
Oct. 23 2002: Lecture 19:

Generalized Conditions for Equilibrium

Last Time

Generalizing Equilibrium to More Degrees of Freedom

Example: Internal Degrees of Freedom

Worked Example: Origin of the Lever Rule

Equilibrium for a System with Internal Degrees of Freedom

For the case of an ideal fluid that has “internal degrees of freedom,” new terms must be added to the internal energy. To illustrate this, we considered that particular case numbers of molecules of each type (of a possible number of C types) was variable in each of the j possible phases.

$$dU = TdS - PdV + \sum_{i=1}^C \mu_i dN_i \quad (19-1)$$

or in general

$$dU = TdS - PdV + \sum_{i=1}^f \sum_{j=1}^c \mu_i^j dN_i^j \quad (19-2)$$

The condition that we applied to find the conditions of equilibrium [$(\delta S)_{\delta U=0, \delta V=0} \leq 0$, or, equivalently $(\delta U)_{\delta S=0, \delta V=0} \geq 0$] previously were not practical. It is difficult to arrange to do experiments where $U = \text{constant}$ and $V = \text{constant}$. They are difficult to arrange in the lab.

Question: Consider that you are doing an experiment to determine the equilibrium properties of a material? What kinds of experimental conditions would be the most straightforward to implement?

Equilibrium with constraints that are more practical

Consider that a system with internal degrees of freedom placed inside a giant reservoir at constant P_R and T_R (i.e. the atmosphere or the conditions inside a furnace, etc.) (R for reference or reservoir)

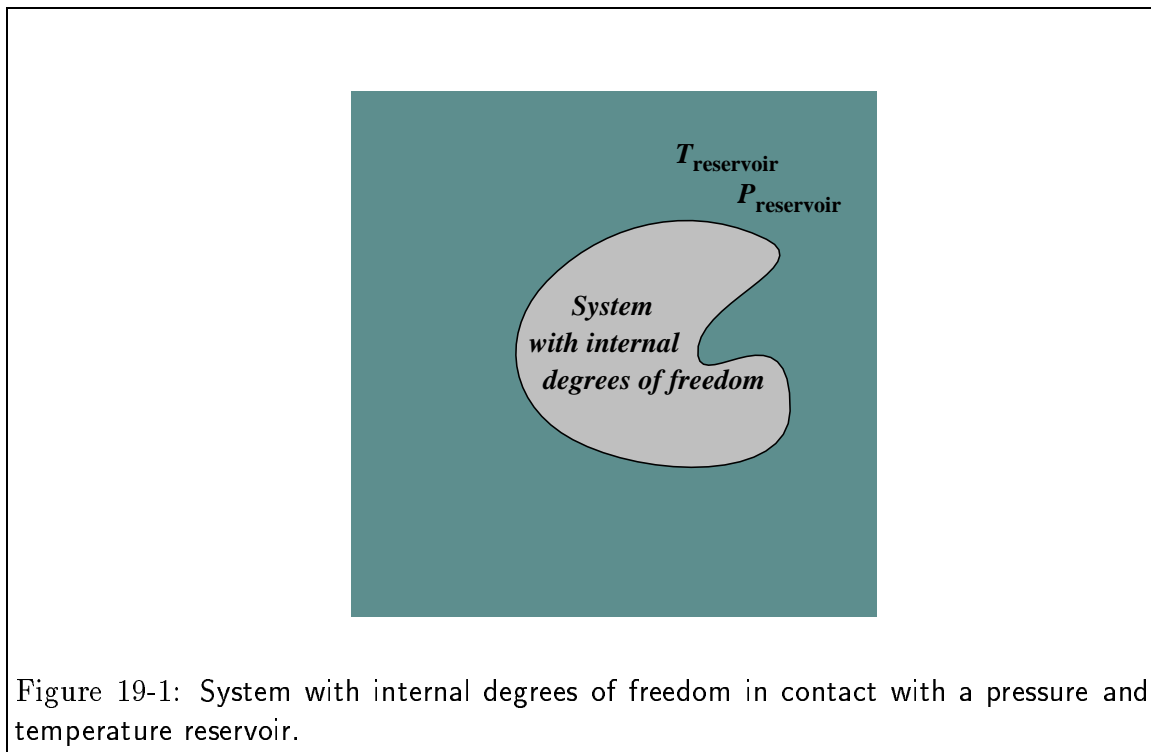


Figure 19-1: System with internal degrees of freedom in contact with a pressure and temperature reservoir.

We have already shown that for equilibrium:

$T_{sys} = T_R$ and $P_{sys} = P_R$ for a system that can exchange energy and volume with its environment.

The condition that a spontaneous change can take place is (in other words, the system is *not* in equilibrium):

$$dS_{\text{universe}} = dS_{\text{system}} + dS_{\text{reservoir}} > 0 \quad (\text{spontaneous})$$

$$dS_{\text{reservoir}} = \frac{dq_{\text{reservoir}}}{T_{\text{reservoir}}} \quad (19-3)$$

Apply the first law to the entire system:

$$dS_{\text{reservoir}} = \frac{-dU_{\text{system}} - P_{\text{reservoir}}dV_{\text{system}}}{T_{\text{reservoir}}} \quad (19-4)$$

so that:

$$dS_{\text{universe}} = dS_{\text{system}} + \frac{-dU_{\text{system}} - P_{\text{reservoir}}dV_{\text{system}}}{T_{\text{reservoir}}} > 0 \quad (\text{spontaneous}) \quad (19-5)$$

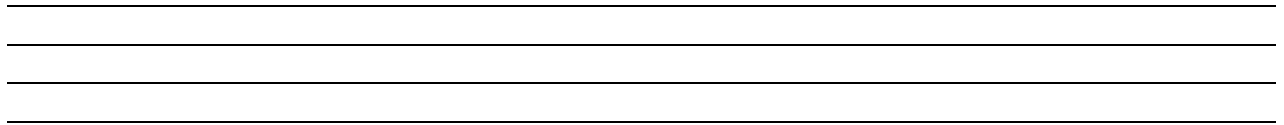
or

$$dU_{\text{system}} + P_{\text{reservoir}}dV_{\text{system}} - T_{\text{reservoir}}dS_{\text{system}} < 0 \quad (\text{spontaneous}) \quad (19-6)$$

or, comparing with Equation 20-1,

$$\sum_{i=1}^f \sum_{j=1}^c \mu_j^i dN_j^i < 0 \quad (\text{spontaneous}) \quad (19-7)$$

Note that the sum in Equation 20-7 is really a placeholder for the “internal degrees of freedom” for a system in equilibrium with a reservoir of constant P and T . Equation 20-7 as it is written, with chemical potentials and changes in the compositions, is the “normal case” and the one that is the best to remember.

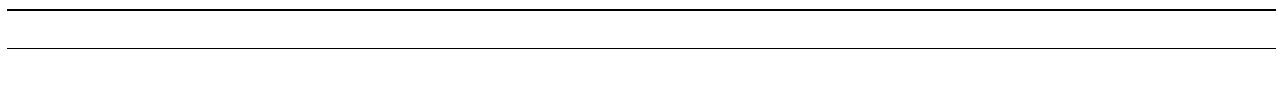


That which is Minimized at Equilibrium for Constant P and T

Letting

$$\begin{aligned} G &\equiv U - TS + PV \\ dG &= dU - TdS + PdV \quad (\text{constant temperature and pressure}) \\ \implies dG_{\text{system}} &= \sum_{i=1}^f \sum_{j=1}^c \mu_j^i dN_j^i < 0 \quad (\text{spontaneous at constant pressure and temperature}) \end{aligned} \quad (19-8)$$

If the Gibbs free energy is a minimum at constant P and T , then the system is at equilibrium: $(\delta G)_{\delta P=0, \delta T=0} \geq 0$



That which is Minimized at Equilibrium for Constant V and T

Note that if we had considered a system at constant V , then $dV = 0$ in the above and

$$dF = d(U - TS) = dU - TdS \quad (\text{constant temperature}) \quad (19-9)$$

then

$$dF < 0 \quad (\text{spontaneous at constant } T, V) \quad (19-10)$$

and

If the Helmholtz free energy is a minimum at constant V and T , then the system is in equilibrium. $(\delta F)_{\delta V=0, \delta T=0} \geq 0$.

The Potential to add a Chemical Species

A very important quantity is identified when the Gibbs free energy is introduced as in Equation 20-8.

$$dG = \sum_{i=1}^c \mu_i dN_i \quad (\text{constant pressure and temperature for the system})$$

$$d\bar{G} = \sum_{i=1}^c \mu_i dX_i \quad (\text{constant pressure and temperature for the system per mole})$$

$$dG^\alpha = \sum_{i=1}^c \mu_i^\alpha dN_i^\alpha \quad (\text{constant pressure and temperature for the } \alpha \text{ subsystem})$$

$$d\bar{G}^\alpha = \sum_{i=1}^c \mu_i^\alpha dX_i^\alpha \quad (\text{constant pressure and temperature per mole of the } \alpha \text{ subsystem}) \quad (19-11)$$

so that

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial N_i} \right)_{\text{const } P, \text{const } T, \text{const } N_j \text{ where } j \neq i} = \left(\frac{\partial \bar{G}^\alpha}{\partial X_i} \right)_{\text{const } P, \text{const } T, \text{const } X_j \text{ where } j \neq i} \quad (19-12)$$

Note that the chemical potential is an intensive variable as a potential should be.

$\mu_i^\alpha(P, T)$ is the chemical potential of species i in phase α : it is rate at which reversible work that must be done on a the subsystem α to add a species i at constant P and T .

Question: How would Equation 20-8 be modified if the chemical species that were being added were charged?

Question: How would the equilibrium condition Equation 20-8 (or more generally Equation 20-1) be modified if the chemical species that were being added were charged?

Work out in the space provided below, the general conditions on equilibrium for a closed system (i.e., one that has a fixed numbers of independent chemical species) at fixed pressure and temperature. Let the system have f different phases.