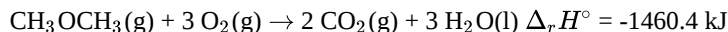


6.3: Enthalpy and Gibbs Energy of Formation- Hess's Law examples

Given that the basis set of formation reactions can be used to calculate the thermodynamic data on any conceivable chemical transformation, we will now work several examples starting with the combustion reaction of dimethyl ether:



The reaction enthalpy is determined from:

$$\Delta_r H^\circ = \sum_{\text{products}} v \cdot \Delta_f H_m^\circ - \sum_{\text{reactants}} v \cdot \Delta_f H_m^\circ \quad (6.3.1)$$

Likewise:

$$\begin{aligned} \Delta_r G^\circ &= \sum_{\text{products}} v \cdot \Delta_f G_m^\circ - \sum_{\text{reactants}} v \cdot \Delta_f G_m^\circ \quad (6.3) \\ &= \sum_{\text{products}} v \cdot (\Delta_f H_m^\circ - T \Delta_f S_m^\circ) - \sum_{\text{reactants}} v \cdot (\Delta_f H_m^\circ - T \Delta_f S_m^\circ) \end{aligned} \quad (6.3.2)$$

where v is the stoichiometric number of moles that each species contributes to the reaction and the symbol $^\circ$ means that the data are measured under standard conditions (25 °C and 1 bar pressure). These equations comprise Hess's Law, which is really just a restatement that energy is conserved (also known as the 1st Law of Thermodynamics).

Back to task- we can determine the enthalpy of burning dimethyl ether by summation of the formation enthalpies of 3 mol×water and 2 mol×carbon dioxide minus the same for 3 mol×oxygen and 1 mol×dimethyl ether:

$$\begin{aligned} \Delta_r H^\circ &= \sum_{\text{products}} v \cdot \Delta_f H_m^\circ - \sum_{\text{reactants}} v \cdot \Delta_f H_m^\circ = 3 \text{ mol} \times -285.83 \frac{\text{kJ}}{\text{mol}} + 2 \text{ mol} \times -393.509 \frac{\text{kJ}}{\text{mol}} - 3 \text{ mol} \\ &\quad \times 0.0 \frac{\text{kJ}}{\text{mol}} - 1 \text{ mol} \times 184.1 \frac{\text{kJ}}{\text{mol}} = -1460.4 \text{ kJ/mol} \end{aligned}$$

and:

$$\begin{aligned} \Delta_r G^\circ &= \sum_{\text{products}} v \cdot \Delta_f G_m^\circ - \sum_{\text{reactants}} v \cdot \Delta_f G_m^\circ = 3 \text{ mol} \times -237.129 \frac{\text{kJ}}{\text{mol}} + 2 \text{ mol} \times -394.359 \frac{\text{kJ}}{\text{mol}} - 3 \text{ mol} \\ &\quad \times 0.0 \frac{\text{kJ}}{\text{mol}} - 1 \text{ mol} \times 135.2 \frac{\text{kJ}}{\text{mol}} = -1364.9 \text{ kJ/mol} \end{aligned}$$

Note that $\Delta_r G^\circ$ could have been calculated from the enthalpies and entropies as:

$$\Delta_r G^\circ = \sum_{\text{products}} v \cdot (\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ) - \sum_{\text{reactants}} v \cdot (\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ)$$

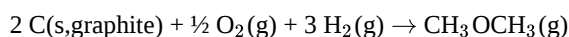
For example, take the thermochemical data on dimethyl ether:

Material	S_m° (J/K/mol)	$\Delta_f G_m^\circ$ (kJ/mol)	$\Delta_f H_m^\circ$ (kJ/mol)	$C_{P,m}^\circ$ (J/K/mol)
CH ₃ OCH ₃ (g)	342.2	-135.2	-184.1	65.57

From this we can get $\Delta_f G_m^\circ$ from $\Delta_f H_m^\circ = -184.1 \text{ kJ/mol}$ and $S_m^\circ = 342.2 \text{ J/K/mol}$, which is:

$$-184.1 \frac{\text{kJ}}{\text{mol}} - -298.15 \text{ K} \times 0.3422 \frac{\text{kJ}}{\text{K} \cdot \text{mol}} = -286.12 \frac{\text{kJ}}{\text{mol}}$$

Wait! Something is wrong, this isn't the same molar Gibbs formation energy as in the table ($\Delta_f G_m^\circ = -135.2 \text{ kJ/mol}$)! If we retrace our steps we can see that this incorrect result comes about from trying to calculate $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T^\circ \times S_m^\circ$, whereas we should have been using: $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T^\circ \times \Delta_f S_m^\circ$. The former, incorrect equation is using S_m° , but we should instead have calculated $\Delta_f S_m^\circ$ for dimethyl ether using the entropy data for carbon, hydrogen and oxygen. From Table 6-1 this is the entropy of the following reaction:



which is:

$$1\text{mol} \times 342 \frac{\text{J}}{\text{K} \cdot \text{mol}} - 2\text{mol} \times 5.74 \frac{\text{J}}{\text{K} \cdot \text{mol}} - \frac{1}{2}\text{mol} \times 205.14 \frac{\text{J}}{\text{K} \cdot \text{mol}} - 3\text{mol} \times 130.68 \frac{\text{J}}{\text{K} \cdot \text{mol}} = -164.09 \frac{\text{J}}{\text{K}}$$

Since this is the entropy for forming 1 mol of dimethyl ether from its elements in their standard states, we can state that this is the per molar entropy of formation $\Delta_f S_m^\circ = -164.09 \text{ J/K/mol}$. When we use entropy properly we see that the data table is self-consistent:

$$\Delta_f G_m^\circ = \Delta_f H_m^\circ - T^\circ \times \Delta_f S_m^\circ = -184.1 \frac{\text{kJ}}{\text{mol}} - 298.15 \text{ K} \times -0.16409 \frac{\text{kJ}}{\text{K} \cdot \text{mol}} = -135.2 \frac{\text{kJ}}{\text{mol}}$$

The exercise above demonstrates that our understanding of how Gibbs energy is related to enthalpy and entropy is correct. However, we don't recommend going through all of these calculations for the Gibbs energy if a table of $\Delta_f G_m^\circ$'s is already available!

The examples above allowed us to calculate thermodynamic data a variety of ways using Hess's Law. It must be noted that the results are only applicable to a reaction performed at room temperature and 1 bar pressure. You should know from your lab experiences that we often heat reactions (and in more advanced labs you sometime cool them!); how do you go about calculating thermodynamic values when you are no longer at the standard state? This is the subject of the next section on Kirchoff's Law.

6.3.1 Non-standard state reactions and Kirchoff's Law. Not all chemical reactions will occur at exactly 1 bar pressure and 25 °C if they are not spontaneous. And of course you know that "not spontaneous" means $\Delta_r G^\circ(298 \text{ K}) > 0 \text{ J}$, which also means that total entropy does not increase as required by the 2nd Law. Our intuition also tells us that heating a chemical reaction to a higher temperature T_2 will often make it "go", i.e., become spontaneous, which means $\Delta_r G(T_2) < 0 \text{ J}$ at this higher temperature. As a result, we often must adjust our thermochemical data for conditions other than the standard state. Here we will focus on temperature, starting with the relationships we derived in Chapter 3 for the temperature dependence of enthalpy:

$$\partial H = \partial U + \partial(PV) = \partial U + nR\partial T = C_v\partial T + nR\partial T = (C_v + nR)\partial T = C_P\partial T$$

While it is tempting to simply integrate the above to yield $\Delta H = C_P\Delta T$, this is an oversimplification. This is because when we integrate we need to know the upper and lower limits. Since we are adjusting the standard state thermochemical data from Table 6.1 the lower limit should be the standard temperature $T^\circ = 25 \text{ °C} = 298.15 \text{ K}$. The upper limit is the temperature at which we need to know the enthalpy; we will call T_2 . Let's not forget that we need to do everything on a per molar basis as well. Thus:

$$\int_{\Delta_f H_m^\circ}^{\Delta_f H_m(T_2)} \partial \Delta_f H_m = \Delta_f H_m(T_2) - \Delta_f H_m^\circ(298.15 \text{ K})$$

likewise:

$$\int_{T^\circ=298.15 \text{ K}}^{T_2} C_{P,m} \partial T = C_{P,m}(T_2 - 298.15 \text{ K})$$

assuming that the heat capacity is not temperature dependent which is not fully correct. Since the above are equal, $\Delta_f H_m(T_2) - \Delta_f H_m^\circ(298.15 \text{ K}) = C_{P,m}(T_2 - 298.15 \text{ K})$, we can find $\Delta_f H_m(T_2)$:

$$\Delta_f H_m(T_2) = \Delta_f H_m^\circ(298.15 \text{ K}) + C_{P,m}(T_2 - 298.15 \text{ K}) \quad \text{left(6.5\right) \nonumber}$$

Using Equation 6.5 we can calculate the formation enthalpy at a new temperature for a single chemical substance, we then determine the same for all the participants in the reaction and then use these data as part of a normal Hess's Law calculation:

$$\Delta_r H(T_2) = \sum_{\text{products}} v \cdot \Delta_f H_m(T_2) - \sum_{\text{reactants}} v \cdot \Delta_f H_m(T_2)$$

Recall that our goal is to determine the change in Gibbs Energy, and for this we must determine how the absolute entropy of a chemical changes with temperature. As we already discussed how to adjust the entropy as temperature increases in Sec. 6.1, which we will adapt here starting at the standard state temperature:

$$S_m(T_2) = S_m^\circ + C_{P,m} \times \ln\left(\frac{T_2}{T^\circ = 298.15 \text{ K}}\right) \quad (6.6)$$

With the knowledge of the proper entropy change of every chemical species in the reaction, the net entropy change is thus: $\Delta_r S = \sum_{products} \nu \cdot S_m(T_2) - \sum_{reactants} \nu \cdot S_m(T_2)$. Combined with the enthalpy change we now know: $\Delta_r G(T_2) = \Delta_r H(T_2) - T_2 \times \Delta_r S(T_2)$.

You may have noticed that these calculations are extremely tedious. However, there is a time-saving method to perform this calculation called Kirchoff's Law. First, note that the heat capacity is used to alter the enthalpy and entropy of each species individually. What if we calculate the reaction difference in heat capacities in the usual manner- products minus reactants:

$$\Delta_r C_P^\circ = \sum_{products} \nu \cdot C_{P,m}^\circ - \sum_{reactants} \nu \cdot C_{P,m}^\circ$$

and then use that to determine the reaction enthalpy at temperature T_2 :

_____ , _____ ,

$$\Delta_r H(T_2) = \Delta_r H^\circ(298.15 K) + \Delta_r C_P^\circ \times (T_2 - 298.15 K)$$

Likewise, the change in the reaction entropy at T_2 :

$$\Delta_r S(T_2) = \Delta_r S_m^\circ(298.15 K) + \Delta_r C_P^\circ \times \ln\left(\frac{T_2}{298.15 K}\right)$$

to give us the change in Gibbs Energy at temperature T_2 :

$$\Delta_r G(T_2) = \Delta_r H(T_2) - T_2 \times \Delta_r S(T_2)$$

This is the exact same thing as adjusting for the individual species' $\Delta_f H_m$ and S_m based on temperature, but faster as the example problems 6.1 & 6.2 illustrate.

6.3.2 Gibbs-Helmholtz approach. In example problems 6.1 & 6.2 we demonstrated examples of chemical reactions that require an increase the temperature to lower $\Delta_r G$. How could we have known this would work before going through all that tortuous calculator work? After all, maybe we needed to cool the reactions! To this end we can use a derivate of the Gibbs-Helmholtz relation, Equation 5.10 that we learned in Chapter 5:

$$\left(\frac{\partial\left(\frac{\Delta_r G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_r H}{T^2} \quad (6.3.3)$$

From this we can immediately see that, if $\Delta_r H$ is positive (the reaction is endothermic), then the derivative $\left(\frac{\partial\left(\frac{\Delta_r G}{T}\right)}{\partial T}\right)_P$ is negative. Thus, if the temperature increases (∂T is positive), then $\partial\left(\frac{\Delta_r G}{T}\right)$ is negative. And since T itself is positive, then a negative $\partial\left(\frac{\Delta_r G}{T}\right)$ requires that $\Delta_r G$ decreases. To summarize, $\Delta_r G$ decreases with increasing temperature for endothermic reactions, and of course $\Delta_r G$ increases with increasing temperature for exothermic reactions. We can make this clearer if we integrate the Gibbs-Helmholtz equation $\partial\left(\frac{\Delta_r G}{T}\right) = -\frac{\Delta_r H^\circ}{T^2} \partial T$ as shown here:

$$\int_{\frac{\Delta_r G^\circ}{T^\circ=298.15 K}}^{\frac{\Delta_r G(T_2)}{T_2}} \partial\left(\frac{\Delta_r G}{T}\right) = \int_{T^\circ=298.15 K}^{T_2} \frac{-\Delta_r H^\circ}{T^2} \partial T$$

where we assume the lower limit is the standard state temperature. The quantity we are trying to calculate, $\Delta_r G(T_2)$, is in the upper limit of the left-hand integral. Solving for it yields:

$$\frac{\Delta_r G(T_2)}{T_2} - \frac{\Delta_r G^\circ}{298.15 K} = \Delta_r H^\circ \left(\frac{1}{T_2} - \frac{1}{298.15 K}\right)$$

which simplifies to:

$$\Delta_r G(T_2) = \Delta_r H^\circ + \frac{(\Delta_r G^\circ - \Delta_r H^\circ) \times T_2}{298.15 K} \quad (6.8)$$

This equation looks a lot easier to work with than the calculations in example problems 6.1 & 6.2! In fact, if we plug in values for the steam forming reaction into the above, we find that $\Delta_r G(T_2) = 0 \text{ kJ}$ at a temperature of 960 K (686.8 °C). This is close, *but not identical*, to the result from the example problem which was 606.3 °C. Why is that? If we insert the fact that $\Delta_r G^\circ = \Delta_r H^\circ - 298.15 \text{ K} \times \Delta_r S^\circ$ into Equation 6.8 above then we can show that:

$$\Delta_r G(T_2) = \Delta_r H^\circ - T_2 \times \Delta_r S^\circ$$

This result is rather trivial as it is simply the standard state Gibbs energy: $\Delta_r G^\circ = \Delta_r H^\circ - T^\circ \times \Delta_r S^\circ$, where $T^\circ = 298.15 \text{ K}$, with a non-standard temperature T_2 inserted for T° . While solving Equation 6.8 is much easier than using Kirchoff's Law as in the example problems of the previous section, it clearly cannot be as accurate.

Where did we go wrong? A simplification must have been made when we integrated the Gibbs-Helmholtz equation, but where? A clue comes from the fact that Equation 6.8 doesn't incorporate the reaction heat capacity ($\Delta_r C_P^\circ$) to adjust the enthalpy for a non-standard temperature. In other words, the temperature dependence of $\Delta_r H$ was ignored when solving the $\int_{T_1=298.15 \text{ K}}^{T_2} \frac{-\Delta_r H^\circ}{T^2} \partial T$ integral. We treated the enthalpy as temperature-independent, which is not very accurate. To resolve, we can add in the temperature dependence of enthalpy when solving the integral as:

$$\int_{\frac{\Delta_r G^\circ}{T^\circ=298.15 \text{ K}}}^{\frac{\Delta_r G(T_2)}{T_2}} \partial \left(\frac{\Delta_r G}{T} \right) = \int_{T^\circ=298.15 \text{ K}}^{T_2} \frac{-(\Delta_r H^\circ + \Delta_r C_P^\circ \times (T - 298.15 \text{ K}))}{T^2} \partial T$$

again assuming that the lower temperature limit is the standard state T° . And when we do so, after some calculus and a significant amount of algebra, we end up with the same equation in the Kirchoff's Law discussion in Sec. 6.3.1.

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