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]

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

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

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

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.

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

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

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

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

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

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

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

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

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

$$G = \sum_{i=1}^{C} \mu_i N_i \tag{24-15}$$

and compare it to our previous expression for dG:

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

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

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.