**Master Equation**

Two important laws of thermodynamics describe spontaneous change in a closed system.

**First Law** \[ dU = q - p \cdot dV \] (a)

**Second Law** \[ T \cdot dS = q + A \cdot d\xi; \quad A \cdot d\xi \geq 0 \] (b)

Heat \( q \) is common to these equations which we combine. The result is a very important equation.

\[
\frac{dU}{dT} = -\frac{dS}{\xi} - p \cdot dV - A \cdot d\xi
\]

We use the description ‘Master Equation’. A case can be made for the statement that chemical thermodynamics is based on this Master Equation.

The Master Equation describes the differential change in the thermodynamic energy of a closed system.

\[
dU = T \cdot dS - p \cdot dV - A \cdot d\xi
\]

where

\[
T = \left( \frac{\partial U}{\partial S} \right)_V,\xi \quad \text{and} \quad p = -\left( \frac{\partial U}{\partial V} \right)_S,\xi
\]

Symbol \( \xi \) represents the chemical composition of the system (and quite generally molecular organization).

The thermodynamic energy of a closed system containing \( k \) chemical substances is defined by the independent variables \( S, V \) and amounts of each chemical substance.

\[ U = U[S, V, n_1, n_2, \ldots, n_k] \] (f)

We assert that we can independently add \( \delta n_j \) moles of any one of the \( k \) chemical substances in the system and that the entropy \( S \) and \( V \) can change independently. Based on equation (f), the following (often called the Gibbs equation) is a key relationship.

\[
dU = \left( \frac{\partial U}{\partial S} \right)_{V,n(i)} \cdot dS + \left( \frac{\partial U}{\partial V} \right)_{S,n(i)} \cdot dV + \sum_{j=1}^{k} \left( \frac{\partial U}{\partial n_j} \right)_{S,V,n(i \neq j)} \cdot \delta n_j
\] (g)
Here \( n(i) \) represents the amounts of each of the \( k \) chemical substances in the system. Hence from equation (e),

\[
dU = T \cdot dS - p \cdot dV + \sum_{j=1}^{j=k} \left( \frac{\partial U}{\partial n_j} \right)_{S,V,n(i=\bar{j})} \cdot dn_j \quad (h)
\]

The importance of these equations is indicated by imagining a closed system held at constant volume \((dV = 0)\) and entropy \((dS = 0)\). Under these constraints \(dU(S \text{ and } V = \text{constant}) = -A \cdot d\xi\). But according to equation (c), the product \( A \cdot d\xi \) is always positive for spontaneous reactions. Hence \(dU(S \text{ and } V = \text{constant})\) is negative. In other words, all spontaneous chemical reactions in a closed system at constant \(S\) and constant \(V\) proceed in a direction which lowers the thermodynamic energy \(U\) of the system. This conclusion is universal, independent of the type of chemical reaction and of the mechanism of chemical reaction. For this reason the thermodynamic energy is the thermodynamic potential function for processes in closed systems at constant \(S\) and constant \(V\) [1].

There is however a problem in terms of practical chemistry. We can envisage designing a reaction vessel which has constant volume. In fact we would probably use heavy steel walls because the conclusions reached above tell us nothing about a possible change in pressure as we face the challenge of holding the volume constant. But it is not obvious what we have to do to hold the entropy constant. Clearly the line of argument is important. Indeed a similar analysis based on the definitions of enthalpy \(H\), Helmholtz energy \(F\) and Gibbs energy \(G\) leads to the following three key equations for changes in enthalpy, Helmholtz energy and Gibbs energy respectively.

\[
dH = T \cdot dS + V \cdot dp + \sum_{j=1}^{j=k} \left( \frac{\partial H}{\partial n_j} \right)_{S,p,n(i=\bar{j})} \cdot dn_j \quad (i)
\]

\[
dF = -S \cdot dT - p \cdot dV + \sum_{j=1}^{j=k} \left( \frac{\partial F}{\partial n_j} \right)_{T,V,n(i=\bar{j})} \cdot dn_j \quad (j)
\]

\[
dG = -S \cdot dT + V \cdot dp + \sum_{j=1}^{j=k} \left( \frac{\partial G}{\partial n_j} \right)_{T,p,n(i=\bar{j})} \cdot dn_j \quad (k)
\]
The four partial derivatives with respect to \( n_j \) in the four equations define the chemical potential, \( \mu_j \).

\[
\mu_j = \left( \frac{\partial U}{\partial n_j} \right)_{S,V,n_j} = \left( \frac{\partial H}{\partial n_j} \right)_{S,p,n_j}
= \left( \frac{\partial F}{\partial n_j} \right)_{T,V,n_j} = \left( \frac{\partial G}{\partial n_j} \right)_{T,p,n_j}
\]

For example, \( dG = -S \cdot dT + V \cdot dp + \sum_{j=1}^{j=k} \mu_j \cdot dn_j \)  

In context of chemistry, the latter equation is very important.

**Footnote**

[1] An analogy is drawn with electric potential. In an electrical circuit, electric charge flows spontaneously from high to low electric potential.