Biology 3550: Physical Principles in Biology
Fall Semester - 2016

Additional Notes on ΔE, ΔF ΔH, and ΔG

I. Introduction

From discussions in class, I now realize that I was unclear about some aspects of these thermodynamic functions, and downright wrong in a few!

I think that the major goof that I made was in defining ΔH as the heat absorbed during a process at constant pressure *and* constant temperature. In fact, ΔH is the heat absorbed at constant pressure, but it can be defined for processes that involve a temperature change. For our purposes, we are largely restricting ourselves to processes at constant temperature, and some of the relationships involving ΔH that I have used are based on this assumption. But, that assumption is not intrinsic to the definition of ΔH.

Something that I didn't say clearly, but should have, is that the equation for ΔG:

$$\Delta G = \Delta H - T\Delta S_{\text{sys}}$$

only applies for a reaction or process when the beginning and ending states have the same temperature. Actually, the equation only makes sense for a single temperature!

I apologize for the confusion and hope that these notes will help clarify things.

II. ΔE, the change in internal energy.

In classical treatments, the change in internal energy for a process, ΔE, is defined by the first law of thermodynamics, stated as $\Delta E = q + w$, where q is the heat absorbed by the system and w is the work done on the system. Heat, in turn, is defined as the flow of energy that can increase temperature (but doesn't necessarily for a given process), and work is the integral of force with respect to distance.

The internal energy of the system, E, is a state function, and ΔE is independent of the path taken from the beginning state to the ending state. The heat, q, and work, w, however, are path dependent. But, whatever the path ΔE must equal $q + w$.

Although these definitions stand on their own, it is helpful to have a molecular interpretation. The two distinguishable components of the internal energy are the kinetic energy and potential energy. In the simplest case, an ideal gas, there is only the kinetic energy associated with translational motion, and $E = 3nRT/2$, for n moles at temperature T. Since the particles making up the gas have no internal structure, there is no potential energy or internal thermal motions. Any change in internal energy, ΔE, is due only to a change in temperature. If the temperature is the same at the beginning and end of the process, $\Delta E = 0$.

When we deal with real molecules, even in the gas phase, things get more complicated. There are now internal motions that contribute to the kinetic energy, and the internal structures of the molecules give rise to potential energy. The potential energy represents

energy that can be converted to heat or mechanical energy if the structures of the molecules change, such as by the formation or breaking of chemical bonds. Potential energy can also be absorbed or released by changes that do not involve covalent bonds, such as the formation or breaking of hydrogen bonds or other "weak" interactions.

In liquids and solids, there are additional forms of potential energy, due to interactions among molecules.

For systems involving real molecules, the first law ($\Delta E = q + w$) still holds for any process, but there may be redistributions of kinetic and potential energy within the system that do not change the total internal energy, E. These redistributions will not be reflected in ΔE.

III. ΔF, the Helmholtz free energy

The Helmholtz free energy, F, is defined as:

$$F = E - TS_{\text{sys}}$$

Because E, the temperature (T) and the system entropy (S_{sys}) are all state functions, F must also be a state function. If the beginning and end states of a process have the same temperature, then the change in F is given by:

$$\Delta F = \Delta E - T\Delta S_{\text{sys}}$$

If, however, T is not constant, then things are generally more complicated. Not only does the temperature change during the process, but E and S_{sys} are likely to change as well. Calculating ΔF then requires evaluating an integral that includes expressions for E and S as functions of temperature. This is why we have generally focused on processes at constant temperature!

Recall that the entropy change at constant temperature is defined by the heat absorbed by the system, q, for the reversible process connecting the two states.

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

Therefore, the term $T\Delta S_{\text{sys}}$ in the expression for ΔF (at constant temperature) represents q_{rev}. Since, from the first law, $\Delta E = q_{\text{rev}} + w_{\text{rev}}$, we can also write:

$$\Delta F = \Delta E - T\Delta S_{\text{sys}} = q_{\text{rev}} + w_{\text{rev}} - q_{\text{rev}}$$
$$= w_{\text{rev}}$$

This, then provides a clear physical meaning for ΔF: The work done on the system during the reversible path between the beginning and end states. For a favorable process, ΔF is negative, and its absolute value represents the maximum work that can be obtained. For an unfavorable process, ΔF is positive, and its value represents the minimum amount of work required to drive the system in that direction.

IV. ΔH, the enthalpy change

J. Willard Gibbs introduced enthalpy, H, in order to make thermodynamic calculations associated with chemical reactions more convenient. A basic problem with the internal energy, E, is that there is no direct way to measure it, and measuring ΔE requires measuring both q and w for a specific process.

The formal definition of enthalpy is:

$$H = E + PV$$

where P and V are pressure and volume respectively. Like E, P and V are state functions, so H must be also. At first glance, however, determining H or ΔH doesn't look any easier than determining E or ΔE!

But, for chemical reactions, especially in relatively dilute solutions, we can often impose additional restrictions. First, and most important, we can specify that the the process occurs under constant pressure. Using the subscripts 1 and 2 to indicate the beginning and ending states, respectively, the change in enthalpy can then be written:

$$\Delta H = H_2 - H_1 = E_2 - E_1 + PV_2 - PV_1$$
$$= \Delta E + P\Delta V$$

If ΔV is not zero, the volume change represents work, as we discussed in the case of gas expansion or compression. For most chemical reactions, this is the only form of work associated with the reaction.[1] If the volume of the system increases, then work is done *by* the system, and w is negative. If this form of work is designated w_p, then we can write:

$$w_p = -P\Delta V$$

Assuming that this is the only form of work associated with the process at constant pressure, and designating the associated heat absorbed q_p, we have:

$$\Delta H = \Delta E + P\Delta V = q_p + w_p - w_p$$
$$= q_p$$

This gives the usual working definition for ΔH: The heat absorbed by the system at constant pressure. (ΔH does not imply constant temperature, as I mistakenly indicated in class and in earlier notes!) Although q is not, in general a state function, because q_p refers to a specific path between two states, it is a state function. This makes it relatively easy to measure ΔH for a reaction, using a calorimeter.

With the above restrictions, we can also express ΔH in terms of ΔE:

$$\Delta H = \Delta E - w_p$$

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[1] Notable exceptions are found in the molecular motors in living organisms, as well as some synthetic systems, but here we are focusing on relatively simple chemical reactions.

V. ΔG, the change in Gibbs free energy.

The free energy function named for Gibbs, G, is defined in a way analogous to the definition of the Helmoltz free energy:

$$G = H - TS_{\text{sys}}$$

and the change in G *at constant temperature* is:

$$\Delta G = \Delta H - T\Delta S_{\text{sys}}$$

As noted earlier, the term $T\Delta S_{\text{sys}}$ represents the heat absorbed during the reversible path. As argued above, ΔH is the heat absorbed by the process at constant pressure, and with no work other than w_{p}. Recall that the entropy change for the surroundings for a specific process is defined as:

$$\Delta S_{\text{surr}} = -\frac{q}{T}$$

For the constant pressure process (assuming constant temperature):

$$\Delta S_{\text{surr}} = -\frac{q_{\text{p}}}{T} = -\frac{\Delta H}{T}$$

and, for any constant temperature process:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

If we then restrict ourselves to processes where both pressure and temperature are constant, the total entropy change for the universe is:

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = -\frac{\Delta H}{T} - \Delta S_{\text{sys}}$$

$$= -\frac{\Delta G}{T}$$

This result demonstrates that the sign of ΔG indicates whether or not the process is spontaneous: If ΔG is negative, ΔS_{univ} is positive and the process is favorable. If ΔG is positive, ΔS_{univ} is negative and the process is unfavorable.

As noted earlier, the Helmoltz free energy change, ΔF, represents the work associated with the reversible process, w_{rev}, which is the maximum amount of work that can be obtained from a favorable process, or the minimum work required to drive an unfavorable process. ΔG is also related to w_{rev}, but in a slightly more complicated way.

Consider the difference between ΔG and ΔF:

$$\begin{aligned} \Delta G - \Delta F &= (\Delta H - T\Delta S_{\text{sys}}) - (\Delta E - T\Delta S_{\text{sys}}) \\ &= \Delta H - \Delta E \end{aligned}$$

Since $\Delta H = q_{\text{p}}$ and $\Delta E = q + w$ for any path, we can write:

$$\begin{aligned} \Delta G - \Delta F &= \Delta H - \Delta E \\ &= q_{\text{p}} - (q_{\text{p}} + w_{\text{p}}) \\ &= -w_{\text{p}} \end{aligned}$$

Replacing ΔF with w_{rev} gives:

$$\begin{aligned} \Delta G - w_{\text{rev}} &= -w_{\text{p}} \\ \Delta G &= w_{\text{rev}} - w_{\text{p}} \end{aligned}$$

Therefore, ΔG represents the maximum work obtainable from a favorable process *minus* the work associated with a change in volume at constant pressure. Because the change in volume is typically quite small for reactions in solution, ΔG usually represents the maximum amount of work available from a process under those conditions (or the minimum amount of work required to drive an unfavorable process).