6.3: ΔA, ΔG, and Maximum Work

The functions A and G are oftentimes referred to as **free energy** functions. The reason for this is that they are a measure of the maximum work (in the case of ΔA) or non p-V work (in the case of ΔG) that is available from a process. To show this, consider the total differentials.

First, consider the differential of A.

$$dA = dU - TdS - SdT$$

Substituting the combined first and second laws for dU, but expressing the work term as dw, yields

$$dA = TdS - dw - TdS - SdT$$

And cancelling the TdS terms gives

$$dA = dw - SdT$$

or at constant temperature ($dT = 0$)

$$dA = dw$$

Since the only assumption made here was that the change is reversible (allowing for the substitution of TdS for dq), and dw for a reversible change is the maximum amount of work, it follows that dA gives the maximum work that can be produced from a process at constant temperature.

Similarly, a simple expression can be derived for dG. Starting from the total differential of G.

$$dG = dU + pdV – pdV + Vdp – TdS – SdT$$

Using an expression for $dU = dq + dw$, where $dq = TdS$ and dw is split into two terms, one (dw_{pV}) describing the work of expansion and the other (dw_e) describing any other type of work (electrical, stretching, etc.)

$$dU - TdS + dW_{pV} + dW_e$$

dG can be expressed as

$$dG = \; T\cancel{dS} - \; p\cancel{dV} + dw_e + \; p\cancel{dV} + Vdp – \; T\cancel{dS} – SdT$$

Cancelling the TdS and pdV terms leaves

$$dG = +dw_e + Vdp – SdT$$

So at constant temperature ($dT = 0$) and pressure ($dp = 0$),

$$dG = dw_e$$

This implies that dG gives the maximum amount of non p-V work that can be extracted from a process.

This concept of dA and dG giving the maximum work (under the specified conditions) is where the term “free energy” comes from, as it is the energy that is *free* to do work in the surroundings. If a system is to be optimized to do work in the soundings (for example a steam engine that may do work by moving a locomotive) the functions A and G will be important to understand. It will, therefore, be useful to understand how these functions change with changing conditions, such as volume, temperature, and pressure.

Contributors

- Patrick E. Fleming (Department of Chemistry and Biochemistry; California State University, East Bay)