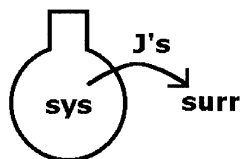


Chapter 19

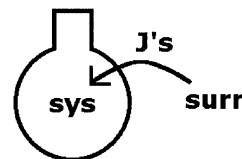
ENERGY, Part 2

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The last Chapter introduced many of the essentials for our discussion of energy and its role in your world. Our emphasis as we continue will be with enthalpy. Remember the exo/endo picture from last Chapter, which I repeat here since it provides a very useful summary.



exothermic (J's exit system)
system gives J's to surroundings
enthalpy of the system decreases
 $H_{\text{final}} < H_{\text{initial}}$
 ΔH is negative



endothermic (J's into system)
system gets J's from surroundings
enthalpy of the system increases
 $H_{\text{final}} > H_{\text{initial}}$
 ΔH is positive

We will now dive into more details on enthalpy in chemical applications.

19.1 Four important aspects: one you knew and three are new.

Here are four important aspects related to ΔH and reactions. I already talked about the first in the last Chapter. I'm saying it again because it's so important.

- IMPORTANT ASPECT 1. ΔH is a transfer amount of some J's.

ΔH is an overall, net difference between final and initial conditions. It does not matter how the process occurs. It does not matter if you do it in one step or in 43 steps. It is how many J's you end up with minus how many J's you began with. That's it.

- IMPORTANT ASPECT 2. When a process is reversed, ΔH takes the opposite sign.

This is simple economics again. You go to the mall. You buy a new lab coat for \$58. The transaction is -\$58 with regards to your assets. You find out later that it's the wrong shade of paisley and you return it for the original amount. This return transaction is +\$58. Overall, when a process is reversed, the transaction amount is the same number of dollars but opposite sign. We also say "negated": when a process is reversed, the sign for the transaction amount is negated, meaning it takes the negative of what it had before. Let's bring back our vaporization example from the last Chapter.



The reverse of vaporization is condensation, which is when the gas phase condenses to a liquid phase. We could write this as



In reversing vaporization, we negate its ΔH to get the ΔH for condensation. Notice that condensation is exothermic while vaporization is endothermic. Even this is conservation of energy: if you pay 44.00 kJ to evaporate one mole of water, then you get that back when you condense that mole back to liquid.

- IMPORTANT ASPECT 3. Quantities for ΔH apply for the reaction as written.

Look again at condensation.



If you condense one mole, the transaction amount is -44.00 kJ. If you condense two moles, the amount is -88.00 kJ. This will lead to stoichiometric calculations for energy, which we'll come back to later.

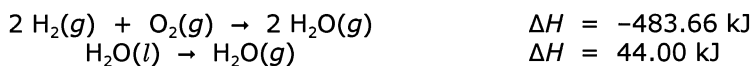
- IMPORTANT ASPECT 4. Reactions are additive; ΔH 's are additive.

You remember the additivity of reactions from Section 6.4, don't you? We talked about multi-step operations and adding up chemical equations to get an overall equation.

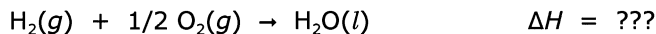
“ The additivity of reactions is a natural consequence of the conservation of matter, the conservation of mass, the conservation of atoms. All atoms are conserved, regardless of the

number of steps. While additivity is introduced here with respect to conservation of matter, it also has a role in the conservation of energy. We'll see that relationship later in Chapter 19. ”

Later is now. The same additivity applies for ΔH . The nice thing about this is that it lets us calculate a ΔH for some reaction using values from other reactions. Let me show you with a simple example. We have been talking since the last Chapter about the combustion of H_2 and the vaporization of H_2O .



Now let's say we want to know the ΔH for the following reaction.

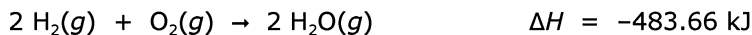


You can derive this value from the prior two equations. First, a point of order here: I have a fractional coefficient in the last equation, which we've been avoiding ever since Chapter 6. Back then, if you recall, I slipped in this little twist.

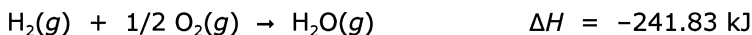
“ Ironically, there are certain definitions of equations which require fractional coefficients, but we won't need these until Chapter 19. ”

Well, here we are in Chapter 19, and we shall indeed see types of equations which require fractional coefficients. So, we'll leave the one-half on O_2 and keep it as the combustion of one mole of H_2 . Here's something else of note: some of you may have thought that this new equation is just one-half of the combustion reaction which we already did. No, it's not. The product is now liquid phase water, not gas phase. Does it matter? You bet it does.

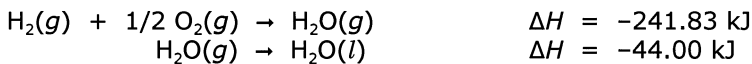
How do we get the ΔH for this new equation? We construct this equation as the sum of the other two for which we already have ΔH 's. First, take the original combustion (which gave gas phase product).



Take one-half of that.

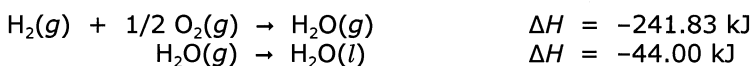


Did you notice the one-half of ΔH also? That's Important Aspect 3 above. Now, take this equation and add it to condensation (reverse of vaporization).

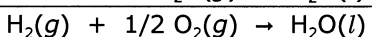


Sum: $H_2(g) + 1/2 O_2(g) + H_2O(g) \rightarrow H_2O(g) + H_2O(l)$

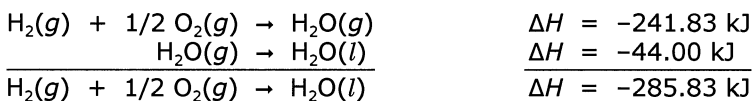
As always, cancel where able, but watch those phases! The $H_2O(g)$ on each side drops out. (Go ahead, scratch them out.) The $H_2O(l)$ stays.



Our final equation is:

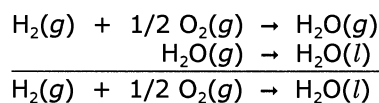


Now, add the J's.



That's it. The combustion to liquid phase water releases more J's overall because you're not paying for gas phase. Remember, gas phases cost more than liquid phases because gas phase packs more energy.

I hope you can see how these things add up. The primary trick is to get them to add in such a way that their sum is the equation you want. We first saw this back in Section 6.4 and it applies here again. Sometimes you need to reverse an equation, just like we did to get condensation from vaporization. Sometimes you need to multiply an equation, just like we did to get the combustion for only one mole of H_2 . Once you get the equations to add, then their ΔH 's also will add. By the way, this practice frequently goes by the historical name of Hess's law but, in modern parlance, it's just another consequence of the conservation of mass/energy. Let me show this connection. The additivity of chemical equations from Chapter 6 represents the conservation of mass, represented by the summation as shown.



By conservation of mass/energy, then the energies must also be conserved through the same summation.

$$\begin{array}{r}
 \Delta H = -241.83 \text{ kJ} \\
 \Delta H = -44.00 \text{ kJ} \\
 \hline
 \Delta H = -285.83 \text{ kJ}
 \end{array}$$

You can't escape these fundamental conservation laws. There are no joule thieves in Nature.

19.2 How good are your standards?

Now we get even more picky.

As mentioned in the prior Chapter, numerous factors define the state of a system and, taken together, these factors determine the value for the enthalpy, H , of that state. We saw that temperature can have a sizeable effect as reflected by heat capacity. Pressure can also have an effect, especially for those systems which deal with gases. For example, the enthalpy of one mole of H_2 at one atm is different from the enthalpy of one mole of H_2 at two atm. Even solutes can be affected: for example, the enthalpy of one mole of $\text{NaCl}(aq)$ differs depending on its concentration. Thus, when we want to measure ΔH of some reaction, we must take these various conditions into account.

To get around these problems, they've adopted a set of conditions which are considered "standard" and which are called "standard conditions". For an experiment run under standard conditions, the system starts at standard conditions and it ends at standard. Don't forget: the middle doesn't matter. Start at standard and end at standard. That's what counts. Let's get into these standards at this time.

The standard for pressure for many years was one atm. They changed it a ways back. The current, thermodynamic standard pressure is one bar where bar relates to barometric. A bar is another pressure unit: one bar is 0.987 atm. To be honest here, this change has not entirely caught on and, besides, the effect on actual energies is so small that most texts and instructors at this level pretty much stay with one atm. You might want to check with your instructor and see what s/he wants you to do. As far as I'm concerned, I'll stay away from bars. We'll just use one atm as standard pressure.

For a solute, the standard for concentration is one mole of solute per kg of solvent. For typical systems which use water as solvent, this is approximately the same as molarity so we'll just use molarity here since we're used to that unit. (There's a reason for using kg of solvent. It involves another concentration unit, which we'll get to later in Chapter 42.)

Interestingly, there is no standard temperature specification. The most commonly available thermodynamic data are for 298.15 K (25.00 °C) and this has become a standard by practice, although it is not a standard by definition. Be mindful of this. I will do 25.00 °C for the most part and you can assume that temperature if I just say standard conditions. If I do a different temperature for standard conditions, then I'll say so at that time.

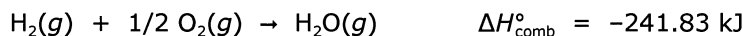
There's a catch here, going back to Chapter 16 with gases: the historical STP for gas studies is one atm and 0 °C. The thermodynamic standard pressure is close to one atm, and that's close enough to STP pressure. The thermodynamic standard for temperature, however, is not defined although it is commonly assumed to be 25 °C. This disagrees with the standard temperature of 0 °C for an STP gas. So, we're stuck with different standards. It's just something you have to remember.

Another term is "standard state" which refers to the overall sample. The standard state for an element or compound is simply its pure form at standard conditions. The standard state for a solute is simply its dissolved form in solution at standard conditions.

Finally, enthalpy. Actually, the important aspect is the enthalpy change. The "standard enthalpy of reaction" is the change in enthalpy (ΔH) for any reaction or process which begins at standard conditions and ends at standard conditions. This also goes by the name, "standard heat of reaction". Remember the underlined part. It's important. It can also be confusing. When we say that a reaction was conducted under standard conditions, you must understand that this really means that its final and initial conditions were standard. The middle conditions might be 4,000 atm, but who cares? As long as it goes to one atm at the end, that's all that matters.

For studies at standard conditions, the symbol for ΔH gets "°" added to it: the full symbol is now ΔH° . This is pronounced "delta-H-zero" or "delta-H-naught". All values for prior ΔH 's were actually ΔH° 's.

Subscripts can also be employed, such as $\Delta H_{\text{rxn}}^\circ$. Specific reactions can be indicated: for example, $\Delta H_{\text{comb}}^\circ$ is the standard enthalpy of combustion for one mole of compound. Since it's defined for one mole of compound, this can lead to cases where fractional coefficients are required. I warned you of this above when we did the combustion of one mol of H_2 .



Earlier, we also dealt with other examples of defined reactions including vaporization and condensation; these lead to the standard enthalpy of vaporization and the standard enthalpy of condensation. These are also defined for one mole of the stated reactant.

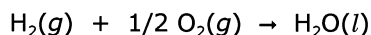


There are yet others. Your instructor may give additional types.

I need to introduce a new type of reaction which is of primary importance in thermodynamic applications. It's called a formation reaction. For any particular substance, its formation reaction is defined as that reaction which produces one mole of that substance from its elements. I'll show you this in a moment, but there's a hitch for some elements and that hitch is allotropes. We first introduced allotropes way back in Section 2.6; I mentioned O_2 and O_3 as the common allotropes of oxygen at that time, along with a couple of other examples for other elements. If you forget, go back and look. The hitch for now is that different allotropes will have different H 's; that's no good when we're trying to establish one overall standard value. The way to get around this is to assign one allotrope as the reference form for each element. They made these assignments based on the most stable allotrope and/or a commonly available allotrope at standard pressure and 25 °C. The reference form for oxygen is $\text{O}_2(g)$ and not $\text{O}_3(g)$. The reference form for carbon is graphite, not diamond. This case of carbon presents a notation problem: both graphite and diamond are networks, so they use their empirical formula, C. Furthermore, both are solid phase (s), so $\text{C}(s)$ can mean either graphite or diamond. Due to this ambiguity, we indicate graphite as $\text{C}(s, \text{graph})$ or just $\text{C}(\text{graph})$, and we indicate diamond as $\text{C}(s, \text{diam})$ or just $\text{C}(\text{diam})$.

You are already familiar with many of the reference forms for many elements. For Group 18, it's just the monatomic gases. Thus, the reference forms are $\text{He}(g)$, $\text{Ne}(g)$, $\text{Ar}(g)$, etc. The common diatomic gases are also reference forms, including $\text{H}_2(g)$, $\text{N}_2(g)$, $\text{O}_2(g)$ and the halogen gases, $\text{F}_2(g)$ and $\text{Cl}_2(g)$. The two other common halogens are liquid and solid diatomics, $\text{Br}_2(l)$ and $\text{I}_2(s)$, in their reference forms. Again, carbon's reference form is $\text{C}(\text{graph})$. Metals are typically indicated simply by their solid phase, such as $\text{Fe}(s)$ and $\text{Co}(s)$. Although some of the solid metals have two or more solid forms, I'm not going to worry about those; we'll stick with just (s) for metals. Mercury is an oddball, however, since it's a liquid at 25 °C; its reference form is $\text{Hg}(l)$.

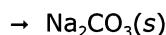
OK, let's get back to the idea of the formation reaction; I'll modify the prior definition to incorporate reference forms. For any particular substance, its formation reaction is defined as that reaction which produces one mole of that substance and which starts from the reference forms of its elements. When you write a "formation equation" for a substance, one mole of that substance will be the only item on the right side of the equation; the reference elements will be on the left side in whatever numbers are required for balance. Here's a simple example, the formation equation for $\text{H}_2\text{O}(l)$.



Notice that only one mole can be given on the right, by the definition for a formation equation. This requires that a fractional coefficient be used on the left for O_2 in order to achieve balance.

Now, let's work through a fresh example: write the formation equation for sodium carbonate(s).

► Start with one mole of that substance on the right side of the equation.



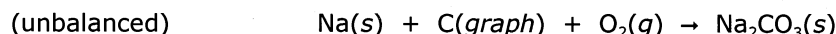
► What elements are present in the substance?

►► Sodium, carbon and oxygen

► What are the reference forms for these elements?

►► $\text{Na}(s)$, $\text{C}(\text{graph})$ and $\text{O}_2(g)$

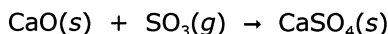
► Enter these on the left of the equation.



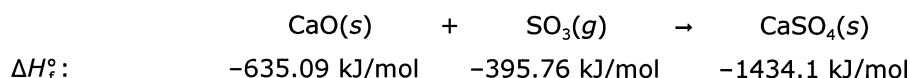
19.3 We are finally getting to where we want to be.

The entire reason that I have brought you here is to show you how to determine $\Delta H_{\text{rxn}}^{\circ}$ for any reaction whatsoever. Not just formation, not just combustion. Anything. The keys to doing this are formation enthalpies and the conservation of mass/energy as contained within the additivity of reactions. The derivation of this can be tedious and I won't cover it here. It's really the end result which is important and thither I thus lead.

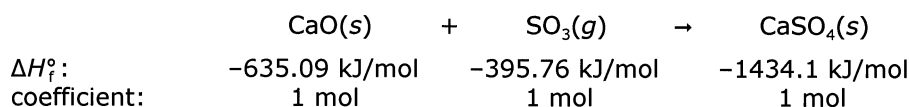
Any enthalpy of any reaction can be calculated merely using the ΔH_f° 's of every reactant and product in the balanced equation. The manner by which this is done is to multiply each ΔH_f° of each item by its coefficient in the balanced equation. You then add up the amounts for all products and subtract the amounts for all reactants. That gives you your $\Delta H_{\text{rxn}}^{\circ}$ and it works for any reaction whatsoever. This is complicated to explain but it's easier to illustrate. Let's get an example started. Calculate the standard enthalpy for the following reaction.



Very first thing to do: look up the values of ΔH_f° for each reactant and product. Here're the values from Appendix A.



You multiply each ΔH_f° by the coefficient from the balanced equation. That's easy here, since everything is one mole.



The results from each multiplication are added for all products and subtracted for all reactants. This sets up as follows.

$$\Delta H_{\text{rxn}}^{\circ} = \overbrace{+ 1 \text{ mol CaSO}_4 \times \frac{-1434.1 \text{ kJ}}{\text{mol CaSO}_4}}^{\text{Add for product(s)}} - \overbrace{1 \text{ mol CaO} \times \frac{-635.09 \text{ kJ}}{\text{mol CaO}} - 1 \text{ mol SO}_3 \times \frac{-395.76 \text{ kJ}}{\text{mol SO}_3}}^{\text{Subtract for reactants}}$$

Notice that all mole terms drop out. This will always be true, so we can write it more simply as

$$\Delta H_{\text{rxn}}^{\circ} = 1(-1434.1 \text{ kJ}) - 1(-635.09 \text{ kJ}) - 1(-395.76 \text{ kJ}) = -403.2 \text{ kJ}$$

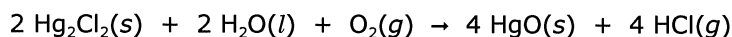
That's the standard enthalpy for the given reaction, -403.2 kJ. Notice that it's negative, so this is exothermic. That means if you run the reaction beginning at standard conditions and ending at standard conditions, the reaction would release 403.2 kJ to the surroundings.

Once again: you add for all products and you subtract for all reactants. We can tidily summarize this as "products minus reactants" but remember to bring in the coefficients, too.

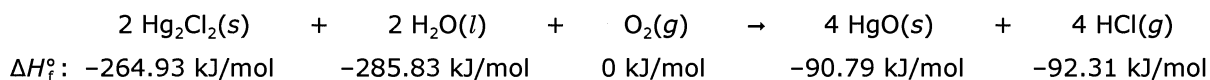
We have a sigfig technicality to report. We are executing multiplication by exact numbers followed by addition/subtraction. There is some parallel with determination of a molar mass, so I will invoke the same sigfig policy: use the +/- rule and round off according to the entry (ΔH_f°) with the fewest decimals. For the above example, two values of ΔH_f° had two decimals but one had only one decimal; thus, the answer rounded to one decimal. Once again, different instructors handle this differently, so check with yours.

That was an easy sampler. Let's do one that's not so easy.

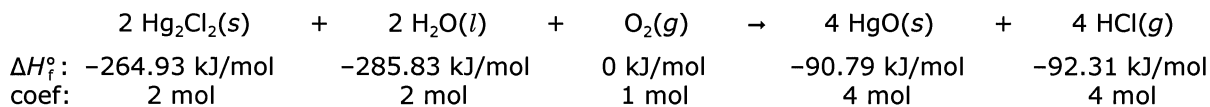
Example 1. Find ΔH° for the following reaction.



First, we look up the ΔH_f° for each item in the equation.



Notice that O_2 is a big zero. It's a standard element reference form, so it's exactly zero and it will not enter into a sigfig round-off decision. If you spot the standard reference forms right away, you know you don't have to look up the ΔH_f° because it's zero. Now, multiply each entry above by its coefficient in the balanced equation.



Don't forget: mole terms drop. Proceed to products minus reactants.

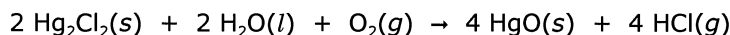
$$\begin{array}{ccccccc}
 & \text{products} & & \text{minus} & & \text{reactants} & \\
 & \text{HgO} & & \text{HCl} & & \text{Hg}_2\text{Cl}_2 & & \text{H}_2\text{O} & & \text{O}_2 \\
 \Delta H_{\text{rxn}}^\circ = & 4(-90.79 \text{ kJ}) & + & 4(-92.31 \text{ kJ}) & - & 2(-264.93 \text{ kJ}) & - & 2(-285.83 \text{ kJ}) & - & 1(0 \text{ kJ})
 \end{array}$$

Plug it in, punch it out, round it off. You get 369.12 kJ. That's positive. That's endothermic. That's what it costs to do that reaction for the amounts given in the balanced equation.

A word of caution. One of the most common ways to screw up these calculations is to mess up the signs. Sometimes you're adding positive kJ's, sometimes you're subtracting negative kJ's, sometimes you're subtracting positive kJ's and sometimes you're adding negative kJ's. Be careful.

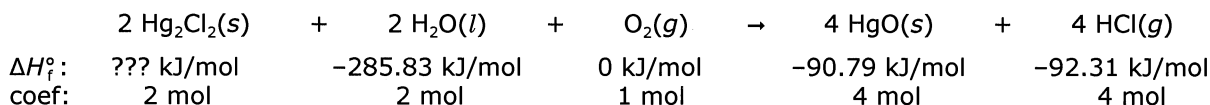
A variation on this method is to calculate a ΔH_f° for some compound from a given $\Delta H_{\text{rxn}}^\circ$. Here's an Example, using the same reaction as above so you can compare the two ways.

Example 2. You want to determine the heat of formation of mercury(I) chloride. (Pretend you don't know it from the above Example 1 or from Appendix A.) Instead, you do have $\Delta H_{\text{rxn}}^\circ = 369.12 \text{ kJ}$ for the following.



You also have the heats of formation of all other reactants and products. From this, calculate ΔH_f° for Hg_2Cl_2 .

Set up your equation and line up the ΔH_f° 's which you are given, along with their coefficients.



Set up everybody, inserting the given value for $\Delta H_{\text{rxn}}^\circ$, 369.12 kJ.

$$\begin{array}{ccccccc}
 & \text{products} & & \text{minus} & & \text{reactants} & \\
 & \text{HgO} & & \text{HCl} & & \text{Hg}_2\text{Cl}_2 & & \text{H}_2\text{O} & & \text{O}_2 \\
 \Delta H_{\text{rxn}}^\circ = & 369.12 \text{ kJ} = & 4(-90.79 \text{ kJ}) & + & 4(-92.31 \text{ kJ}) & - & 2(??? \text{ kJ}) & - & 2(-285.83 \text{ kJ}) & - & 1(0 \text{ kJ})
 \end{array}$$

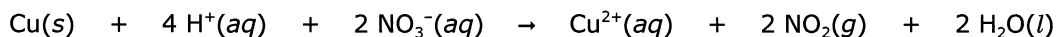
Then, you re-arrange and solve for ???. Go ahead and punch this out. Be sure you get -264.93. If you didn't, check your signs, although some people do forget one or more of the coefficient multipliers.

Your turn. You can do a net ionic equation. We'll retrieve the reaction of copper metal and nitric acid from Chapter 14.

Example 3. Find ΔH° for the following reaction.



You'll need some values for ΔH_f° and you'll need some coefficients. You can leave out the mol units.



ΔH_f° (kJ only): _____ kJ _____ kJ _____ kJ _____ kJ

coef: _____

Why are we not bothering with $\text{Cu}(s)$ and $\text{H}^+(aq)$?

Plug in what you need to plug in.

$$\Delta H_{\text{rxn}}^\circ =$$

Did you get -850.7 kJ? I hope not, because it's the wrong answer. It's from messing up a sign. The real answer is -30.7 kJ. If you got this, then good. If not, then you may have messed up another sign or a coefficient. Do it again.

These types of problems are fairly routine. Be sure you can do them. Calculations which use products minus reactants are among the most important type of thermodynamic problem at this level. These same steps will apply to other things, too, including entropy and free energy. We'll see this beginning in Chapter 44. For now, we stick with enthalpy. Practice. Practice. Practice.

19.4 Stoichiometry

Back in Important Aspect 3, I mentioned that you can do stoichiometry with kJ's. Let's continue with the mercury(I) chloride reaction from above as an example. $\Delta H_{\text{rxn}}^\circ$ is 369.12 kJ and that's what the surroundings must pay for the reaction to occur in the amounts given by the equation. The equation is written for 2 mol Hg_2Cl_2 . What if you don't want to do 2 mol Hg_2Cl_2 ? What if you want to do some other amount like 183.6 g Hg_2Cl_2 ? How many kJ's must be paid for that? That's where stoichiometry comes in.

$\Delta H_{\text{rxn}}^\circ$ now provides a new type of rxn ratio for use in stoichiometry. Recall that the rxn ratio was the link between different items in the chemical equation. Now, ΔH° is an item. As a rxn ratio, it can be used in a conversion factor and it can be used right-side up or upside-down. For example, the rxn ratio for kJ and mol Hg_2Cl_2 is the following.

$$\frac{369.12 \text{ kJ}}{2 \text{ mol Hg}_2\text{Cl}_2} \quad \text{OR} \quad \frac{2 \text{ mol Hg}_2\text{Cl}_2}{369.12 \text{ kJ}}$$

This can be done for any member of the balanced equation. Here's the rxn ratio for kJ and HCl.

$$\frac{369.12 \text{ kJ}}{4 \text{ mol HCl}} \quad \text{OR} \quad \frac{4 \text{ mol HCl}}{369.12 \text{ kJ}}$$

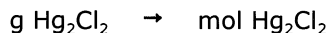
These kinds of rxn ratios can enter into a stoichiometry calculation. Just remember: the ΔH° of an equation is for the equation as written and it relates to the coefficients as written.

Let's return to the question: how many kJ's must be paid for the reaction of 183.6 g Hg_2Cl_2 ?

This still follows the typical stoichiometry procedure but frequently we get away with one less Step.

Step 1. Balanced equation is given.

Step 2. Convert g Hg_2Cl_2 to mol, using molar mass.



Step 3. Convert mol Hg_2Cl_2 to kJ, using the rxn ratio.



Step 4. There is no Step 4: the rxn ratio already took us to kJ, which is the final requested unit.

Go ahead, do the string.

$$\begin{array}{ccccccc} \text{g Hg}_2\text{Cl}_2 & \rightarrow & \text{mol Hg}_2\text{Cl}_2 & \rightarrow & \text{kJ} & & \\ 183.6 \text{ g Hg}_2\text{Cl}_2 & \times & \frac{\text{mol Hg}_2\text{Cl}_2}{472.1 \text{ g Hg}_2\text{Cl}_2} & \times & \frac{369.12 \text{ kJ}}{2 \text{ mol Hg}_2\text{Cl}_2} & = & 71.78 \text{ kJ} \end{array}$$

That means 71.78 kJ must be paid in order to react the desired amount of Hg_2Cl_2 .

Let's do a combustion example. I'm getting tired of blowing up hydrogen. Let's do something else. Think food. Think grilling. Think about getting ready and then finding out that your gas tank is empty. Time for LPG. That's liquified petroleum gas. It's used in all sorts of things, not just grills. Some vehicles use it instead of gasoline. Some tractors, trucks, buses, fork lifts, zambonis and even some cars. LPG is primarily propane, C_3H_8 . It's a gas at normal pressure but, at high pressure, some will condense to a liquid. If you pick up a gas tank and jiggle it, you can feel the liquid inside sloshing around but, when it's attached to the grill and you open the burners, the stuff that comes out is all of a sudden back to normal pressure and you get gas phase. That's vaporization again. At the burners, the propane gas burns in air. That's combustion and that's the part we want for now. Let's consider two questions.

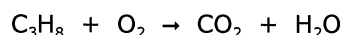
Example 4. What is the standard enthalpy of combustion for propane gas? How many kJ's can you get from the combustion of 1.000 g propane at standard conditions?

OK, where do you want to start? You should start by thinking about what you have, where you're going and what you need to get there. There are several parts here. Break them down.

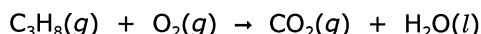
- The standard enthalpy of combustion is defined for the combustion of one mole of the compound. The first thing we need is a balanced combustion equation, written for one mole of propane.
- Once we have that, we can do products minus reactants with ΔH_f° 's to get ΔH_{rxn}° . Since our reaction is combustion, then ΔH_{rxn}° is ΔH_{comb}° . That gives us the answer for the first question.
- We get the answer for the second question by doing a stoichiometry calculation with ΔH_{comb}° .

Now, let's start.

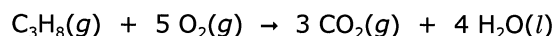
We need the balanced equation for the combustion of C_3H_8 . Don't forget the stuff you knew in Chapter 6 about combustion reactions. The other reactant is O_2 . The products are CO_2 and H_2O .



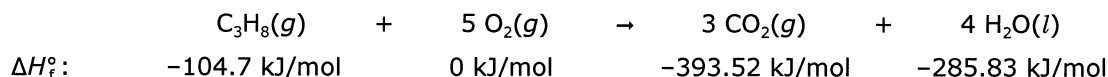
Now you need to include phases. You were told to use propane gas. O_2 and CO_2 are gases. Water is the only ambiguity, since we can set it up for gas phase water or liquid phase water. Some instructors will specify that you should use only one or the other, so heed if you need. I'll use liquid phase in this example.



Balance.



This is our equation for the combustion of one mole of propane. Now, we need ΔH_{comb}° . For this part, we set up the routine for products minus reactants. We need the ΔH_f° 's for everyone involved.



We can leave out the zero for O_2 . Get your other coefficients and set up for products minus reactants.

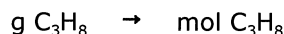
$$\Delta H_{comb}^\circ = \text{_____} (\text{_____ kJ}) + \text{_____} (\text{_____ kJ}) - \text{_____} (\text{_____ kJ})$$

Punch it out, round it off: you get $\Delta H_{comb}^\circ = -2,219.2$ kJ, which is a lot of J's. That's the first part of the problem.

The second part is the stoichiometry: we want the number of kJ's for 1.000 g C_3H_8 . Notice that the reaction as written involves $-2,219.2$ kJ and one mol C_3H_8 ; these will make up the rxn ratio.

$$\frac{-2,219.2 \text{ kJ}}{\text{mol } C_3H_8} \quad \text{OR} \quad \frac{\text{mol } C_3H_8}{-2,219.2 \text{ kJ}}$$

Start: convert g C_3H_8 to mol, using molar mass.



Convert mol C_3H_8 to kJ, using the rxn ratio. This leaves you with the requested unit of kJ.



Put it all together.

$$\begin{array}{ccccccc}
 \text{g C}_3\text{H}_8 & \rightarrow & \text{mol C}_3\text{H}_8 & \rightarrow & \text{kJ} & & \\
 1.000 \text{ g C}_3\text{H}_8 & \times & \frac{\text{mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} & \times & \frac{-2,219.2 \text{ kJ}}{\text{mol C}_3\text{H}_8} & = & -50.33 \text{ kJ}
 \end{array}$$

This result says that 50.33 kJ will be released from the combustion of 1.000 g propane. Notice that signs are preserved in stoichiometry. The enthalpy change is still negative and the heat is being released to the surroundings. So don't stand too close, please.

Too much talk about grilling. Now I'm hungry.

19.5 Calories from the Sun

I hope this has whetted your appetite. It's time to serve up some Calories.

Propane is just one of many fuels which we use to power our lifestyles, but the fuels which we use to power our lifestyles are not the fuels which we use to power our bodies. Nature developed that differently.

The majority of what you eat and what you can digest is water and fuel; after that, toss in some nutrients for good measure. The fuel is combusted and this provides the bulk of your energy needs throughout your life. The fuel needs an oxidant and that is why you breathe. Water has no energy value (no Calories) because it combusts no further, but it's a major part of the mass of all biological tissue including foods. Thus, you take in a lot of water in what you eat, in addition to what you drink. Furthermore, you make more water chemically as you combust your fuels. Since much of your body is water, proper water balance is essential and you need a constant source just to replenish losses. On the other hand, just like any other engine, the human engine has waste products. CO₂ is exhaled. H₂O is ultimately respired, transpired, sweated, and passed in urine. Undigestibles and some other things are excreted.

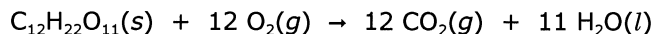
All of this constitutes the primary explanation for why you eat, drink and breathe. It's alimentary, dear Watson. Nature genetically programmed humans with an appetite for combustible fuels in order to power their bodies to breathe, to pump blood, to digest, to work, to contemplate, to recreate and to procreate. And, of course, to seek out chocolate.

The principal fuels for humans are classified as fats, carbohydrates (carbos) and proteins. Some fats, carbos and proteins have structural roles also but the net utilization on a typical day would be for fuel. The reactions are combustion using O₂. The Calories came from the Sun, courtesy of plants to whom all animals on Earth owe their existence. There are no flames. Nature designed the combustion to go through a bunch of steps, releasing small amounts of energy at a time. Because of the additivity of reactions (conservation of mass/energy), we can just add up all the steps and get one big overall equation. Another way you can think of this is that all of the little steps are the middle parts and the only things that matter are initial states (fats, carbos, proteins and O₂) and final states (combustion products). Again, the middle doesn't matter, and it's the same number of kJ's regardless. There is one technicality here and that is that human body temperature is 37 °C, but I'll continue to use 25 °C as we've been doing. The numbers aren't very different between the two temperatures.

So let's combust some fuels. I'll illustrate this for several carbos and a fat.

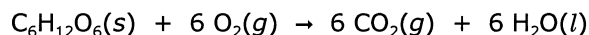
Carbohydrates include the simple and complex sugars. Another name is saccharides, and these can take a numerical prefix depending on how many "sugar units" are bonded within the molecule. The simplest are monosaccharides which are composed of one sugar unit; for example, we mentioned two monosaccharides, fructose (fruit sugar) and glucose (blood sugar), in Section 3.2 as isomers with the formula C₆H₁₂O₆. Disaccharides are composed of two sugar units within their molecules, and examples include sucrose (cane or table sugar) and lactose (milk sugar), which are isomers of the formula C₁₂H₂₂O₁₁. Polysaccharides can involve many sugar units; examples include starch and cellulose.

The combustion reaction for sucrose is the following.



For this, $\Delta H_{\text{comb}}^\circ = -5,640$ kJ. The combustion equation for lactose is the same equation since lactose and sucrose are isomers, but $\Delta H_{\text{comb}}^\circ$ is different because it's a different compound. Although different, they're still close: $\Delta H_{\text{comb}}^\circ$ for lactose is $-5,630$ kJ.

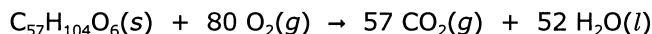
The combustion reaction for fructose and glucose is



The $\Delta H_{\text{comb}}^\circ$ is $-2,810$. kJ for fructose and $-2,803$ kJ for glucose.

One thing to note with these examples is that the combustion enthalpies can be large. Sugars can be large molecules, which means that they can pack more energy. Just look at how the disaccharides have roughly twice the enthalpy of combustion of a monosaccharide.

Let's do a fat. The term "fats" can refer to many different compounds but I'll just do one for illustration: $\text{C}_{57}\text{H}_{104}\text{O}_6$. Fats are big molecules.



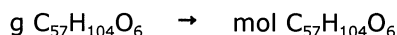
Those big molecules have a lot to burn and their combustion packs a wallop; for $\text{C}_{57}\text{H}_{104}\text{O}_6$, $\Delta H_{\text{comb}}^\circ = -34,900$ kJ.

Taken together, combustions of carbos, fats and proteins provide the majority of your energy. They also provide you with energy storage, especially in the form of stored fats. Nature designed animals to store fats in times of plenty so that they can survive in times of not-so-plenty. For humans, these aspects get into nutritional areas related to losing fat, and this is part of the thermodynamics of nutrition. Let's say you want to burn off one pound of fat: how many Calories must you burn? Well, that's just another combustion problem with stoichiometry. Let's do an Example.

Example 5. Using $\text{C}_{57}\text{H}_{104}\text{O}_6$ as a sample fat, how many Cal are involved in the combustion of one pound (453.6 g) of that fat?

We have the balanced equation and $\Delta H_{\text{comb}}^\circ$ above. Together, these give us the rxn ratio: $-34,900$ kJ per mol of $\text{C}_{57}\text{H}_{104}\text{O}_6$. The only thing different here is that we want Cal in the end, not kJ. I mentioned that conversion in the last Chapter: it's one Cal = 4.184 kJ.

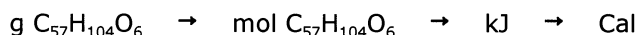
Convert g $\text{C}_{57}\text{H}_{104}\text{O}_6$ to mol, using molar mass.



Convert mol $\text{C}_{57}\text{H}_{104}\text{O}_6$ to kJ, using the rxn ratio.



Convert kJ to Cal.



Put it all together.

$$453.6 \text{ g C}_{57}\text{H}_{104}\text{O}_6 \times \frac{\text{mol C}_{57}\text{H}_{104}\text{O}_6}{885.40 \text{ g C}_{57}\text{H}_{104}\text{O}_6} \times \frac{-34,900 \text{ kJ}}{\text{mol C}_{57}\text{H}_{104}\text{O}_6} \times \frac{\text{Cal}}{4.184 \text{ kJ}} = -4,270 \text{ Cal}$$

This says that the combustion of that pound of fat involves the release of 4,270 Cal of energy. Since that fat is part of your system, YOU must release 4,270 Cal as heat and/or work as you combust that pound of fat to CO_2 and H_2O . So get going. How? If you're into walking, you would typically burn that many Calories in 13 - 16 hours of walking. Running? Only 5 - 7 hours. But that's misleading, too, since human exercise is not that simple. You burn mostly carbos during exercise; it's only partly fat. There's another technicality here which is on your side: the 4,270 Cal is for a pound of fat only. Body weight is not straight fat, so nutritionists use a value of $\sim 3,500$ Cal per pound of body weight. Maybe you should run the treadmill as you read this. Just don't pull a George Jetson.

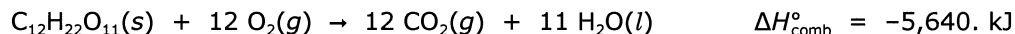
Fats pack a lot of energy per molecule and that's why animals were designed to store fats so readily. It's not just Cal's or kJ's per molecule that Nature is concerned with; it's also Cal's or kJ's per gram. The goal for Nature is simple: store a lot of energy into a compound without making it too heavy to carry around all the time. If it's too heavy, you're wasting more energy just carrying the fuel around before you get to use it for breathing or whatever. This is not just Nature, either. Humans have picked up on this and have taken serious consideration of this energy per mass relationship in vehicle design. This is especially true for air and space travel, where the mass is extremely critical.

Let's look at the thermodynamics involved in the energy-per-mass relationships. It's still combustion, but now we want to know the ratio of stored energy per mass of fuel. The stored energy is

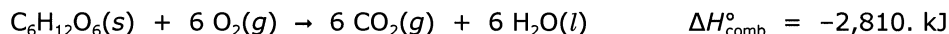
the chemical energy which is the amount released during combustion. The ratio can be expressed as kJ/g or Cal/g. We did a similar example in the prior Section when we calculated the number of kJ's for the combustion of 1.000 g of propane. The enthalpy change was -50.33 kJ for 1.000 g; we can say that the energy released was 50.33 kJ/g or that the available energy is 50.33 kJ/g. I want to work with Cal right now, so we can convert that (via 4.184 kJ per Cal) to 12.03 Cal/g. That's propane's energy-per-mass ratio.

Let's go back to our carbohydrates and do sucrose and fructose as an Example.

Example 6. Calculate the enthalpy change for the combustion of 1.000 g sucrose



and for the combustion of 1.000 g fructose.



I'm just going to the full strings. Compare this to the earlier Examples if you don't follow. Don't forget that we are converting to Cal at the end. OK, sucrose:

$$\begin{array}{ccccccc} \text{g sucrose} & \rightarrow & \text{mol sucrose} & \rightarrow & \text{kJ} & \rightarrow & \text{Cal} \\ 1.000 \text{ g sucrose} & \times & \frac{\text{mol sucrose}}{342.30 \text{ g sucrose}} & \times & \frac{-5,640. \text{ kJ}}{\text{mol sucrose}} & \times & \frac{\text{Cal}}{4.184 \text{ kJ}} = -3.938 \text{ Cal} \end{array}$$

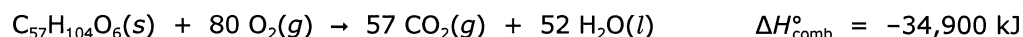
This amount is for 1.000 g, so we can say that sucrose packs 3.938 Cal/g of available energy; that's how much is released upon full combustion. Now let's do the same calculation for 1.000 g fructose.

$$\begin{array}{ccccccc} \text{g fructose} & \rightarrow & \text{mol fructose} & \rightarrow & \text{kJ} & \rightarrow & \text{Cal} \\ 1.000 \text{ g fructose} & \times & \frac{\text{mol fructose}}{180.16 \text{ g fructose}} & \times & \frac{-2,810. \text{ kJ}}{\text{mol fructose}} & \times & \frac{\text{Cal}}{4.184 \text{ kJ}} = -3.728 \text{ Cal} \end{array}$$

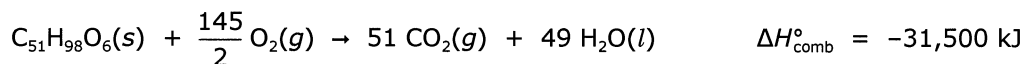
Fructose packs 3.728 Cal/g of available energy, which is close to the value for sucrose above. If you do the same for a bunch of different sugars, they average out to about 4 Cal/g.

Let's do a couple fats.

Example 7. Calculate the change in enthalpy for the combustion of 1.000 g $\text{C}_{57}\text{H}_{104}\text{O}_6$



and for the combustion of 1.000 g $\text{C}_{51}\text{H}_{98}\text{O}_6$.



You can plug everything in.

$$1.000 \text{ g } \text{C}_{57}\text{H}_{104}\text{O}_6 \times \text{_____} \times \text{_____} \times \text{_____} = -9.42 \text{ Cal}$$

This tells us that this fat carries 9.42 Cal/g. Now for $\text{C}_{51}\text{H}_{98}\text{O}_6$.

$$1.000 \text{ g } \text{C}_{51}\text{H}_{98}\text{O}_6 \times \text{_____} \times \text{_____} \times \text{_____} = -9.35 \text{ Cal}$$

The values are close. If you do the same calculation for a bunch of fats, they average out to about 9 Cal/g.

I won't do a specific protein combustion, but these come out to about 4 Cal/g, similar to carbohydrates.

I know that's a bunch of stoichiometry calculations which we went through, but there's a reason. The significance of these was to demonstrate what Nature has been doing for millions of years: providing

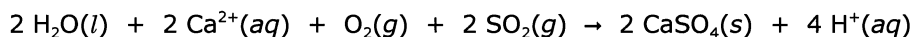
fuel for life. Of the various fuels for humans, fats pack the most stored energy per mass. I also did these for another reason, something you may be familiar with: perhaps you've heard the numbers 9-4-4 in relation to nutrition. They are the general guides for Calorie content per gram of fuel: 9 Cal per gram of fat, 4 Cal per gram of carbo, and 4 Cal per gram of protein. They even appear on some nutritional labeling. Where do the numbers come from? We just derived them. They are combustion values.

If you are what you eat, then you are thermodynamics. Yes, these things are part of your world.

Problems

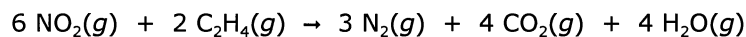
- True or false.
 - ΔH_f° for $\text{H}^+(\text{aq})$ is zero.
 - Diamond is the standard form of the element carbon.
 - The standard enthalpy of formation of $\text{F}_2(\text{g})$ is zero.
 - When you reverse a process, the ΔH takes the opposite sign.
 - The reverse of an exothermic process is endothermic.
 - Humans obtain energy from the combustion of foods.
- List five standard elemental reference forms for elements other than metals.
- Write formation equations for each of the following compounds.
 - $\text{Zn}(\text{NO}_3)_2(\text{s})$
 - $\text{C}_2\text{H}_5\text{I}(\text{l})$
 - $\text{HClO}_3(\text{l})$
 - $\text{BrNO}(\text{l})$
 - $\text{Hg}_2\text{O}(\text{s})$

- The following equation is balanced.



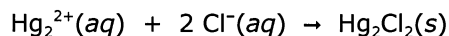
What is the ΔH° (in kJ) for this reaction?

- The following equation is balanced.



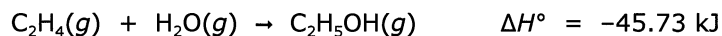
What is the ΔH° (in kJ) for this reaction?

- The net ionic equation for the precipitation of mercury(I) chloride is the following.

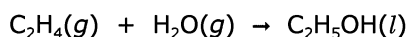


What is the ΔH° (in kJ) for this reaction?

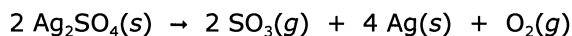
- The reaction of ethylene, C_2H_4 , with water can produce ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, according to the following equation.



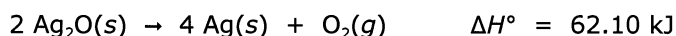
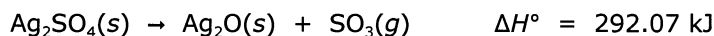
The vaporization of ethyl alcohol, $\Delta H_{\text{vap}}^\circ$, is 42.59 kJ. Use this information to find ΔH° for the following reaction.



- At high temperature, silver sulfate reacts to form elemental Ag metal, SO_3 and O_2 . The overall equation is the following.

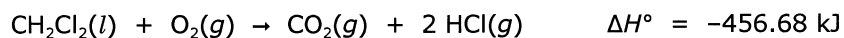


Consider this overall reaction as derived from two Steps, with Ag_2O as an intermediate.



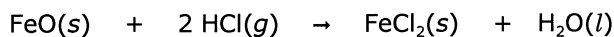
What is ΔH° (in kJ) for the overall equation?

9. The following equation is balanced.



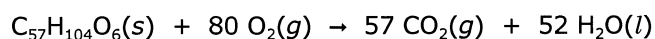
For the reaction which uses 50.0 g CH_2Cl_2 , what is ΔH° (in kJ)?

10. The heat of combustion of sucrose (table sugar), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is $-5,640$. kJ. How many nutritional Calories are involved for one pound (453.6 g) of sucrose?
11. Solid zinc oxide can be prepared by direct combustion of $\text{Zn}(s)$ with $\text{O}_2(g)$. What is the change in enthalpy (in kJ) for this reaction when 16.2 g of zinc are reacted?
12. The following equation is balanced.



What is the change in enthalpy (in kJ) if the reaction is conducted using 64.2 g FeO ?

13. Assume an individual burns 2000. Cal per day. Also assume that 46.0% of this energy (920. Cal) is provided from the combustion of fats. The combustion reaction of a typical fat is shown below.



$$\Delta H^\circ = -34,900 \text{ kJ}$$

When 920. Cal is released according to this equation, how much water (in g) is also produced?