Thermodynamics and Equilibrium: Important Equations

Second Law of Thermodynamics

Entropy S is a measure of the disorder of a system: the greater the disorder the greater the entropy. The *second law of thermodynamics* tells us the direction of spontaneous (natural) change in the universe. The law states that in any spontaneous change the entropy of the universe increases, and in an equilibrium process it remains unchanged: $\Delta S_{universe} \geq 0$ (where the equality applies at equilibrium). A process for which $\Delta S_{universe} < 0$ is impossible (much like going backwards in time)!

Gibbs Free Energy

A much more convenient criteria for spontaneity which can be derived from the second law involves changes in *Gibbs free energy G*, where $G \equiv H - TS$. A change is spontaneous (product-favored) in the direction written at a constant temperature T and constant pressure p if ΔG for the change is negative. Mathematically, for a spontaneous change we must have

$$(\Delta G)_{p,T} \; < \; 0 \tag{1}$$

At equilibrium, $(\Delta G)_{p,T} \; = \; 0$. If $(\Delta G)_{p,T} \; > \; 0$, the change cannot occur in the direction written (but will be spontaneous in the opposite direction).

There are a number of ways to calculate ΔG . Since $G \equiv H - TS$, when the temperature T is constant

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{3}$$

In these equations (and in all which follow), the temperature is in Kelvin. At standard conditions (superscript "*o*" means standard conditions):

$$\Delta G^{o} = \sum_{\text{products}} n_{prod}\Delta G_{f}^{o}(prod) - \sum_{\text{reactants}} n_{react}\Delta G_{f}^{o}(react) \tag{4}$$

$$\Delta H^{o} = \sum_{\text{products}} n_{prod}\Delta H_{f}^{o}(prod) - \sum_{\text{reactants}} n_{react}\Delta H_{f}^{o}(react) \tag{5}$$

$$\Delta S^{o} = \sum_{\text{products}} n_{prod}S^{o}(prod) - \sum_{\text{reactants}} n_{react}S^{o}(react) \tag{6}$$

Another method of calculating ΔG follows from the connection between the criteria for spontaneous change, $(\Delta G)_{p,T} \; < \; 0$, and our earlier $Q < K$ criteria. Recall that when $Q < K$, reaction is predicted to proceed forward until $Q = K$. It can be shown that

$$\Delta G = - RT \ln K \; + \; RT \ln Q \tag{7}$$

Note that this equation predicts (as required) that when $Q < K$, $\Delta G < 0$. Also, when $Q = K$, $\Delta G =$

0.

By definition at *standard conditions* all reactants and products are in their standard states: they are pure if solid or liquid, and at 1 M concentration if dissolved. It follows that at standard conditions, $Q = 1$ and $\ln Q = 0$. Thus, Eq(7) reduces to

$$\Delta G^o = - RT \ln K \tag{8}$$

where, as always, the "*o*" superscript means standard conditions. Rearranging Eq(8) gives us a convenient equation for calculating K:

$$\ln K = - \frac{\Delta G^o}{RT} \quad \text{or} \quad K = e^{- \Delta G^o / RT} \tag{9}$$

Finally, Eq(7) and Eq(8) may be combined to give

$$\Delta G = \Delta G^o + RT \ln Q \tag{10}$$

The table below summarizes our equations for ΔG under various conditions. Note how the more specialized equations are easily derived from those for the general case.

General Case	$\Delta G = - RT \ln K + RT \ln Q$ $\Delta G = \Delta G^o + RT \ln Q$ $\Delta G = \Delta H - T \Delta S$
Equilibrium Conditions	$Q = K$ $\Delta G = 0$ $\Delta H = T \Delta S$
Standard Conditions	$Q = 1$ $\Delta G = \Delta G^o$; $\Delta H = \Delta H^o$; $\Delta S = \Delta S^o$ $\Delta G^o = - RT \ln K$ $\Delta G^o = \Delta H^o - T \Delta S^o$

Third Law of Thermodynamics

You may have noticed the difference in notation in the ΔS^o equation, Eq(6), as compared to that in Eq(4) and Eq(5). The reason for the difference is that entropy values are *absolute*. They are based on the *third law of thermodynamics* which says that the entropy of a perfect crystalline substance is zero at the absolute zero of temperature (0 K). We therefore assign the value of zero entropy to perfect crystals at absolute zero. All non-perfect crystals and all substances (including pure elements) at temperatures above 0 K have positive entropy. Entropy increases with temperature, since disorder increases when the temperature is raised.

In contrast the zero of enthalpy and zero of free energy are undefined. We follow the convention of setting the heat of formation ΔH^o_f and free energy of formation ΔG^o_f of a pure element in its standard state equal to zero.