9.16: Internal Entropy and the Second Law

For every incremental part of any process, we have $dS + d\hat{S} \geq 0$. Let us define a new quantity, the ***external entropy*** change, as $d_eS = -d\hat{S}$. The change criteria become $dS - d_eS \geq 0$. Now, let us define the ***internal entropy*** [1] change as $d_iS = dS - d_eS$. The entropy change for a system is the sum of its internal and external entropy changes, $dS = d_iS + d_eS$. We use d_iS and d_eS to represent incremental changes. To represent macroscopic changes, we use $\Delta_i S$ and $\Delta_e S$. Since two processes can effect different changes in the surroundings while the change that occurs in the system is the same, $\Delta\hat{S}$ and $\Delta_e S$ are not completely determined by the change in the state of the system. Neither the internal nor the external entropy change depends solely on the change in the state of the system. Nevertheless, we see that $d_iS \geq 0$ or $\Delta_i S \geq 0$ is an alternative expression of the thermodynamic criteria.

The external entropy change is that part of the entropy change that results from the interaction between the system and its surroundings. The internal entropy is that part of the entropy change that results from processes occurring entirely within the system. (We also use the term "internal energy." The fact that the word "internal" appears in both of these terms does not reflect any underlying relationship of material significance.) The criterion $d_iS > 0$ makes it explicit that a process is spontaneous if and only if the events occurring within the system act to increase the entropy of the system. In one common figure of speech, we say "entropy is produced" in the system in a spontaneous process. (It is, of course, possible for a spontaneous process to have $d_iS > 0$ while $d_eS < 0$, and $dS < 0$.)

In Section 14.1, we introduce a quantity,

$$\sum_{j=1}^{\omega} \mu_j dn_j$$

that we can think of as a change in the chemical potential energy of a system. The internal entropy change is closely related to this quantity: We find

$$d_iS = -\frac{1}{T}\sum_{j=1}^{\omega} \mu_j dn_j$$

As required by the properties of d_iS, we find that $\sum_{j=1}^{\omega} \mu_j dn_j \leq 0$ is an expression of the thermodynamic criteria for change. Internal entropy is a useful concept that is applied to particular advantage in the analysis of many different kinds of spontaneous processes in non-homogeneous systems.