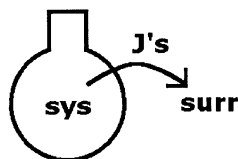


Chapter 19

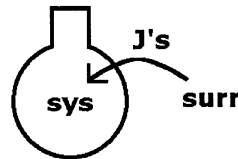
ENERGY, Part 2

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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 in the final state minus how many J's you began with in the initial state. 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 store. 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.

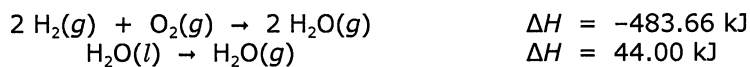
- IMPORTANT ASPECT 4. Reactions are additive; ΔH 's are additive.

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.

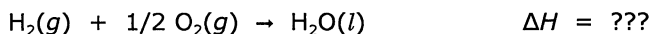
“ The additivity of reactions is a natural consequence of the conservation of matter, the conservation of mass, the conservation of atoms. All atoms are conserved, regardless of the

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.

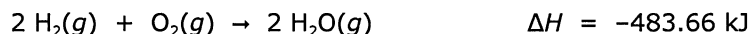


You can derive this value from the prior two equations. First, a point of order here: I have a fractional coefficient in the last equation, which we've been avoiding ever since Chapter 6. Back then, if you recall, I slipped in this little twist.

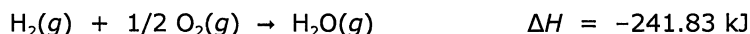
“ Ironically, there are certain definitions of equations which require fractional coefficients, but we won't need these until Chapter 19. ”

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.

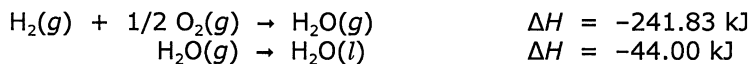
How do we get the ΔH for this new equation? We construct this equation as the sum of the other two for which we already have ΔH 's. First, take the original combustion (which gave gas phase product).



Take one-half of that.

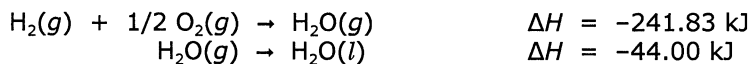


Did you notice the one-half of ΔH also? That's Important Aspect 3 above. Now, take this equation and add it to condensation (reverse of vaporization).



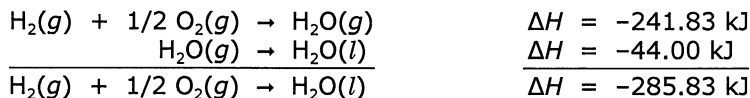
Sum: $H_2(g) + 1/2 O_2(g) + H_2O(g) \rightarrow H_2O(g) + H_2O(l)$

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

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 went by the historical name of Hess's law but, in modern parlance, it's just another consequence of the conservation of mass-energy. 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 $Na^+(aq)$ ions will differ 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 conditions. 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 old, traditional standard for pressure was one atm but they changed that a ways back to one bar. As noted in Chapter 16, one bar and one atm are actually very close, $atm = 1.01325 \text{ bar}$, and the effect on energies is quite small. We will stay away from bars and stick with the traditional standard of one atm.

For a solute, the standard for concentration is one mole of solute per kg of solvent. For dilute solutions with water as solvent, one kg of solvent is close to one L, so standard concentration is acceptably close to one mole of solute per L of solution. That's molarity. As such, we will use one molar as our unit for standard concentration. (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.

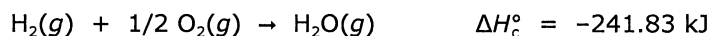
There's a catch here, going back to Chapter 16 with gases: STP uses 0.00 °C for temperature. The thermodynamic standard for temperature is not defined (although it is commonly assumed to be 25.00 °C). Thus, we are stuck with different standards for temperature in these applications. It's just something you have to remember. If it's a ΔH (or related) calculation, then use $T = 25.00 \text{ °C}$; if it's a $PVnRT$ calculation, use $T = 0.00 \text{ °C}$.

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. Caution! Be careful with the part about "dissolved form". If it's a nonelectrolyte, it's the neutral form. If it's a strong electrolyte, it's the fully dissociated form. If it's a weak electrolyte, then it's the undissociated form.

Finally, enthalpy. Actually, the important aspect is the change in enthalpy, ΔH . The "change in standard enthalpy" or the "standard enthalpy change" is the change in enthalpy (ΔH) for any reaction or process which begins at standard conditions and ends at standard conditions. Remember the underlined part. It's important. When we say that a reaction was conducted under standard conditions, you must understand that this really means that its initial and final conditions were standard. The middle conditions might be 500 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 ° tacked onto the end: the symbol is then ΔH° . This is pronounced as "delta-H-zero" or "delta-H-naught". All values for prior ΔH 's, here and in Chapter 18, were actually ΔH° 's.

Subscripts can also be employed for specific reactions or processes. For example, the change in standard enthalpy for the combustion of one mole of compound is given by ΔH_c° . 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 change in standard enthalpy of vaporization and the change in standard enthalpy of condensation. These are also defined for one mole of the stated reactant.



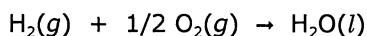
There are yet other standard types of defined equations, and I will bring these in as we need them. Your instructor may give additional types.

Note that I keep saying the "change in standard enthalpy" of a reaction or process. This is often referred to simply as the standard enthalpy of the reaction or process. Keep in mind that a Δ quantity always involves a change of some kind between an initial condition and a final condition.

There is one new type of reaction to introduce now, 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 reference elemental forms. 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 one atm 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 C(s) can mean either graphite or diamond. Due to this ambiguity, we indicate graphite as C(s, *graph*) or just C(*graph*), and we indicate diamond as C(s, *diam*) or just C(*diam*).

You are already familiar with many of the reference elemental forms for many elements. For Group 18, it's just the monatomic gases. Thus, the reference forms are He(*g*), Ne(*g*), Ar(*g*), etc. (except Og, whose phase at standard conditions isn't known yet). 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 C(*graph*). Metals are typically indicated simply by their solid phase, such as Fe(s) and 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 Hg(*l*).

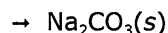
OK, let's get back to the idea of the formation reaction. When you write a "formation equation" for a substance, one mole of that substance will be the only item on the right side of the balanced equation; the reference elements will be on the left side in whatever numbers are required for balance. Here's a simple example, the formation equation for $\text{H}_2\text{O}(l)$.



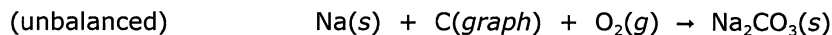
Notice that only one mole can be given on the right, by the definition for a formation equation. This requires a fractional coefficient to be used on the left for O_2 in order to achieve balance.

Let's work through two other examples. First, write the formation equation for sodium carbonate(s).

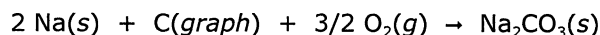
- ▶ Start with one mole of that substance on the right side of the equation.



- ▶ What elements are present in the substance? ➡ ➡ Sodium, carbon and oxygen
- ▶ What are the reference forms for these elements? ➡ ➡ Na(s), C(*graph*) and $\text{O}_2(g)$
- ▶ Enter these on the left of the equation.



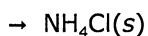
- ▶ Balance the equation. You must keep a coefficient of one on the right.



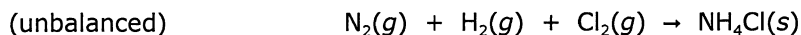
That's it.

Next, write the formation equation for ammonium chloride(s).

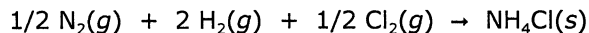
- ▶ Start with one mole of that substance on the right side of the equation.



- ▶ What elements are present in the substance? ➤ ➤ Nitrogen, hydrogen and chlorine
- ▶ What are the reference forms for these elements? ➤ ➤ $\text{N}_2(g)$, $\text{H}_2(g)$ and $\text{Cl}_2(g)$
- ▶ Enter these on the left of the equation.



- ▶ Balance the equation. You must keep a coefficient of one on the right.



That's all there is to these types of equations.

This brings us to the next term, the "standard enthalpy of formation". The standard enthalpy of formation is the change in the standard enthalpy for a formation reaction. It gets its own symbol, ΔH_f° , where the subscript f is for formation. This is often called a standard "heat of formation" but, as already pointed out, heat is not the only form of energy contained within enthalpy. Regardless, values of ΔH_f° are the bases for extremely important calculations in thermodynamics which we shall be getting to momentarily.

Many ΔH_f° 's for many substances have been measured over the years. Some are listed in Appendix A at the end of this text. (Be sure to pick from the correct column in that Appendix. We won't get to those other columns until Chapters 44 and 45.) Take a look at Appendix A at this time and let me make a few notes.

- Values of ΔH_f° can range from several kJ up through a thousand or more kJ or kJ/mol.
- Values can be positive or negative.
- Some values are zero but notice which ones those are! They are the reference forms of the elements. This is a consequence of how they set this up: all formation reactions for all substances are relative to their reference elements. All reference forms are assigned $\Delta H_f^\circ = 0$, and every other substance is relative to that. Look at the values of ΔH_f° for $\text{O}_2(g)$, $\text{C}(\text{graph})$, $\text{Na}(s)$ and $\text{Hg}(l)$. They're all zero. Every other allotrope or phase of the various elements is some other value. Look at the other allotrope of oxygen, $\text{O}_3(g)$. It's not zero, is it? Look at $\text{C}(\text{diam})$. It's not zero, is it? There's another consequence to this. If you forget who is a reference form, look up the element in the table and see which allotrope got assigned zero. That's the reference form. What's the reference form for potassium? Look it up: which allotrope or phase has $\Delta H_f^\circ = 0$?
- Look at the value for $\text{H}^+(aq)$. It's zero because it, too, is a reference. It's the reference point for all other aqueous ions. All values of ΔH_f° for ions are relative to the value for $\text{H}^+(aq)$.

Remember these last two points: reference elemental forms and $\text{H}^+(aq)$ are defined to have $\Delta H_f^\circ = 0$. All other substances will have a nonzero ΔH_f° which is measured relative to those.

I should mention that data for ΔH_f° have derived from different sources over the years. The result is that different tables may have slightly different values, especially if they're rounded off differently. The numbers which I use may not be exactly the same as in some other source. Don't worry about it. They should be close.

We had written the formation equation for $\text{H}_2\text{O}(l)$ above. What's its ΔH_f° ? Look it up: you'll find that ΔH_f° for $\text{H}_2\text{O}(l)$ is -285.83 kJ/mol. We can represent this process as



(This equation also happens to be the combustion reaction for $\text{H}_2(g)$ to $\text{H}_2\text{O}(l)$, for which we had previously derived $\Delta H_c^\circ = -285.83$ kJ.) As a practical matter, the units for any ΔH_f° can be taken to be kJ or kJ/mol. The difference doesn't matter much, since formation is defined for one mole anyway. We can say:

- ▶ The standard enthalpy for the formation reaction of one mole of $\text{H}_2\text{O}(l)$ is -285.83 kJ.

OR

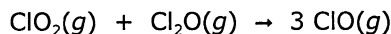
- ▶ The standard enthalpy of formation for $\text{H}_2\text{O}(l)$ is -285.83 kJ per mole.

The message is the same either way for our purposes. In some applications, the use (or not) of the per mol term becomes more important, but we generally won't require that distinction. On the other hand, your instructor may be more specific in this usage, so heed if there's need.

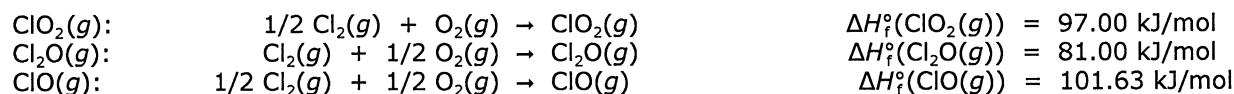
OK, enough of this terminology for now. Time for a coffee break. Where's the standard $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$?

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

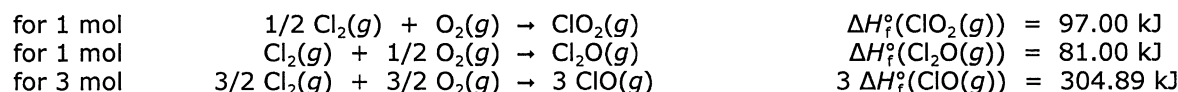
The entire reason that I have brought you here is to show you how to determine ΔH° for any reaction whatsoever. The keys to doing this are the standard formation enthalpies and the conservation of mass-energy as contained within the additivity of reactions. I will first show you the full, gory details of how this works, and then we'll cut to the chase and spell out a simple approach. We begin with the following reaction, for which we will derive ΔH° . This is our target equation.



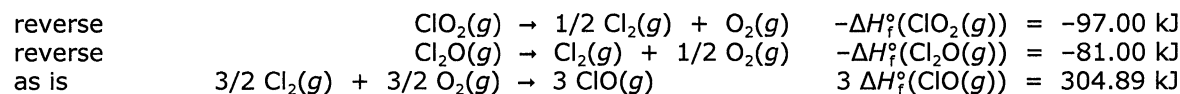
We start by spelling out the formation reactions for each item in the balanced equation. We also bring in the ΔH_f° values from Appendix A.



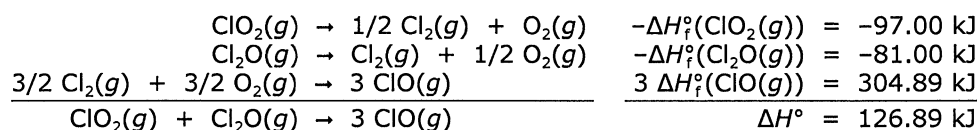
We then use these formation equations to derive the target equation, according to the additivity of reactions. For each reactant and product in the target equation, we multiply its formation equation by its coefficient in the target equation; this will also multiply ΔH_f° . The coefficients for ClO₂(g) and for Cl₂O(g) in the target equation are one mol; the coefficient for ClO(g) is three mol, so we triple its formation equation.



We must also reverse the formation equations for all reactants in the target equation; this will negate the ΔH_f° values of the reactants. On the other hand, keep the direction as is for the product ClO(g).



Now, add the equations (Cl₂(g) and O₂(g) will cancel out) and add the enthalpies.

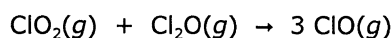


That gives you your target equation and its ΔH° . Notice that the reaction is endothermic. If you run the reaction beginning at standard conditions and ending at standard conditions, the reaction would require 126.89 kJ from the surroundings.

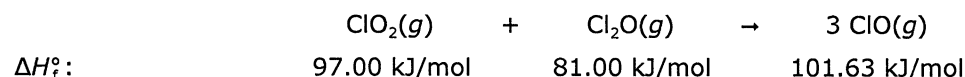
By spelling out the whole process, you can see the importance of the formation equations and the manipulation of the ΔH_f° values. Yes, this was a very lengthy procedure, but we can break this down to a simple shortcut. Check out what we did here.

- ✓ We started with the ΔH_f° for each item in the target equation.
- ✓ We multiplied each ΔH_f° by the coefficient in the target equation.
- ✓ We added the values for all products and subtracted the values for all reactants.

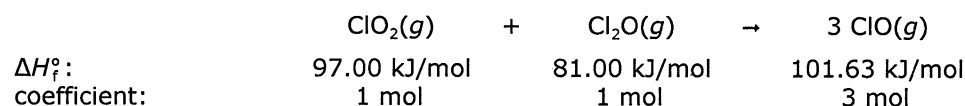
To derive a ΔH° for any reaction whatsoever, you can execute these same steps without writing down any formation equation. To illustrate, let's do the shortcut for the same reaction. Start over.



Bring in the values of ΔH_f° for each reactant and product.



Multiply each ΔH_f° by its coefficient in the balanced equation.



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

$$\Delta H^\circ = \overbrace{+ 3 \text{ mol ClO} \times \frac{101.63 \text{ kJ}}{\text{mol ClO}}}^{\text{Add for product(s)}} - \overbrace{1 \text{ mol ClO}_2 \times \frac{97.00 \text{ kJ}}{\text{mol ClO}_2} - 1 \text{ mol Cl}_2\text{O} \times \frac{81.00 \text{ kJ}}{\text{mol Cl}_2\text{O}}}^{\text{Subtract for reactants}}$$

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

$$\Delta H^\circ = 3(101.63 \text{ kJ}) - 1(97.00 \text{ kJ}) - 1(81.00 \text{ kJ}) = 126.89 \text{ kJ}$$

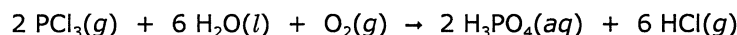
There's the answer without getting bogged down in the actual formation equations.

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, all three values of ΔH_f° had two decimals; thus, the answer goes to two decimal places. Once again, different instructors handle this differently, so check with yours.

That was an easy sampler. Let's do one a bit more involved.

Example 1. Find ΔH° for the following reaction.



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

$$\begin{array}{cccccc} 2 \text{ PCl}_3(g) & + & 6 \text{ H}_2\text{O}(l) & + & \text{O}_2(g) & \rightarrow & 2 \text{ H}_3\text{PO}_4(aq) & + & 6 \text{ HCl}(g) \\ \Delta H_f^\circ: & -288.70 \text{ kJ/mol} & -285.83 \text{ kJ/mol} & & 0 \text{ kJ/mol} & & -1,288.3 \text{ kJ/mol} & & -92.31 \text{ kJ/mol} \end{array}$$

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

$$\begin{array}{cccccc} 2 \text{ PCl}_3(g) & + & 6 \text{ H}_2\text{O}(l) & + & \text{O}_2(g) & \rightarrow & 2 \text{ H}_3\text{PO}_4(aq) & + & 6 \text{ HCl}(g) \\ \Delta H_f^\circ: & -288.70 \text{ kJ/mol} & -285.83 \text{ kJ/mol} & & 0 \text{ kJ/mol} & & -1,288.3 \text{ kJ/mol} & & -92.31 \text{ kJ/mol} \\ \text{coef:} & 2 \text{ mol} & 6 \text{ mol} & & 1 \text{ mol} & & 2 \text{ mol} & & 6 \text{ mol} \end{array}$$

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

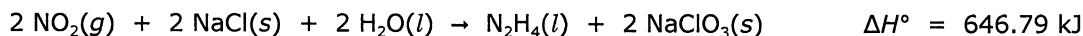
$$\Delta H^\circ = \overbrace{2(-1,288.3 \text{ kJ}) + 6(-92.31 \text{ kJ})}^{\text{products}} - \overbrace{2(-288.70 \text{ kJ}) - 6(-285.83 \text{ kJ}) - 1(0 \text{ kJ})}^{\text{reactants}}$$

Plug it in, punch it out, round it off. You get -838.1 kJ . That's negative, so the reaction is exothermic. That's the total energy released to the surroundings starting from standard conditions and ending at standard conditions.

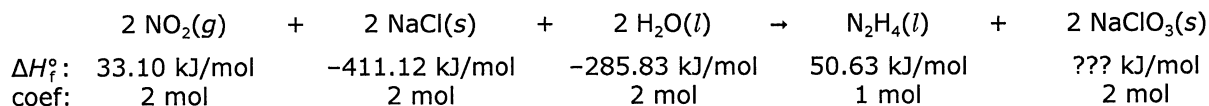
A word of caution. One of the most common ways to screw up these calculations is to mess up the signs. Sometimes you're adding positive kJ's, sometimes you're subtracting negative kJ's, sometimes you're subtracting positive kJ's and sometimes you're adding negative kJ's. Be careful.

A variation on this type of problem is to calculate a ΔH_f° for one reagent in a given reaction, given ΔH_f° values for the other reagents and ΔH° . Here's an Example.

Example 2. From the following equation and the given ΔH° , determine ΔH_f° for $\text{NaClO}_3(s)$.



Line up the available ΔH_f° 's from Appendix A, along with the coefficients. $\text{NaClO}_3(s)$ is not in Appendix A, and its value is the unknown.



Set up everybody, inserting the given value for ΔH° , 646.79 kJ.

$$\begin{array}{ccccccc}
 & & \text{products} & \text{minus} & & \text{reactants} & \\
 & & \underbrace{\hspace{10em}} & & \underbrace{\hspace{10em}} & & \\
 & & \text{N}_2\text{H}_4 & \text{NaClO}_3 & \text{NO}_2 & \text{NaCl} & \text{H}_2\text{O} \\
 \Delta H^\circ = 646.79 \text{ kJ} = & 1(50.63 \text{ kJ}) & + & 2(???) & - & 2(33.10 \text{ kJ}) & - & 2(-411.12 \text{ kJ}) & - & 2(-285.83 \text{ kJ})
 \end{array}$$

Then, re-arrange and solve for ???. Go ahead and punch this out. Be sure you get -365.77 kJ. If you didn't, check your signs, although some people do forget one or more of the coefficient multipliers.

Your turn. We'll do an aqueous reaction. Here's an important point to note: if any reagent in an aqueous reaction is a strong electrolyte, then you must work in net ionic format for the balanced equation. Tables of ΔH_f° values are generally compiled for the net ionic approach. If you check Appendix A, you will find $\text{NaCl}(s)$ but you will not find $\text{NaCl}(aq)$. In net ionic format, $\text{NaCl}(aq)$ would be written as $\text{Na}^+(aq) + \text{Cl}^-(aq)$; ΔH_f° values for both of those ions are in Appendix A and you add them together to get the value for $\text{NaCl}(aq)$. This is important now and it will be important later in Chapters 39 and 44. Despite this minor detail, the calculation for ΔH° is still the same: products minus reactants. OK, now you can get started. We'll retrieve the reaction of copper metal and nitric acid from Chapter 14. That was done then in net ionic format, and here it is again.

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.

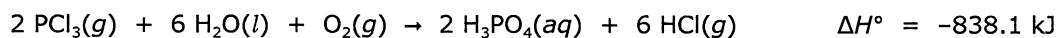
$\Delta H^\circ =$

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. Or you just pulled the wrong number out of Appendix A. Try 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 reaction from Example 1.



If you conduct this reaction in the mole amounts given by the coefficients of the balanced equation, it will release 838.1 kJ. But let's say you want to run the reaction using 50.0 g PCl_3 instead of 2 mol PCl_3 . How many kJ's would be released under those conditions? That's where stoichiometry comes in.

Every ΔH° 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 PCl_3 is the following.

$$\frac{-838.1 \text{ kJ}}{2 \text{ mol PCl}_3} \quad \text{OR} \quad \frac{2 \text{ mol PCl}_3}{-838.1 \text{ kJ}}$$

You can write rxn ratios for any member of the equation. Here's the rxn ratio for kJ and HCl.

$$\frac{-838.1 \text{ kJ}}{6 \text{ mol HCl}} \quad \text{OR} \quad \frac{6 \text{ mol HCl}}{-838.1 \text{ kJ}}$$

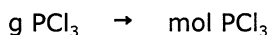
These kinds of rxn ratios can enter into a stoichiometry calculation. Just remember: the ΔH° of an equation is for the equation as written and it relates to the coefficients as written.

OK, back to the question: how many kJ's would be released from the reaction of 50.0 g PCl_3 ?

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 PCl_3 to mol, using molar mass.



Step 3. Convert mol PCl_3 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.

$$\begin{array}{ccccccc} \text{g PCl}_3 & \rightarrow & \text{mol PCl}_3 & \rightarrow & \text{kJ} & & \\ 50.0 \text{ g PCl}_3 & \times & \frac{\text{mol PCl}_3}{137.32 \text{ g PCl}_3} & \times & \frac{-838.1 \text{ kJ}}{2 \text{ mol PCl}_3} & = & -153 \text{ kJ} \end{array}$$

That means 153 kJ would be released for the reaction of 50.0 g of PCl_3 .

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 sometimes 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.

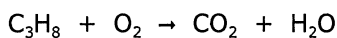
Example 4. What is the standard enthalpy of combustion for propane gas? How many kJ's can you get from the combustion of 1.000 g propane at standard conditions?

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.

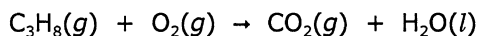
- The standard enthalpy of combustion is defined for the combustion of one mole of the compound. The first thing we need is a balanced combustion equation, written for one mole of propane.
- Once we have that, we can do products minus reactants with ΔH_f° 's to get ΔH_c° . That gives us the answer for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

Now, proceed.

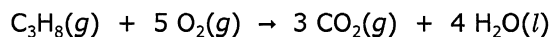
We need the balanced equation for the combustion of C_3H_8 . Don't forget the stuff you knew in Chapter 6 about combustion reactions. The other reactant is O_2 . The products are CO_2 and H_2O .



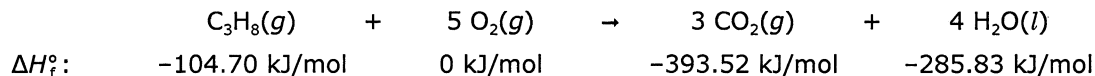
Now you need to include phases. You were told to use propane gas. O_2 and CO_2 are gases. Water is the only ambiguity, since we can set it up for gas phase water or liquid phase water. Some instructors will specify that you should use only one or the other, so heed if you need. I'll use liquid phase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



Balance.



This is our equation for the combustion of one mole of propane. Now, we need ΔH_c° . 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.

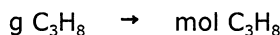
$$\Delta H_c^\circ = \text{_____} (\text{_____ kJ}) + \text{_____} (\text{_____ kJ}) - \text{_____} (\text{_____ kJ})$$

Punch it out, round it off: you get $\Delta H_c^\circ = -2,219.18 \text{ kJ}$, which is a lot of J's. That's the first part of the problem.

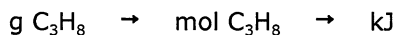
The second part is the stoichiometry: we want the number of kJ's for 1.000 g C_3H_8 . Notice that the reaction as written involves $-2,219.18 \text{ kJ}$ and one mol C_3H_8 ; these will make up the rxn ratio.

$$\frac{-2,219.18 \text{ kJ}}{\text{mol C}_3\text{H}_8} \quad \text{OR} \quad \frac{\text{mol C}_3\text{H}_8}{-2,219.18 \text{ kJ}}$$

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.

$$\text{g C}_3\text{H}_8 \rightarrow \text{mol C}_3\text{H}_8 \rightarrow \text{kJ}$$

$$1.000 \text{ g C}_3\text{H}_8 \times \frac{\text{mol C}_3\text{H}_8}{44.09 \text{ g C}_3\text{H}_8} \times \frac{-2,219.18 \text{ kJ}}{\text{mol C}_3\text{H}_8} = -50.33 \text{ kJ}$$

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 we use to power our bodies. Nature developed that differently.

Most 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 does not combust, 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. CO_2 is exhaled. H_2O is ultimately respired, transpired, sweated, and passed in urine. Undigestibles and some other things are excreted.

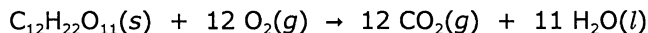
All of this constitutes the primary explanation for why you eat, drink and breathe. It's alimentary, my dear Watson. Nature genetically programmed humans with an appetite for combustible fuels in order to power their bodies to breathe, to pump blood, to digest, to work, to contemplate, to recreate and 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 O_2 . 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, 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 O_2) 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 fats.

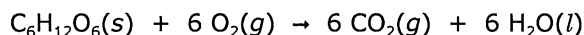
Carbohydrates include the simple and complex sugars. Another name is saccharides, and these can take a numerical prefix depending on how many "sugar units" are bonded within the molecule. The simplest are monosaccharides which are composed of one sugar unit; for example, we mentioned two monosaccharides, fructose (fruit sugar) and glucose (blood sugar), in Section 3.2 as isomers with the formula $C_6H_{12}O_6$. 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 $C_{12}H_{22}O_{11}$. Polysaccharides can involve many sugar units; examples include starch and cellulose.

The combustion reaction for sucrose is the following.



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

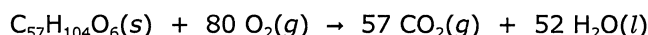
The combustion reaction for fructose and glucose is



The ΔH_c° 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 combustion enthalpy 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: $C_{57}H_{104}O_6$. Fats are big molecules.



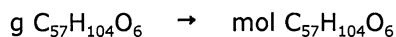
Those big molecules have a lot to burn and their combustion packs a wallop; for $C_{57}H_{104}O_6$, $\Delta H_c^\circ = -34,900$ kJ.

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 $C_{57}H_{104}O_6$ 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 ΔH_c° above. Together, these give us the rxn ratio: $-34,900$ kJ per mol of $C_{57}H_{104}O_6$. 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.

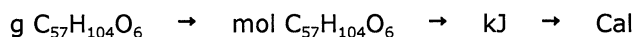
Convert g C₅₇H₁₀₄O₆ to mol, using molar mass.



Convert mol C₅₇H₁₀₄O₆ to kJ, using the rxn ratio.



Convert kJ to Cal.



Put it all together.

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

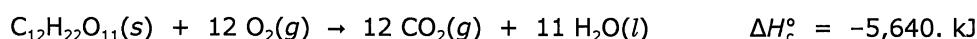
This says that the combustion of that pound of fat involves the release of 4,270 Cal of energy. Since that fat is part of your system, YOU must release 4,270 Cal as heat and/or work as you combust that pound of fat to CO₂ and H₂O. So get going. How? If you're into walking, you would typically burn that 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 ~3,500 Cal per pound of body weight. Maybe you should run on the treadmill as you read this.

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 mole 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.

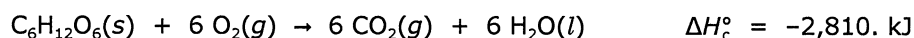
Let's look at the thermodynamics involved in the energy-per-mass relationships. It's still combustion, but now we want to know the ratio of stored energy per mass of fuel. The stored energy is the chemical energy which is the amount released during combustion. The ratio can be expressed as kJ/g or Cal/g. 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 50.33 kJ/g is released 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:

$$1.000 \text{ g sucrose} \times \frac{\text{mol sucrose}}{342.30 \text{ g sucrose}} \times \frac{-5,640. \text{ kJ}}{\text{mol sucrose}} \times \frac{\text{Cal}}{4.184 \text{ kJ}} = -3.938 \text{ Cal}$$

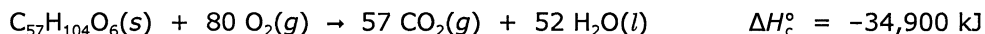
This amount is for 1.000 g, so we can say that sucrose packs 3.938 Cal/g of available energy; that's how much is released upon full combustion. Now let's do the same calculation for 1.000 g fructose.

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

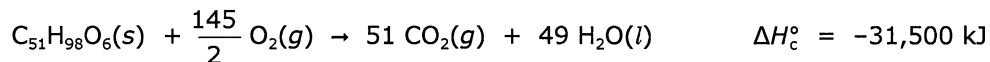
Fructose packs 3.728 Cal/g of available energy, which is close to the value for sucrose above. If you do the same for a bunch of different sugars, they come out to about 4 Cal/g.

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.

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

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

$$1.000 \text{ g C}_{51}\text{H}_{98}\text{O}_6 \times \text{_____} \times \text{_____} \times \text{_____} = -9.33 \text{ Cal}$$

The values are close. If you do the same calculation for a bunch of fats, they come 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.

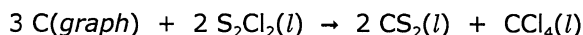
I know that's a bunch of stoichiometry calculations which we went through, but there's a reason. The significance of these was to demonstrate what Nature has been doing for millions of years: providing fuel for life. Of the various fuels for humans, fats pack the most stored energy per mass. I also did 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.

Yes, these things are very much a part of your world.

Problems

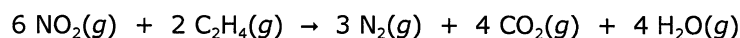
- True or false.
 - The reverse of an exothermic process is still exothermic.
 - Enthalpies of reactions are additive.
 - ΔH_f° for $\text{H}^+(aq)$ is zero.
 - The standard enthalpy of formation of $\text{Br}_2(g)$ is zero.
 - Every formation equation shows one mole of one product on the right side of the equation.
 - 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.
 - $\text{Zn}(\text{NO}_3)_2(s)$
 - $\text{C}_2\text{H}_5\text{I}(l)$
 - $\text{BrNO}(l)$
 - $\text{HgO}(s)$
 - $\text{C}_2\text{F}_6\text{Xe}(s)$

4. The following equation is balanced.



What is the ΔH° (in kJ) for this reaction? Is the reaction exothermic or endothermic?

5. The following equation is balanced.



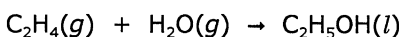
What is the ΔH° (in kJ) for this reaction? Is the reaction exothermic or endothermic?

6. Consider the precipitation reaction resulting from mixing aqueous solutions of calcium nitrate and of sodium carbonate. Derive the net ionic equation for this reaction, and use that to find ΔH° for this reaction. Is the precipitation exothermic or endothermic?

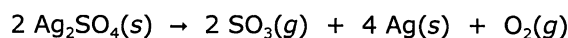
7. The reaction of ethylene, C_2H_4 , with water can produce ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, according to the following equation.



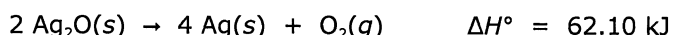
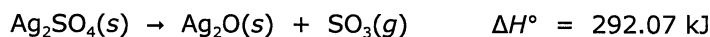
The standard enthalpy of vaporization of ethyl alcohol, $\Delta H_{\text{vap}}^\circ$, is 42.59 kJ. Use this information to find ΔH° (in kJ) for the following reaction.



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

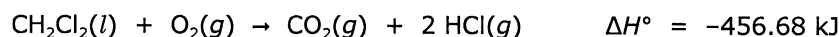


Consider this overall reaction as derived from two Steps, with Ag_2O as an intermediate.



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

9. The following equation is balanced.

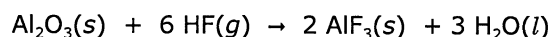


For the reaction which uses 50.0 g CH_2Cl_2 , what is the change in enthalpy (in kJ)?

10. The standard enthalpy 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?

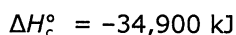
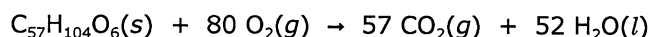
11. Solid zinc oxide can be prepared by direct combustion of $\text{Zn}(s)$ with $\text{O}_2(g)$. What is the change in enthalpy (in kJ) for this reaction when 16.2 g of zinc are reacted?

12. The following equation is balanced.



What is the change in enthalpy (in kJ) for the production of 57.2 g AlF_3 ?

13. Assume an individual burns 2,000. 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.



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