Nov. 15 2002: Lecture 24:

Implications of Equilibrium and Gibbs-Duhem

Last Time

Drawing Curves Correctly

Stability, Global Stability, Metastability, Instability

Equilibrium States With More Than One Variable

For a system of fixed composition, $\delta U(S, V)$ can be expanded[25]

$$\begin{aligned}\delta U = & \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV \\ & + \frac{1}{2}\left[\frac{\partial^2 U}{\partial S^2}(dS)^2 + 2\frac{\partial^2 U}{\partial S \partial V} dS dV + \frac{\partial^2 U}{\partial V^2}(dV)^2\right] + \dots\end{aligned} \tag{24-1}$$

For a local equilibrium

$$\frac{\partial U}{\partial S} = T_\circ \quad \text{and} \quad \frac{\partial U}{\partial V} = -P_\circ \tag{24-2}$$

so that

$$(dS, dV)\begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} \\ \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial V^2} \end{pmatrix}\begin{pmatrix} dS \\ dV \end{pmatrix} > 0 \tag{24-3}$$

[25] Assuming that $U(S, V)$ has continuous derivatives near the point (S, V) that it is being expanded around.

The matrix is called the Hessian of the system and for the inequality to be true it must be "positive definite" for a two-by-two matrix.

Necessary conditions for a local minimum are:

$$\frac{\partial^2 U}{\partial S^2} > 0 \tag{24-4}$$

and

$$\frac{\partial^2 U}{\partial S^2}\frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 > 0 \tag{24-5}$$

evaluated at the extrema.

Therefore:

$$\frac{\partial^2 U}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \tag{24-6}$$

$C_V > O$ for stability (If you add heat to a system, then its entropy must rise)

The second part (Eq. 24-5) that must also positive can be written in terms of the Jacobian

$$\frac{\partial((\frac{\partial U}{\partial S})_V, (\frac{\partial U}{\partial V})_S)}{\partial(S,V)} = \frac{\partial(T,-P)}{\partial(S,V)} > 0 \tag{24-7}$$

$$\left(\frac{\partial P}{\partial V}\right)_T \frac{T}{C_V} < 0$$
$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \tag{24-8}$$

for a stable equilibrium.

More Mathematical Thermodynamics: Homogeneous Functions

Consider $U(S, V, N_i)$, if I scale all the extensive variables by multiplying each of the extensive variables with the same "scale factor" λ then

$$U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N_i) \tag{24-9}$$

Functions that have the property of Equation 24-9, like U, are called "homogeneous degree one" (HD1) function of their variables.

Notice that G is *not* a completely homogeneous function:

$$G(\lambda T, \lambda P, \lambda N_i) \neq \lambda G(T, P, N_i) \tag{24-10}$$

i.e., increasing the pressure is *not* like changing an extensive variable.

However,

$$G(T, P, \lambda N_i) = \lambda G(T, P, N_i) \tag{24-11}$$

G is HD1 only in the N_i.

Notice that (here lies a common mistake!)

$$\overline{G}(T, P, \lambda X_i) \neq \lambda \overline{G}(T, P, X_i) \tag{24-12}$$

$\overline{G}$ is a different function than G.
Consider carefully, what can be deduced from Equation 24-11.
Taking the derivative with respect to λ

$$\sum_{i=1}^{C} \frac{\partial G}{\partial(\lambda N_i)} \frac{\partial(\lambda N_i)}{\partial \lambda} = G(T, P, N_i) \qquad (24\text{-}13)$$

We get the following **very important equation**:

$$\sum_{i=1}^{C} \mu_i N_i = G(T, P, N_i) \qquad (24\text{-}14)$$

This corresponds to what has been discussed about the relation of the Gibbs free energy. It corresponds to the internal degrees of freedom.

The Gibbs-Duhem Relation

Consider

$$G = \sum_{i=1}^{C} \mu_i N_i \qquad (24\text{-}15)$$

and compare it to our previous expression for dG:

It follows that (**This is another important equation**):

$$0 = -SdT + V\,dP - \sum_{i=1}^{C} N_i d\mu_i \tag{24-16}$$

This is the Gibbs-Duhem Equation. It will be used again and again.

Notice that Equation 24-16 has the following form:

$$0 = \vec{Y} \cdot d\vec{X} \tag{24-17}$$

At equilibrium, a small virtual change in the system is *normal* to the size of the system.