in the system are:

$$\begin{aligned} N_B &= N_B^\alpha + N_B^\beta = \quad \text{(general)} \quad \sum_{i=1}^{f} N_B^i \\ N_W &= N_W^\alpha + N_W^\beta = \quad \text{(general)} \quad \sum_{i=1}^{f} N_W^i \end{aligned} \tag{18-2}$$

The total number of atoms in the system is

$$N^{\text{total}} = N_B + N_W = \quad \text{(in general)} \quad \sum_{j=1}^{C} N_j \tag{18-3}$$

The average composition in the system is

$$\begin{aligned} \overline{N_B} &\equiv X_B = \frac{N_B}{N^{\text{total}}} \\ \overline{N_W} &\equiv X_W = \frac{N_W}{N^{\text{total}}} \end{aligned} \tag{18-4}$$

Furthermore, we can find the total number of atoms (molecules) in the α-phase:

$$\begin{aligned} N^{\alpha\text{total}} &= N_B^\alpha + N_W^\alpha = \quad \text{(in general)} \quad \sum_{j=1}^{C} N_j^\alpha \\ N^{\beta\text{total}} &= N_B^\beta + N_W^\beta = \quad \text{(in general)} \quad \sum_{j=1}^{C} N_j^\beta \end{aligned} \tag{18-5}$$

$$\text{(general, for phase } i\text{)} \quad N^{i\text{total}} = \sum_{j=1}^{C} N_j^i$$

And the compositions of the phases can be defined as:

$$\begin{aligned} X_B^\alpha &= \frac{N_B^\alpha}{N^\alpha \text{total}} & X_W^\alpha &= \frac{N_W^\alpha}{N^\alpha \text{total}} \\ X_B^\beta &= \frac{N_B^\beta}{N^\beta \text{total}} & X_W^\beta &= \frac{N_W^\beta}{N^\beta \text{total}} \end{aligned} \tag{18-6}$$

An Illustrative Example

To fix our ideas, consider the following figure and think of N_B as the number of black spots

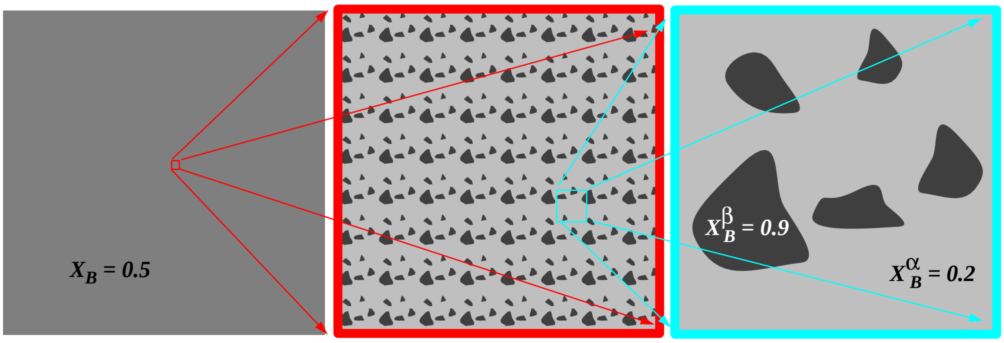

Figure 18-5: Example of a system where the composition is nowhere equal to the average composition.

The phase fractions can be computed as follows:

$$f^{\alpha} = \frac{N^{\alpha}\text{total}}{N\text{total}} \qquad f^{\beta} = \frac{N^{\beta}\text{total}}{N\text{total}}$$
$$\text{generally, } f^{i} = \frac{N^{i}\text{total}}{N\text{total}} \tag{18-7}$$
$$1 = \sum_{i=1}^{f} f^{i}$$

Note that:

$$X_B = f^{\alpha} X_B^{\alpha} + (1 - f^{\alpha}) X_B^{\beta} \tag{18-8}$$

or

$$f^{\alpha} = \frac{X_B - X_B^{\beta}}{X_B^{\alpha} - X_B^{\beta}} \tag{18-9}$$

Notice that nowhere in the system is the actual composition equal to the average composition.

A Concrete Example

To fix this idea even further, consider a brine solution with watery-ice and salty-water. The quantity of interest may be the temperature (or temperatures) that an average composition of $C_{\text{NaCl}} = 0.07$ has an icy-phase in equilibrium with a watery-phase. One possible state of the system may be:

$C_{\text{NaCl}}^{\text{icy}} = 0.0005$ and $C_{\text{NaCl}}^{\text{watery}} = 0.09$
which completely determines the phase fractions.

Note that this doesn't determine what the extent (i.e. $N_{\text{total}}^{\text{icy}}$ and $N_{\text{total}}^{\text{watery}}$) of the system is—it only produces derived intensive quantities.