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.

$$dU = TdS - PdV + \sum_{i=1}^{C} \mu_i dN_i \tag{19-1}$$
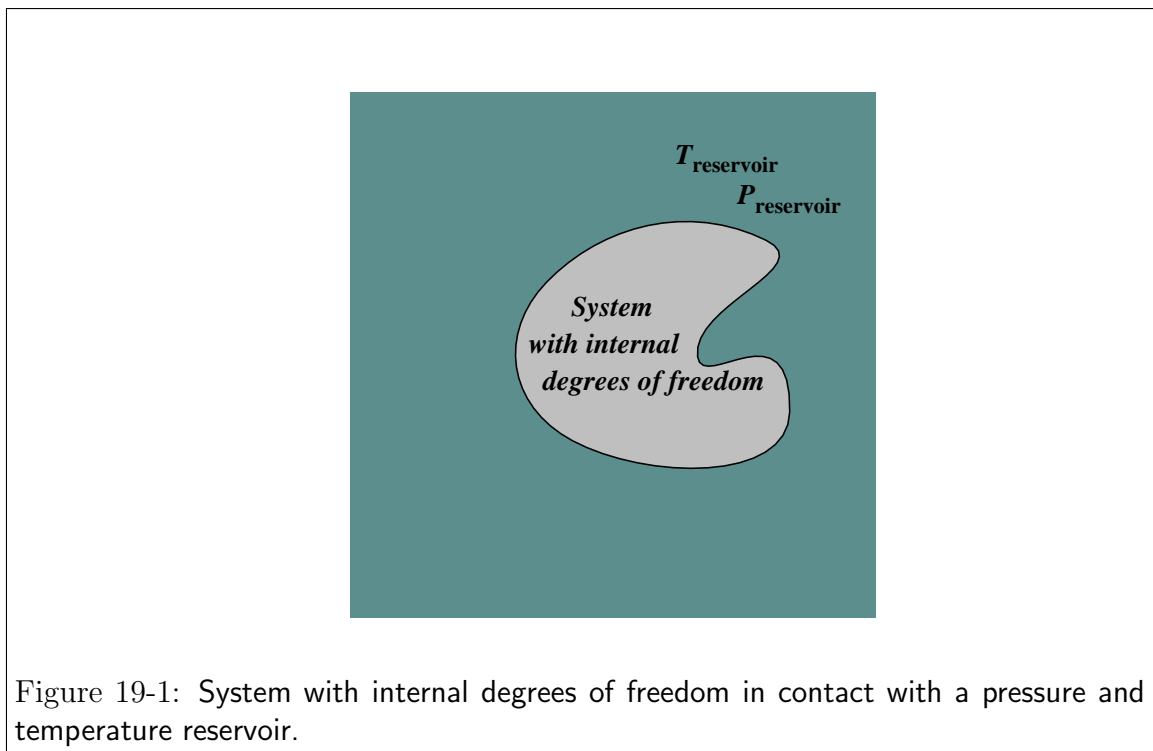
___

or in general

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

___

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 = $ constant and $V = $ 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):

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

$$dS_{\text{reservoir}} = \frac{dq_{\text{reservoir}}}{T_{\text{reservoir}}} \tag{19-3}$$

Apply the first law to the entire system:

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

so that:

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

or

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

or, comparing with Equation 19-1,

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

Note that the sum in Equation 19-7 is really a placeholder for the "internal degrees of freedom" for a system in equilibrium with a reservoir of constant P and T. Equation 19-7 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

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

$$\text{(19-8)}$$

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

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

then

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

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 19-8.

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

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

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

$$d\overline{G^\alpha} = \sum_{i=1}^{C} \mu_i^\alpha dX_i^\alpha \quad \text{(constant pressure and temperature per mole of the } \alpha \text{ subsystem)}$$

$$\tag{19-11}$$

so that

$$\mu_i^\alpha = \left(\frac{\partial G^\alpha}{\partial N_i} \right)_{const\ P\ ,constT\ constN_j}\text{ where }_{j \neq i} = \left(\frac{\partial \overline{G}^\alpha}{\partial X_i} \right)_{const\ P\ ,constT\ constX_j}\text{ where }_{j \neq i}$$

$$\tag{19-12}$$

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 19-8 be modified if the chemical species that were being added were charged?

_____
_____
_____
_____

Question: How would the equilibrium condition Equation 19-8 (or more generally Equation 19-1) 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.