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

$$
\delta U = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV \\
+ \frac{1}{2} \left[ \frac{\partial^2 U}{\partial S^2} (dS)^2 + 2 \frac{\partial^2 U}{\partial S \partial V} dS dV + \frac{\partial^2 U}{\partial V^2} (dV)^2 \right] + \ldots
$$

For a local equilibrium

$$
\frac{\partial U}{\partial S} = T_0 \quad \text{and} \quad \frac{\partial U}{\partial V} = -P_0
$$

so that

$$
(dS, dV) \left( \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial S \partial V} \right) \left( \frac{dS}{dV} \right) > 0
$$

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.

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25Assuming 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:
\[
\frac{\partial^2 U}{\partial S^2} > 0 \quad (24-4)
\]
and
\[
\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left( \frac{\partial^2 U}{\partial S \partial V} \right)^2 > 0 \quad (24-5)
\]
evaluated at the extrema.

Therefore:
\[
\frac{\partial^2 U}{\partial S^2} = \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0 \quad (24-6)
\]

\(C_V > 0\) 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
\[
\frac{\partial (\left( \frac{\partial U}{\partial S} \right)_V, \left( \frac{\partial U}{\partial V} \right)_S)}{\partial (S,V)} = \frac{\partial (T,-P)}{\partial (S,V)} > 0 \quad (24-7)
\]

\[
\left( \frac{\partial P}{\partial V} \right)_T \frac{T}{C_V} < 0 \quad (24-8)
\]
\[
\left( \frac{\partial P}{\partial V} \right)_T < 0
\]
for a stable equilibrium.

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### 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” $\lambda$ then

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

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:

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

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

However,

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

$G$ is HD1 only in the $N_i$.

Notice that (here lies a common mistake!)

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

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$\overline{G}$ is a different function than $G$.

Consider carefully, what can be deduced from Equation 24-11.

Taking the derivative with respect to $\lambda$
\[
\sum_{i=1}^{C} \frac{\partial G}{\partial (\lambda N_i)} \frac{\partial (\lambda N_i)}{\partial \lambda} = G(T, P, N_i) \quad (24-13)
\]

We get the following very important equation:

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

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

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**The Gibbs-Duhem Relation**

Consider

\[
G = \sum_{i=1}^{C} \mu_i N_i \quad (24-15)
\]

and compare it to our previous expression for \( dG \):
It follows that (This is another important equation):

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

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

Notice that Equation 24-16 has the following form:

$$0 = \vec{Y} \cdot d\vec{X}$$  \hspace{1cm} (24-17)

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