5.8: Criteria for Spontaneity

In this section we combine the first and second laws in order to derive some general relations for changes during a reversible or irreversible process of a closed system. The temperature and pressure will be assumed to be practically uniform during the process, even if the process is irreversible. For example, the volume might be changing at a finite rate but very slowly, or there might be a spontaneous homogeneous reaction in a mixture of uniform temperature and pressure.

The second law states that $\mathrm{d}S$ is equal to $\dđ q/T$ if the process is reversible, and is greater than $\dđ q/T$ if the process is irreversible:

$$\mathrm{d}S \geq \dđ q/T$$

$$(5.8.1)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

or

$$\dđ q \leq T\,\mathrm{d}S$$

$$(5.8.2)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

The *inequalities* in these relations refer to an irreversible process and the *equalities* to a reversible process, as indicated by the notation $\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}$.

When we substitute $\dđ q$ from Eq. 5.8.2 into the first law in the form $\mathrm{d}U = \dđ q - p\,\mathrm{d}V + \dđ w'$, where $\dđ w'$ is nonexpansion work, we obtain the relation

$$\mathrm{d}U \leq T\,\mathrm{d}S - p\,\mathrm{d}V + \dđ w'$$

$$(5.8.3)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

We substitute this relation for $\mathrm{d}U$ into the differentials of enthalpy, Helmholtz energy, and Gibbs energy given by Eqs. 5.3.4–5.3.6 to obtain three more relations:

$$\mathrm{d}H \leq T\,\mathrm{d}S + V\,\mathrm{d}p + \dđ w'$$

$$(5.8.4)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

$$\mathrm{d}A \leq -S\,\mathrm{d}T - p\,\mathrm{d}V + \dđ w'$$

$$(5.8.5)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

$$\mathrm{d}G \leq -S\,\mathrm{d}T + V\,\mathrm{d}p + \dđ w'$$

$$(5.8.6)$$
$$\left(\genfrac{}{}{0pt}{}{\text{irrev}}{\text{rev}}, \text{closed system}\right)$$

The last two of these relations provide valuable criteria for spontaneity under common laboratory conditions. Equation 5.8.5 shows that during a spontaneous irreversible change at constant temperature and volume, $\mathrm{d}A$ is less than $\dđ w'$. If the only work is expansion work (i.e., $\dđ w'$ is zero), the Helmholtz energy decreases during a spontaneous process at constant T and V and has its minimum value when the system reaches an equilibrium state.

Equation 5.8.6 is especially useful. From it, we can conclude the following:

- Ben-Amotz and Honig (*J. Chem. Phys.*, **118**, 5932–5936, 2003; *J. Chem. Educ.*, **83**, 132–137, 2006) developed a "rectification" procedure that simplifies the mathematical manipulation of inequalities. Following this procedure, we can write

$$\mathrm{d}S = \dđ q/T + \dđ\theta$$

$$(5.8.7)$$

  where $\dđ\theta$ is an *excess entropy function* that is positive for an irreversible change and zero for a reversible change ($\dđ\theta \geq 0$). Solving for $\dđ q$ gives the expression $\dđ q = T\,\mathrm{d}S - T\,\dđ\theta$ that, when substituted in the first law expression $\mathrm{d}U = \dđ q - p\,\mathrm{d}V + \dđ w'$, produces

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \dđ w' - T\,\dđ\theta$$

$$(5.8.8)$$

  The equality of this equation is equivalent to the combined equality and inequality of Eq. 5.8.3. Then by substitution of this expression for $\mathrm{d}U$ into Eqs. 5.3.4–5.3.6, we obtain equalities equivalent to Eqs. 5.8.4–5.8.6, for example

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \dđ w' - T\,\dđ\theta$$

$$(5.8.9)$$

  Equation 5.8.9 tells us that during a process at constant T and p, with expansion work only ($\dđ w'=0$), $\mathrm{d}G$ has the same sign as $-T\,\dđ\theta$: negative for an irreversible change and zero for a reversible change.