Dec. 4 2002: Lecture 29:

Important Geometrical Constructions

Last Time

Graphical Construction for Extracting Chemical Potentials of Solution

The Common Tangent Construction

The equilibrium condition, that the chemical potentials of components must have equal values in all phases, indicates that at equilibrium compositions that have the same tangent (*i.e., a common tangent*).

This result allows equilibrium to be determined by a geometrical construction: the common tangent construction.

Consider the region of lines that lies inside the common tangent point in Figure 28-5, a mixture of $f^{\text{liquid}} G^{sol\,\text{liquid}}(X_L, T, P) + f^{\text{solid}} G^{sol\,\text{solid}}(X_S, T, P)$ has lowest value of $\overline{G}$ where f^{liquid} is the fraction of the system that is liquid and f^{solid} fraction of system that is solid.

$$f^{\text{solid}} + f^{\text{liquid}} = 1$$

This corresponds to a diagram that maps stable compositions of phase mixtures:

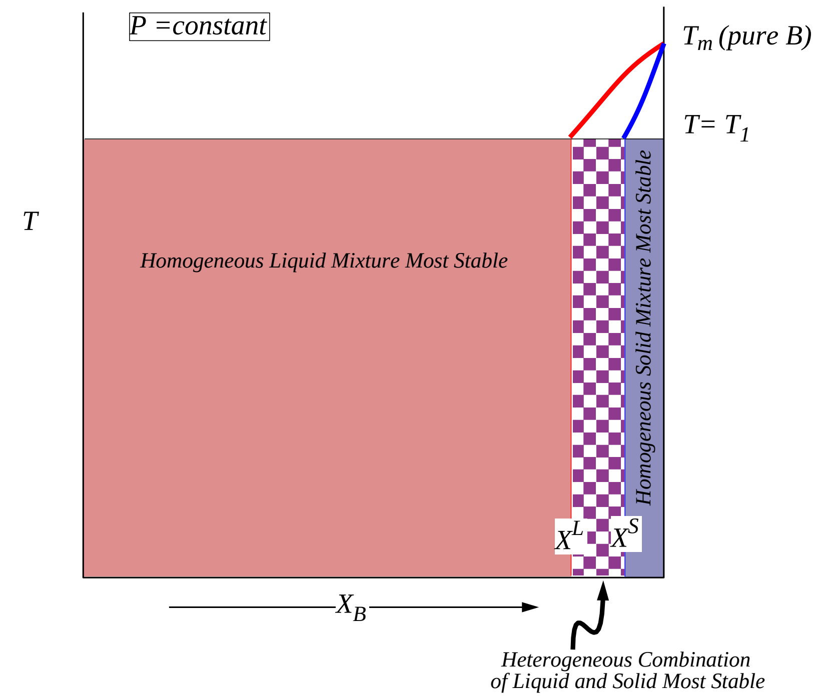

Figure 29-1: Construction of the equilibrium values of the compositions resulting from the lowest free energy in Figure 28-5.

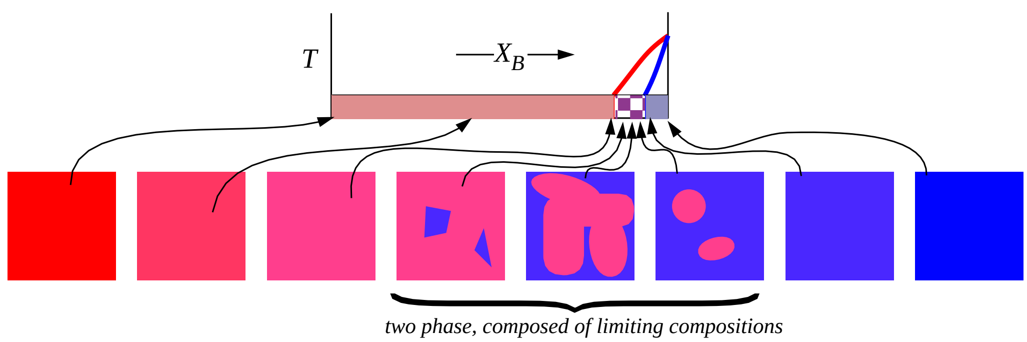

Figure 29-2: Illustration of the physical composition of the states corresponding to the average compositions indicated in Figure 29-1.

There is a range of "average compositions" at $T < T_M^B$ in which the system has as its most stable form a mixture of liquid at composition X_L and solid at composition X_S. The fractions of f^{liquid} and f^{solid} come from the requirements that the average composition is given by:

$$\begin{aligned} \langle X \rangle &= X^{\text{liquid}} f^{\text{liquid}} + X^{\text{solid}} f^{\text{solid}} \\ &= X^{\text{liquid}} f^{\text{liquid}} + X^{\text{solid}} (1 - f^{\text{liquid}}) \end{aligned} \tag{29-1}$$

or, for the general case where the two phases in equilibrium are α and β:

$$f^\alpha = \frac{X^\beta - \langle X \rangle}{X^\beta - X^\alpha} \quad \text{and} \quad f^\beta = \frac{\langle X \rangle - X^\alpha}{X^\beta - X^\alpha} \tag{29-2}$$

Equation 29-2 is called the lever rule:

Figure 29-3: The lever rule as indicated by Equation 29-2—on the balance chubby kids get the short end of the stick.

A Menagerie of Pure Component Phase Diagrams

THe graphics in this section were created by Angela Tong, MIT.

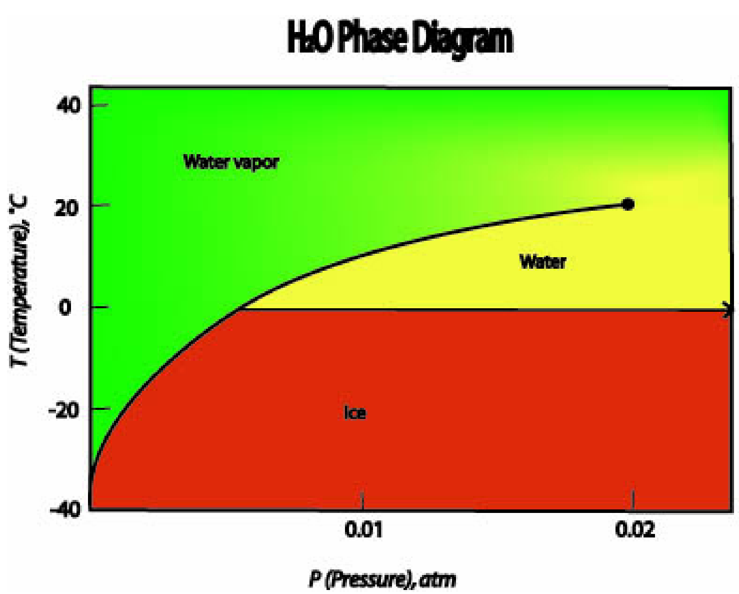

Figure 29-4: T-P phase diagram for pure water.

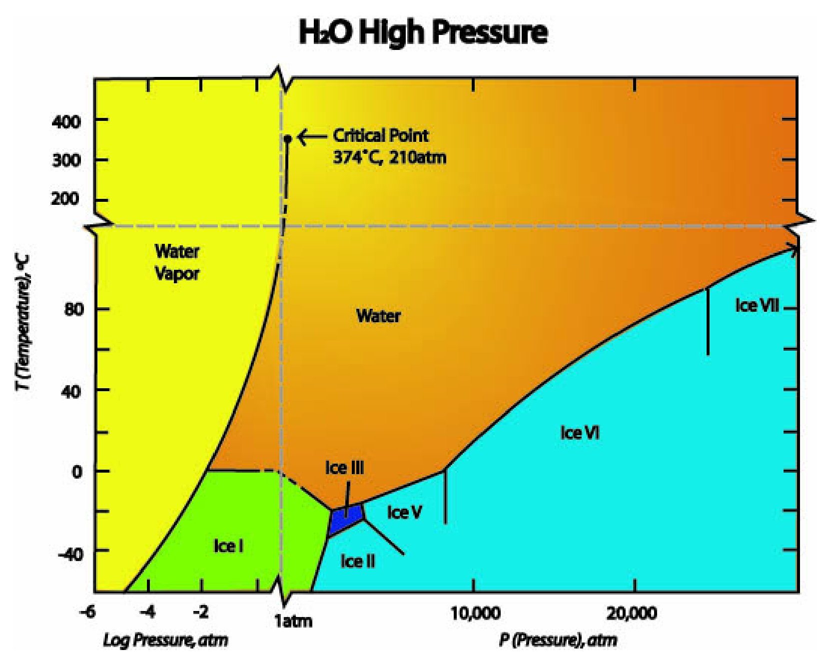

Figure 29-5: T-P phase diagram for pure water showing several different solid phases.

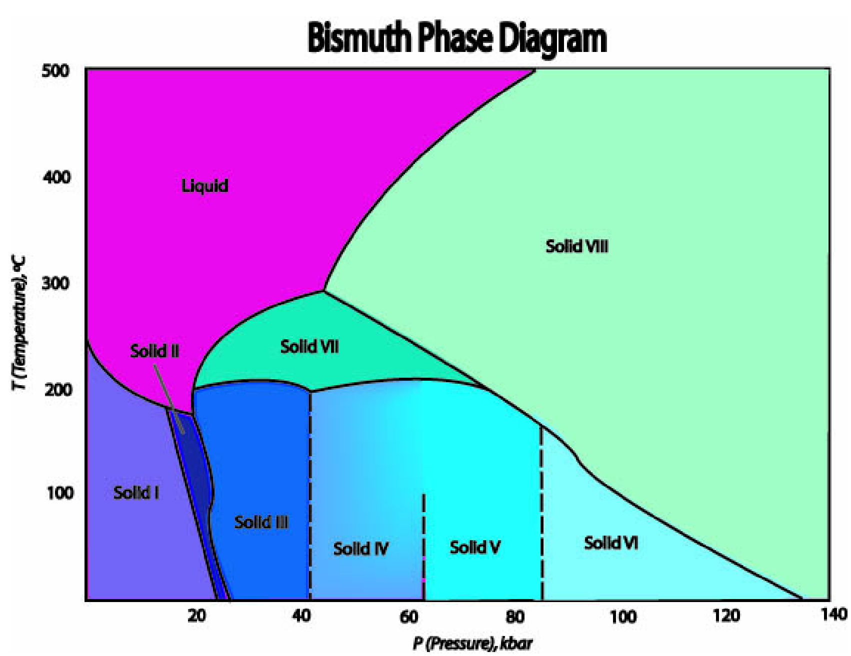

Figure 29-6: T-P phase diagram for Bi. Bismuth's low pressure solid phase has the same volume anomaly as water. What can be said about the symmetries of phases IV and V?

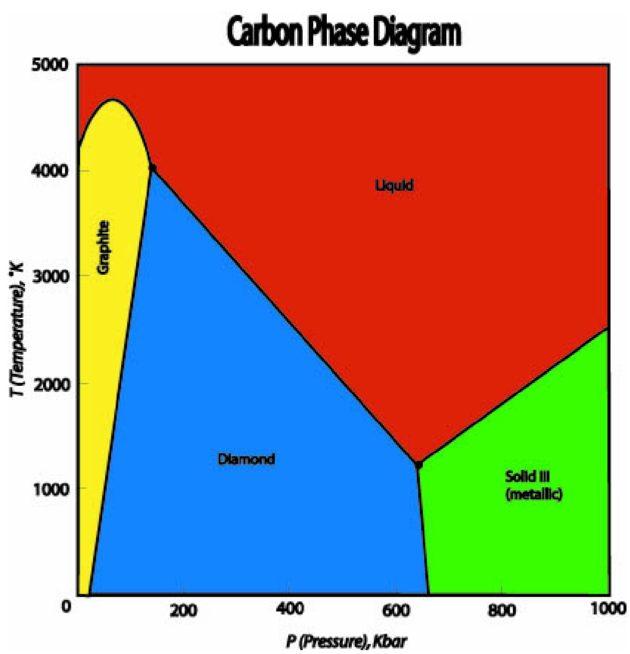

Figure 29-7: T-P phase diagram for carbon—proving that diamonds are not forever.

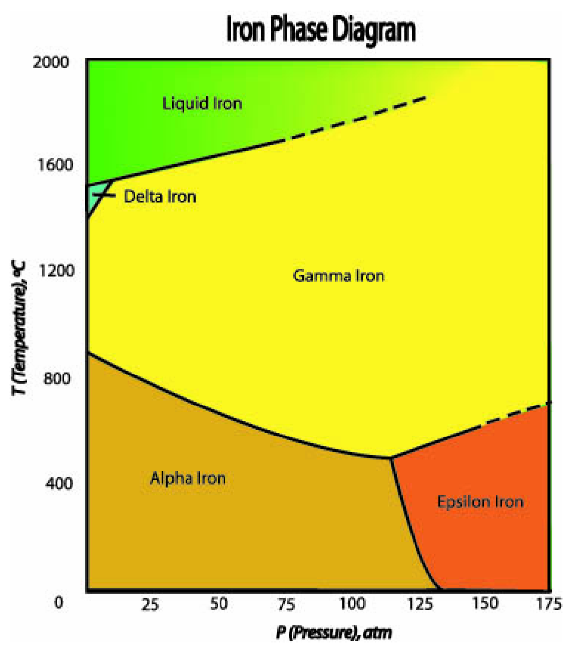

Figure 29-8: T-P phase diagram for iron. I am not sure that I believe that there is a critical point for liquid and γ-Fe.