

4.7 Focus on ΔG

We have found how U , H , and S vary with temperature. For the two energies, the changes with respect to temperature are called heat capacities, and we derived several equations for the change in S with respect to temperature (like equation 3.18, $\Delta S = n \cdot \bar{C} \cdot \ln(T_f/T_i)$, or the integral form previous to equation 3.18 for a nonconstant heat capacity). Since we are making the point that G is the most useful energy state function, how does G vary with temperature?

From the natural variable equation for dG , we found one relationship between G and T :

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (4.40)$$

As temperature changes, the change in G is equal to the negative of the entropy of the system. Notice the negative sign on the entropy in this equation: it implies that as temperature goes up, the free energy goes down, and vice versa. This might seem intuitively wrong at first glance: an energy goes *down* as the temperature increases? But recall the original definition of the Gibbs free energy: $G = H - TS$. The negative sign in front of the term that includes temperature does indeed imply that as T increases, G will be lower.

There is another expression that relates the temperature-dependence of G , but in a slightly different fashion. If we start with the definition of G :

$$G = H - TS$$

we remember that $-S$ is defined by the partial derivative in equation 4.40. Substituting:

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

where the minus signs have canceled. We rearrange this by dividing both sides of the equation by T , and get

$$\frac{G}{T} = \frac{H}{T} + \left(\frac{\partial G}{\partial T}\right)_p$$

Now we further rearrange by bringing all terms in G to one side:

$$\frac{G}{T} - \left(\frac{\partial G}{\partial T}\right)_p = \frac{H}{T} \quad (4.41)$$

Although this might look intractable, we will introduce a simplifying substitution in a roundabout way. Consider the expression G/T . The derivative of this with respect to T at constant p is

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{G}{T^2}\left(\frac{\partial T}{\partial T}\right)_p + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p$$

by strict application of the chain rule. $\partial T/\partial T$ equals 1, so this expression simplifies to

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p$$

If we multiply this expression by $-T$, we get

$$-T \cdot \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = \frac{G}{T} - \left(\frac{\partial G}{\partial T}\right)_p$$

Note that the expression on the right side of the equation is the same as the left side of equation 4.41. We can therefore substitute:

$$-T \cdot \frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = \frac{H}{T}$$

or

$$\frac{\partial}{\partial T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2} \quad (4.42)$$

This is an extremely simple equation, and when expanding our derivation to consider changes in energy, it should not be too difficult to derive, for the overall process:

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2} \quad (4.43)$$

for a physical or chemical process. Equations 4.42 and 4.43 are two expressions of what is called the *Gibbs-Helmholtz equation*. By using substitution [that is, let $u = 1/T$, $du = -(1/T^2) dT$, and so on], you can show that equation 4.43 can also be written as

$$\left(\frac{\partial \Delta G}{\partial \frac{1}{T}}\right)_p = \Delta H \quad (4.44)$$

The form given in equation 4.44 is especially useful. By knowing ΔH for a process, we know something about ΔG . A plot of $\Delta G/T$ versus $1/T$ would be equal to ΔH as a slope. (Remember that a derivative is just a slope.) Further, if

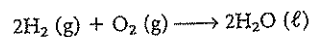
we make the approximation that ΔH is constant over small temperature ranges, we can use equation 4.44 to approximate ΔG at different temperatures, as the following example illustrates.

Example 4.11

By approximating equation 4.44 as

$$\left(\frac{\Delta \Delta G}{\Delta \frac{1}{T}}\right)_p \approx \Delta H$$

predict the value of ΔG (100°C, 1 atm) of the reaction



given that ΔG (25°C, 1 atm) = -474.36 kJ and $\Delta H = -571.66 \text{ kJ}$. Assume constant pressure and ΔH .

Solution

First, we should evaluate $\Delta(1/T)$. Converting the temperatures to kelvins, we find that

$$\Delta \frac{1}{T} = \frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} = -0.000674/\text{K}$$

Using the approximated form of equation 4.44:

$$\left(\frac{\Delta \Delta G}{\Delta \frac{1}{T}}\right)_p \approx -571.66 \text{ kJ}$$

$$\Delta \frac{\Delta G}{T} = 0.386 \frac{\text{kJ}}{\text{K}}$$

Writing $\Delta(\Delta G/T)$ as $(\Delta G/T)_{\text{final}} - (\Delta G/T)_{\text{initial}}$, we can use the conditions given to get the following expression:

$$\left(\frac{\Delta G}{373 \text{ K}}\right)_{\text{final}} - \left(\frac{-474.36 \text{ kJ}}{298 \text{ K}}\right)_{\text{initial}} = 0.386 \frac{\text{kJ}}{\text{K}}$$

$$\Delta G_{\text{final}} = \Delta G(100^\circ\text{C}) = -450. \text{ kJ}$$

This compares to a value of -439.2 kJ obtained by recalculating ΔH (100°C) and ΔS (100°C) using a Hess's-law type of approach. The Gibbs-Helmholtz equation makes fewer approximations and would be expected to produce more accurate values of ΔG .

Try $\Delta G(50^\circ\text{C}, 1 \text{ atm})$

5.5 Changes in Equilibrium Constants

Despite their names, the numerical values of equilibrium constants can vary depending on conditions, usually with varying temperatures. The effects of temperature on equilibria are easy to model. In the last chapter, we derived the Gibbs-Helmholtz equation as

$$\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right)_p = -\frac{\Delta H}{T^2}$$

When applied to a chemical reaction under conditions of standard pressure, it can be rewritten as

$$\frac{\partial}{\partial T} \left(\frac{\Delta_{rxn} G^\circ}{T} \right)_p = -\frac{\Delta_{rxn} H^\circ}{T^2}$$

Since $\Delta_{rxn} G^\circ = -RT \ln K$, we can sub

$$\frac{\partial}{\partial T} (-R \ln K)_p = -\frac{\Delta_{rxn} H^\circ}{T^2}$$

R is a constant, and the two negative signs cancel. This equation rearranges to yield the *van't Hoff equation*:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta_{rxn} H^\circ}{RT^2} \quad (5.18)$$

A qualitative description of the changes in K depends on the sign of the enthalpy of reaction. If $\Delta_{rxn} H$ is positive, then K increases with increasing T and decreases with decreasing T . Endothermic reactions therefore shift towards products with increasing temperatures. If $\Delta_{rxn} H$ is negative, increasing temperatures decrease the value of K , and vice versa. Exothermic reactions therefore shift toward reactants with increasing temperatures. Both qualitative trends are consistent with *Le Chatelier's principle*, the idea that equilibria that are stressed will shift in the direction that minimizes the stress.

A mathematically equivalent form of the van't Hoff equation is

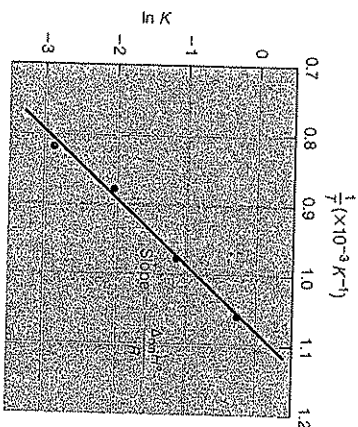
$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{\Delta_{rxn} H^\circ}{R} \quad (5.19)$$

This is useful because it implies that a plot of $\ln K$ versus $1/T$ has a slope of $-(\Delta_{rxn} H^\circ)/R$. Values of $\Delta_{rxn} H$ can be determined graphically by measuring equilibrium constants versus temperature. (Compare this with the analogous plot of the Gibbs-Helmholtz equation. What differences and similarities are there in the two plots?) Figure 5.4 shows an example of such a plot.

A more predictive form of the van't Hoff equation can be found by moving the temperature variables to one side of equation 5.18 and integrating both sides:

$$d \ln K = \frac{\Delta_{rxn} H^\circ}{RT^2} dT$$

$$\int_{K_1}^{K_2} d \ln K = \int_{T_1}^{T_2} \frac{\Delta_{rxn} H^\circ}{RT^2} dT$$



4 Plot of the van't Hoff equation as given in equation 5.19. Plots like this are one way of determining $\Delta_{rxn} H$.

If $\Delta_{rxn} H^\circ$ is assumed to not vary over the temperature range, it can be removed from the integral along with R , and the expression becomes

$$\ln \frac{K_2}{K_1} = \frac{\Delta_{rxn} H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5.20)$$

Using this expression, we can estimate the values of equilibrium constants at different temperatures, knowing the standard enthalpy change. Or, we can estimate the standard enthalpy change knowing the equilibrium constant at two different temperatures, rather than plotting data as suggested by equation 5.19.

Example 5.10

The dimerization of a protein has the following equilibrium constants at the given temperatures: K (4°C) = 1.3×10^7 , K (15°C) = 1.5×10^7 . Estimate the standard enthalpy of reaction for this process.

Solution

Using equation 5.20 and remembering to convert our temperatures into kelvins:

$$\ln \frac{1.3 \times 10^7}{1.5 \times 10^7} = \frac{\Delta_{rxn} H^\circ}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{288 \text{ K}} - \frac{1}{277 \text{ K}} \right)$$

Solving for the enthalpy of reaction:

$$\Delta_{rxn} H^\circ = 8630 \text{ J/mol} = 8.63 \text{ kJ/mol}$$

Product the $K(25^\circ\text{C})$