

## 6.2: Energy, it's all relative

Now that we can calculate the entropy per mole of all chemicals at the standard state, we would like to tabulate it with the Gibbs energy per mole as derived from the enthalpy using:  $G_m = H_m - (298 \text{ K} \times S_m)$ . From there we could evaluate whether any reaction was spontaneous without having to go to a lab, put all the chemicals in a reactor and measure the reaction yields etc. All we do is get the sum of the  $G_m$ 's of the reactants and subtract that from the sum of the same of the products. Given the equations above, all we need to know is the absolute enthalpy per mole  $H_m$  that we can determine using  $H_m = U_m + PV$ .

Unfortunately there is a terrible problem; we need to know  $U_m$  but there is no 3<sup>rd</sup> Law for the absolute internal energy. This is probably confusing because it appeared we defined the internal energy in Chapter 2 via the Equipartition theorem:  $U_m = \frac{1}{2}RT \cdot (\text{degrees of freedom})$ . The Equipartition theorem relates the internal energy to the temperature of a chemical, but now we have to ask, *what kind of energy?* In Chapter 2, we were considering gas molecules' ability to translate through space; maybe it could rotate as well. These types of energies were important because it helped us determine the work done by an expanding piston. What this definition of  $U_m$  **does not do** is allow us to determine the energy of a gas molecule if it reacts with another. Reactions are dependent on bond breaking and making, which has to do with the arrangement of electrons between the atoms. And the energy of electrons must depend on their own degrees of freedom, which is difficult to think about because electrons are very light and behave via the rules of quantum mechanics. For example, do electrons in the  $\sigma$ -bonds of hexane have more or less degrees of freedom of those in the delocalized  $\pi$ -bonds of benzene? And if so, how do you use that information to calculate the internal energy?

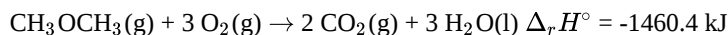
At this point, you are probably confused about energy, and so are the authors of this book! In fact, it is difficult to know whether absolute energy even exists when all we do is measure changes in energy. However, perhaps such knowledge of relative energies is good enough for us to predict the thermodynamics and yields of chemical reactions, which is all that chemists care about anyways. This is in fact true and the subject of the next section.

**6.2.1 Hess's Law and the Gibbs Energy of Chemical Reactions.** Let's consider some chemical reactions related to home fuels. In terms of household heating, one good use of thermochemistry would be to discover a reaction that produces a lot of heat via a large negative enthalpy ( $\Delta_r H^\circ$ , where "r" means "reaction" and  $^\circ$  means the value was measured at the standard state  $T=298.15 \text{ K}$  and  $P = 100 \text{ kPa}$ ). Burning propane is a good example:

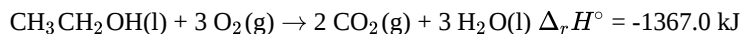


but we see a lot of "bad" carbon dioxide produced. Perhaps there is another reaction that produces heat without as much  $\text{CO}_2(\text{g})$ ? To do so, let's tabulate the  $\Delta_r H^\circ$ 's of all possible chemical reactions and sort them based on exothermicity. We can do this by adding the reactants' enthalpies and subtract that from the sum of the products' enthalpies. However, knowledge of a chemical's absolute enthalpy content is not possible as we just discussed. And with no ability to make predictions, we are going to have to experimentally measure all the enthalpies of all reactions that could ever exist. While the results will be very accurate, this effort will take a huge amount of time and money.

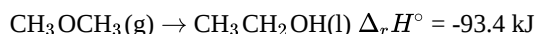
It turns out that we can predict the enthalpies of chemical reactions without actually setting them off; we will demonstrate how this works with some examples. For example, the heat generated from the combustion of dimethyl ether is:



This reaction produces a lot heat but less  $\text{CO}_2$  than propane. Dimethyl ether is easier to transport than propane because it liquefies under mild conditions; perhaps we should use it instead of propane for a home fuel? Let's also examine ethanol. Here we see that ethanol combustion is not as exothermic as dimethyl ether:



but it is a "green" fuel because ethanol can be produced by fermentation, which is a renewable process. Ethanol can also be synthesized from dimethyl ether:

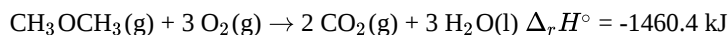


Now here is an important observation- the difference in the enthalpy of combustion of dimethyl ether and ethanol:

$$-1460.4 \text{ kJ} - (-1367.0 \text{ kJ}) = -93.4 \text{ kJ}$$

just happens to be the same as the difference in enthalpy of forming ethanol from dimethyl ether shown above! It's as though we can combine the reactions as though they are equations. If this statement is confusing, let us demonstrate exactly what we mean by

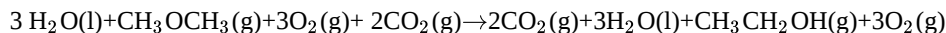
summing the combustion reaction of diethyl ether with the reverse reaction of the combustion of ethanol:



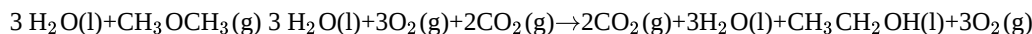
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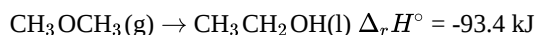
The result is:



The enthalpy ( $\Delta_r H^\circ$ ) of the combustion reaction of ethanol was switched from negative to positive because the reaction is written in reverse. Next, there are identical species (oxygen, water, and carbon dioxide) on the right and left of the net reaction that can be removed because they don't "do" anything if they are on both sides of the equation. This simplification yields:

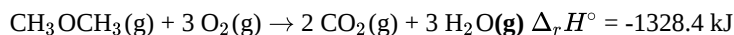


The leftovers are:



These are summarized in Figure 6.2, where we can see that the difference in the enthalpy of the combustion reaction of dimethyl ether and ethanol is the same as the enthalpy difference between forming ethanol from diethyl ether. The combination of all these data form a thermodynamic cycle, which means that we can generate new data on reactions that we haven't actually measured so long as it closes a cycle of other reactions with known thermochemistry.

One more example; let's see what happens if we burn dimethyl ether such that the product is steam (i.e. gaseous water, see Figure 6.3):

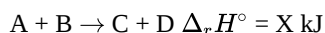


Compared to our previous example that had liquid water as a product, we can use these data to determine  $3 \times$  the enthalpy of vaporization of water:

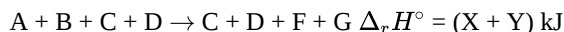
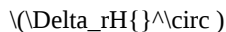
$$-1328.4 \text{ kJ/mol} - (-1460.4 \text{ kJ/mol}) = 132.0 \text{ kJ/mol}$$

(the factor of  $3 \times$  exists because there are three moles of water formed in this reaction). For 1 mol of water this is +44.0 kJ/mol. In fact, if we Google the enthalpy of vaporization of water we quickly discover the same value: +40.0 kJ/mol! Note that this also shows that we must be careful when we do Hess's Law problems that we have to pay attention to the phases of the chemicals in the reaction.

We have covered several specific examples thus far, and maybe it's a bit confusing as to how we are performing these manipulations. So instead let's study some examples for summing chemical reactions for which we will use labels like "A" & "B" etc. for the reactants and products:



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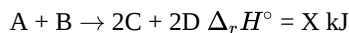


We simply add the chemicals to the left of the " $\rightarrow$ " sign together, and ditto for the right side. Likewise we add the enthalpies together. In the net reaction at the bottom we can eliminate C and D since they are on both sides:  $\text{A} + \text{B} + \text{C} + \text{D} \rightarrow \text{C} + \text{D} + \text{F} + \text{G}$ , leaving:

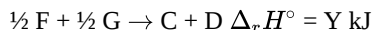


What this example demonstrates is a process that can be applied to calculate the enthalpy for the reaction  $\text{A} + \text{B} \rightarrow \text{F} + \text{G}$ .

Here is a more difficult example. If we are looking to calculate the enthalpy for the reaction  $\text{A} + \text{B} \rightarrow \text{F} + \text{G}$  using the following:



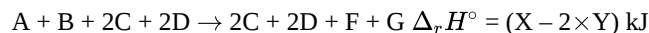
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This is more difficult because we can't directly add these equations together. In fact, we need to reverse the second reaction and then multiply it by 2, and then we can sum the two to get the correct reaction stoichiometry (products, reactants, and relative number of moles). Note that the enthalpy is thus multiplied by -2, where the minus comes about from reversing the reaction:



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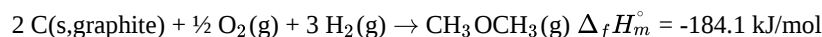


As in the last example we eliminate the species that appear on both left and right sided to yield:  $A + B \rightarrow F + G \quad \Delta_r H^\circ = (X - 2 \times Y) \text{ kJ}$

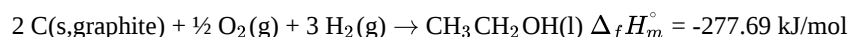
**6.2.2 A reaction basis set.** Let us not forget our end goal, which is to tabulate the enthalpy and Gibbs energy of chemical substances to predict the outcomes of reactions without necessarily having to actually measure them. To meet this goal, we first note that in every example above species "C" and "D" were ultimately removed. What if "C" is  $\text{CO}_2$  and "D" is  $\text{H}_2\text{O}$ , which are always to one side of a combustion reaction? If so, then we can derive the thermochemistry of the reaction  $A + B \rightarrow F + G$  solely using data from combustion reactions. Consequently, if we simply measure the thermochemistry of combusting every chemical we can get our hands on, the data derived from this effort can be mixed and matched as above to determine new thermochemical data for other types of reactions! So, some investment must be made to form a "basis set" of thermochemical combustion data, but that data ultimately produces savings when we want to predict the outcome of other reactions that aren't necessarily related to burning organic compounds.

**6.2.3 Standard state.** The approach outlined above for tabulating thermochemical data from a basis set of combustion reactions for all known chemical substances is a good idea and it can work, except for the fact that not all chemicals react with oxygen, i.e. they don't combust. And for those that do, we need to know the thermochemistry of combustion at exactly 1 bar and 298.15K (standard pressure and temperature). As burning things tends to generate a lot of heat and pressure, there is a bit of a problem here.

To summarize, the idea of tabulating data using a basis set of a particular reaction type is good, but we just have to pick something other than combustion. In this regard there is one reaction that all chemicals must participate in, *which is their own formation*. For example, dimethyl ether can be created from carbon, oxygen, and hydrogen because it is composed of those elements. Ditto for ethanol; and note that the carbon would likely be in the form of graphite since graphite is the most thermodynamically stable form of carbon. Likewise, oxygen and hydrogen are naturally found as gases. Here are examples of such data for dimethyl ether:

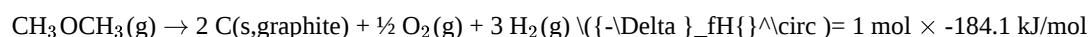


and for ethanol:

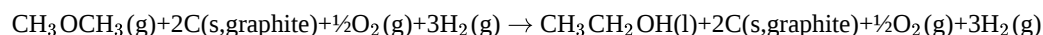


Here we see some new symbols and units for these formation energies. For one, these data are per molar quantities since they are defined by the formation of one mole of dimethyl ether and ethanol. This is why you see the symbol " $H_m^\circ$ " as opposed to " $H^\circ$ " from the previous examples. We also use a subscript "f" for "formation" as opposed to "r" for "reaction". As previously, the  $^\circ$  means standard temperature and pressure.

The enthalpy difference between dimethyl ether and ethanol can be determined by reversing the dimethyl ether reaction and adding it to the formation reaction of ethanol:



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After removing the redundant species that appear on both sides of the equation:



There! We calculated the enthalpy difference between ethanol and dimethyl ether by subtraction of their enthalpies of formation, albeit after some manipulation. We had to multiply the enthalpies of formation by the corresponding number of moles, which is because enthalpy is energy and energy is extensive. There is a slight difference with the result above (-93.6 kJ) from that calculated

using combustion data (-93.4 kJ) in our previous example. This is common, and results from experimental errors, the source of your data, and rounding errors. Table 6.1 has more thermodynamic data that we will be using to work more examples below; more extensive thermodynamic tables can be found in a CRC or on-line.

Material	$S_m^\circ$ (J/K/mol)	$\Delta_f G_m^\circ$ (kJ/mol)	$\Delta_f H_m^\circ$ (kJ/mol)	$C_{P,m}^\circ$ (J/K/mol)
C (s,graphite)	5.74	0.0	0.0	8.64
CO(g)	197.674	-137.168	-110.525	29.14
CO <sub>2</sub> (g)	213.74	-394.359	-393.509	37.1
CH <sub>4</sub> (g)	186.264	-50.72	-74.81	35.31
CH <sub>3</sub> CHO(g)	250.3	-128.9	-199.2	57.3
CH <sub>3</sub> OCH <sub>3</sub> (g)	342.2	-135.2	-184.1	65.57
CH <sub>3</sub> CH <sub>2</sub> OH(l)	160.7	-174.78	-277.69	112.3
H <sub>2</sub> O(g)	188.825	-228.572	-241.818	33.58
H <sub>2</sub> O(l)	69.91	-237.129	-285.83	75.28
H <sub>2</sub> (g)	130.684	0.0	0.0	28.64
N <sub>2</sub> (g)	191.61	0.0	0.0	29.1
NH <sub>3</sub> (g)	192.5	-16.45	-46.11	35.06
(NH <sub>2</sub> ) <sub>2</sub> CO(s)	104.3	-197.4	-333.1	92.8
O <sub>2</sub> (g)	205.138	0.0	0.0	29.41

There are some important data points to note in Table 6.1, such as the fact that the Gibbs energy and enthalpy of C(s,graphite), O<sub>2</sub>(g), and H<sub>2</sub>(g) are 0.0 kJ/mol. This is because no energy is required to form these species starting from themselves, as these are elements in their standard states. Some elements can be found in different forms, called allotropes, and all but the ground state must have non-zero formation energies. For example, diamond is made of pure carbon, but it is not the ground state and requires  $\Delta_f H_m^\circ = 1.86$  kJ/mol to be formed from graphite. Of course, everything including elements in their standard states still have finite values of entropy and heat capacity because these are absolute quantities and are not relative to their formation. Recall we demonstrated this when we calculated the entropy of N<sub>2</sub> gas at the standard state at the beginning of this chapter. In the next section we will demonstrate how to use the data in Table 6.1 starting with the calculation of the thermochemistry of combustion of dimethyl ether.

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