Lecture 23

Mathematics and Stability

<u>Last Time</u>

Legendre Transformations
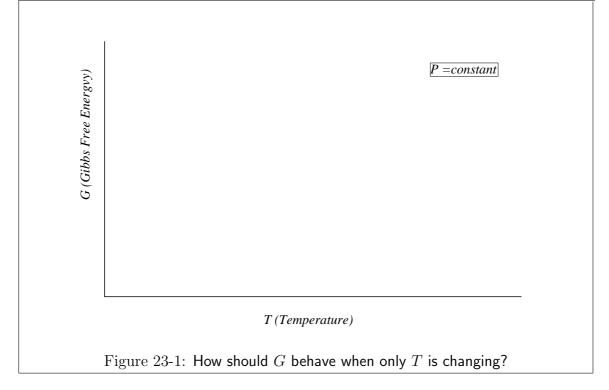
Maxwell's Relations

Change of Variable

⎯⎯ Some Implications of Mathematics in Thermodynamics ⎯⎯

The mathematics of thermodynamics places restrictions on how certain thermodynamic curves must appear when they are graphed.

There is one curve that is often drawn incorrectly by beginners and that is how G changes with temperature at constant pressure and composition. Crusty old materials scientists are fond of pointing out, when this particular mistake is made,[24] that knowing how to take derivatives is important.

An example of the plot is given below:

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[24]I don't know why they focus on this one and not the zillions of others.

Figure 23-1: How should G behave when only T is changing?

First, what is the slope of this curve?

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{23-1}$$

Second, what is the curvature of the curve?

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} < 0 \tag{23-2}$$

Therefore the curve must appear as follows:

Please learn these rules for drawing curves for the future. Someone is likely to ask you how they are drawn—if you make this particular mistake, please say that someone else besides me taught you thermo...

Question: What if another phase is considered? How would it be drawn? What conclusions can be made from the graph?
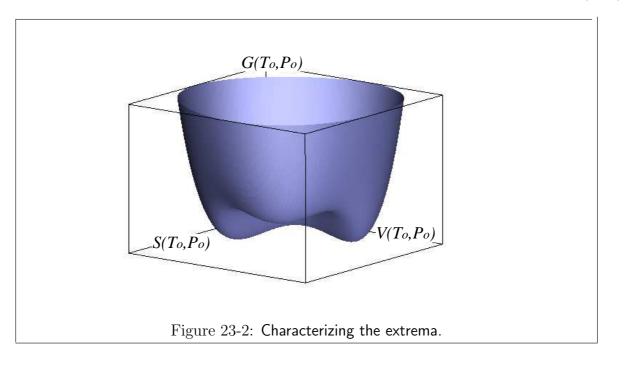
Further Considerations of Equilibrium

Recall the Gibbsian statements of equilibrium

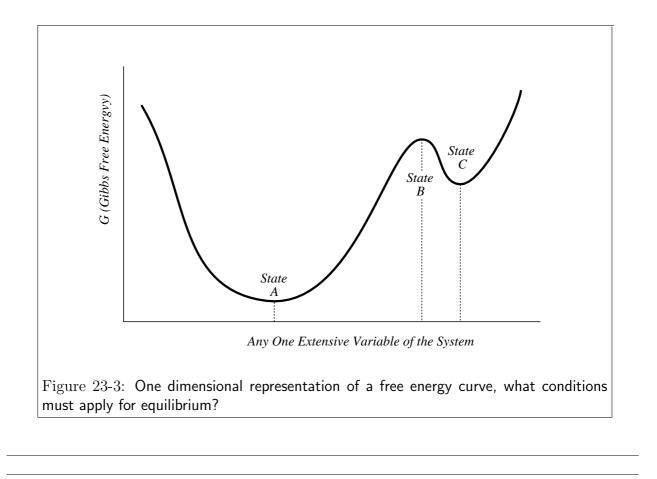$$(\delta G)_{\delta T=0\,,\,\delta P=0} \geq 0 \tag{23-3}$$

> "For equilibrium, any virtual change of the system at
> constant P and T must lead to an increase in the Gibbs
> free energy of the system."

In other words, the Gibbs free energy must be a minimum:

$$G = U - T_\circ S + P_\circ V \tag{23-4}$$

Figure 23-2: Characterizing the extrema.

This is easier to see if we collect all the dependent variables in one coordinate:

Figure 23-3: One dimensional representation of a free energy curve, what conditions must apply for equilibrium?

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Considering the *local* behavior of G:

$$\delta G = G - G_\circ = \frac{\partial G}{\partial X}(G - G_\circ) + \frac{1}{2}\frac{\partial^2 G}{\partial X^2}((G - G_\circ)^2 + \ldots \qquad (23\text{-}5)$$

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The extrema can be characterized:

The points A and C are in local equilibrium.

B is an unstable equilibrium.

A is an absolute equilibrium.

C is a local metastable equilibrium.

Question: What if the extensive variable is held fixed in state B in Fig. 23-3.