

Nov. 22 2002: Lecture 26:

The Gibbs Phase Rule and its Application

Last Time

Symmetry and Thermodynamics

$Cf + 2$ Variables

$C(f - 1)$ Equations for Continuity of Chemical Potential

f Gibbs-Duhem Relations (one for each phase)

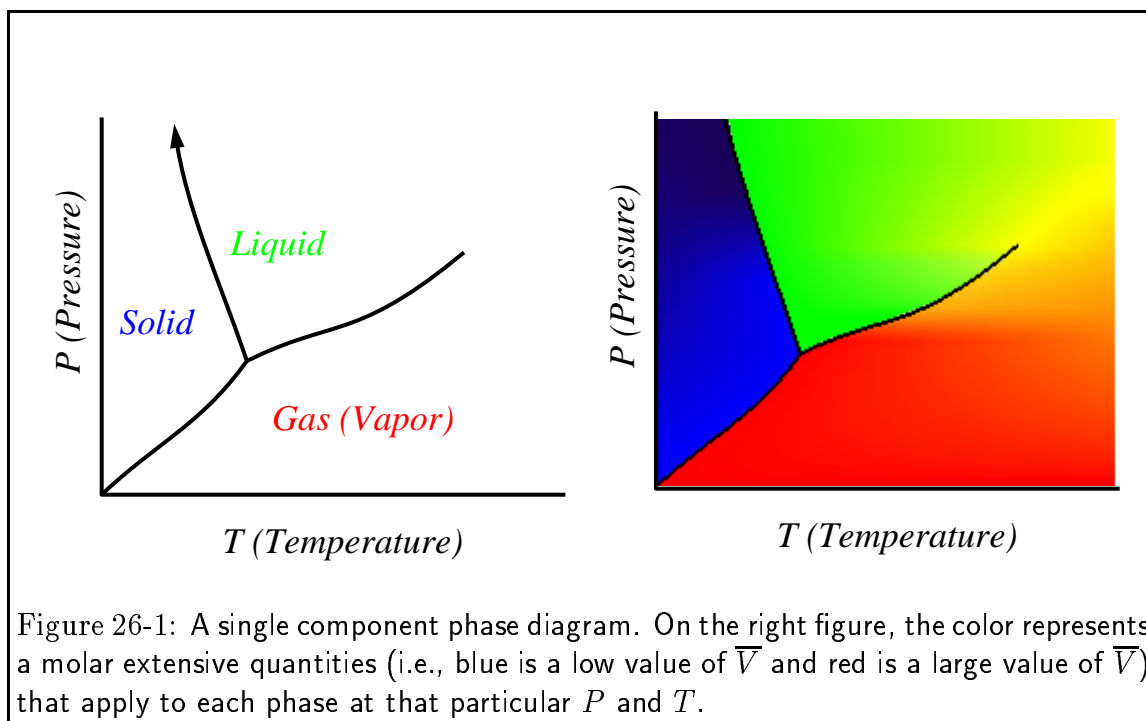
$D = C - f - 2$ Degrees of Freedom Left Over

The Gibbs Phase Rule

$$D + f = C + 2 \quad (26-1)$$

The Gibbs phase rule is a very useful equation because it put precise limits on the number of phases f that can be simultaneously in equilibrium for a given number of components.

What does Equation 26-1 mean? Consider the following example of a single component (pure) phase diagram $C = 1$.



Consider a single-phase region:

$$D = 2 - f + C = 2 - 1 + 1 = 2$$

This implies that two variables (P and T) can be changed independently (i.e., pick any dP and dT) and a single phase remains in equilibrium.

Consider where two phases are in equilibrium:

$$D = 2 - f + C = 2 - 2 + 1 = 1,$$

There is only one degree of freedom—for the two phases to remain in equilibrium, one variable can be changed freely (for instance, dP) but then the change in the other variable (i.e., dT) must depend on the change of the free variables:

$$\frac{dP}{dT} = f(P, T)$$

Finally, consider where three phases are in equilibrium then:

$$D = 2 - 3 + 1 = 0.$$

There can be no change any variable that maintains three phase equilibrium.

Various Confusing Issues on Applications of $D + f = C + 2$

Consider a pure liquid A in contact with the air. The degrees of freedom can be determined in several equivalent ways.

A Consider the system composed of two components, the pure liquid A and air and restrict that the total pressure is 1 atm.

$$(D + f = C + 2) \rightarrow (D + f = C + 1).$$

$$\text{Therefore, } D = 2 - 2 + 1 = 1.$$

B Considering that the system consists of three components: A , O_2 , N_2 and has two additional restrictions: 1) $\Sigma P = 1$ $P_{O_2}/P_{N_2} = \text{constant}$, then $(D + f = C + 2) \rightarrow (D + f = C + 0)$.
 $D = 3 - 2 + 0 = 1$ as before.

C Disregard the air: $C = 1$. $f = 2$ and therefore $D = 1$. The liquid has an equilibrium vapor pressure which is a function of temperature. One can pick either the vapor pressure *or* the temperature independently, but not both.

Single Component Phase Equilibria

When there is only one degree of freedom in a single component phase diagram, it was shown above that there must be a relation between dP and dT for the system to remain in two phase equilibrium. Such a relation can be derived as follows:

$$\begin{aligned}
 0 &= S^{\text{liquid}} dT - V^{\text{liquid}} dP \\
 0 &= S^{\text{solid}} dT - V^{\text{solid}} dP \\
 \Rightarrow \left. \frac{dP}{dT} \right|_{\text{equilibrium}} &= \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T_{\text{eq.}} \Delta V}
 \end{aligned} \tag{26-2}$$

Equation 26-2 is the famous Clausius-Clapeyron equation.

Consider the behavior of the molar free energy (or μ) on slices of Figure 26-1 at constant P and T :

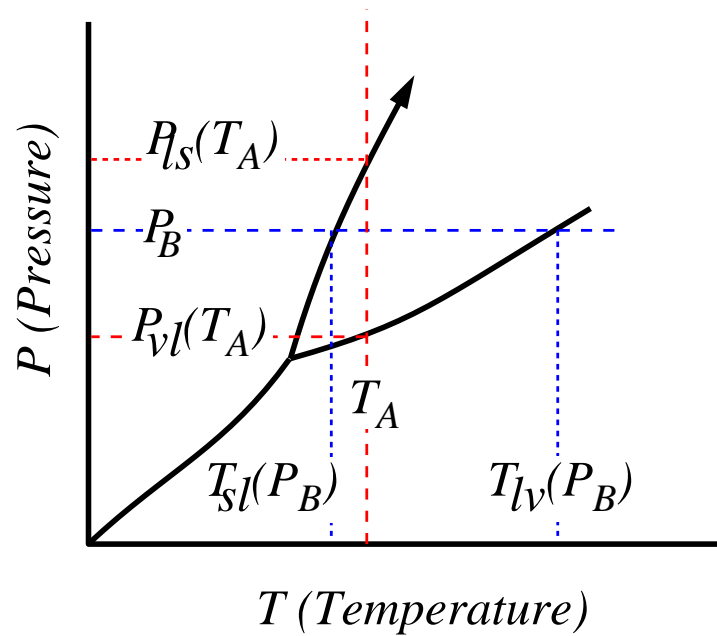


Figure 26-2: Considerations of the molar Gibbs free energy on slices of the single component phase diagram along lines of constant T and constant P .

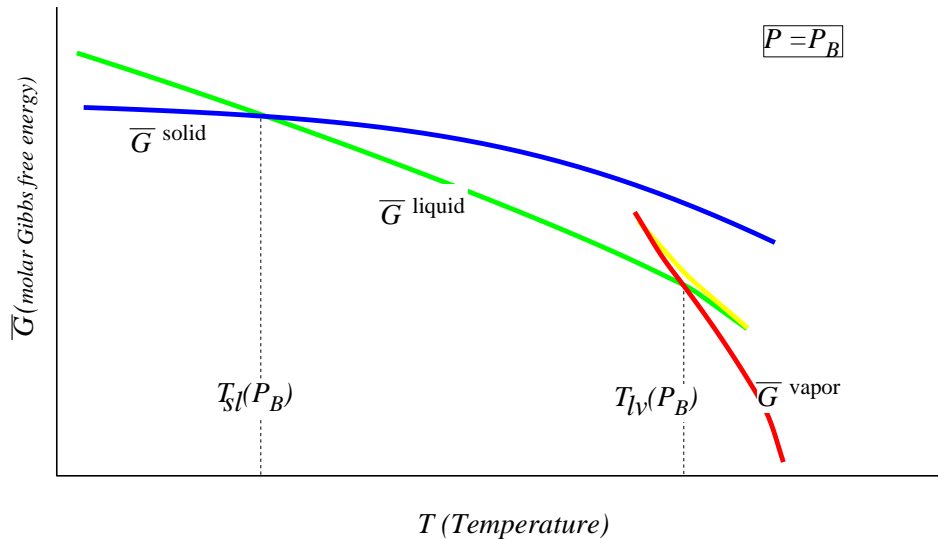
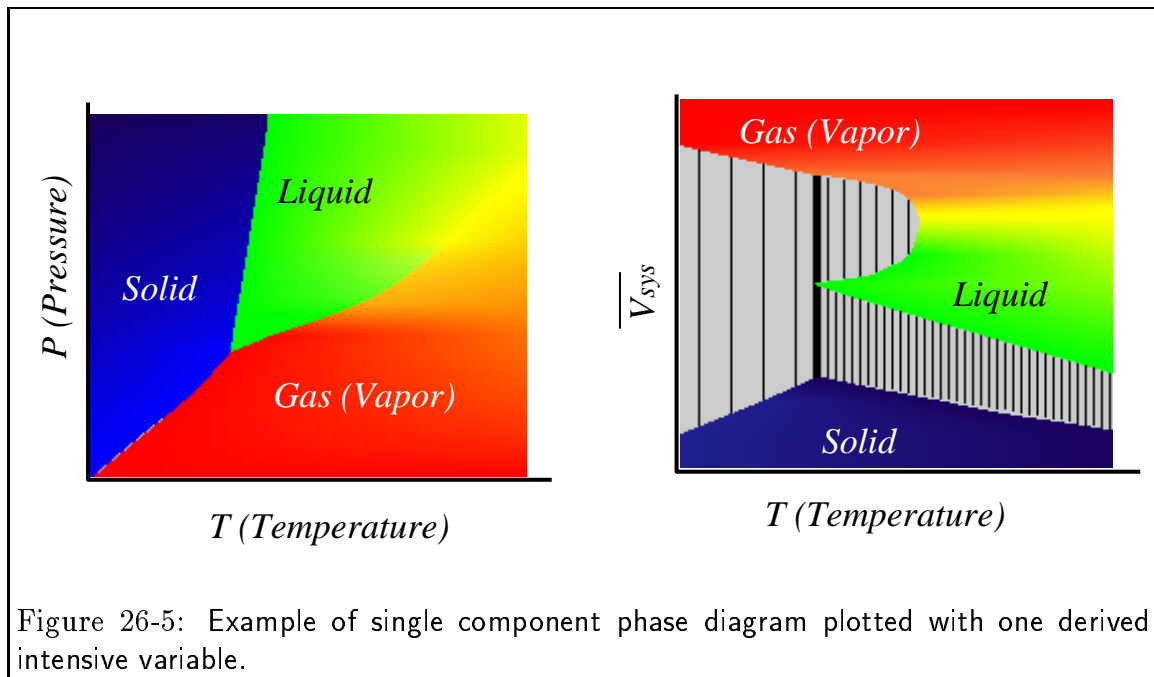
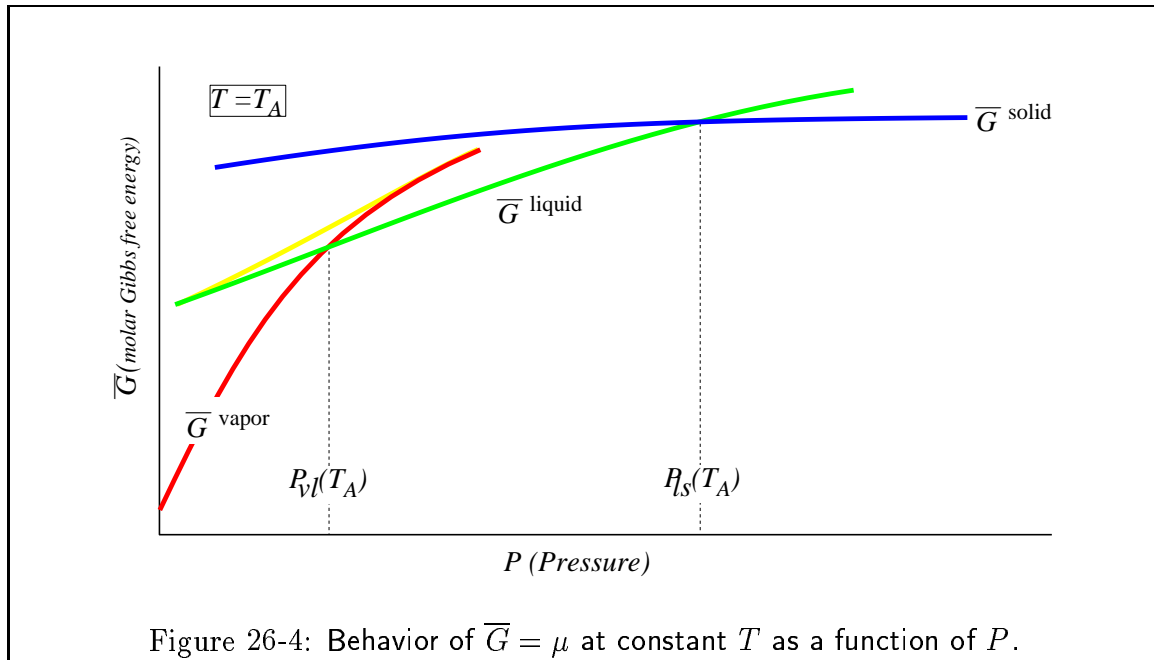


Figure 26-3: Behavior of $\bar{G} = \mu$ at constant P as a function of T . Where the curvature of \bar{G} changes sign, the system is unstable. The liquid and vapor curves must be connected to each other and this is illustrated with the "spiny-looking" curve with opposite curvature. The curve for solid is not connected to the others.



What would the plot look like with two extensive variables plotted?