

Hess' Law of Constant Heat Summation

Using four or more equations and their enthalpies

[Go to Hess' Law - using two equations and their enthalpies](#)

[Go to Hess' Law - using three equations and their enthalpies](#)

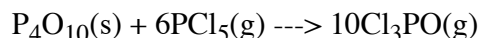
[Go to Hess' Law - using standard enthalpies of formation](#)

[Go to Hess' Law - using bond enthalpies](#)

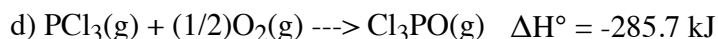
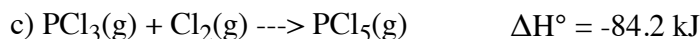
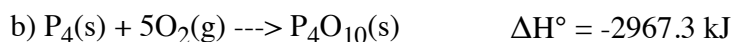
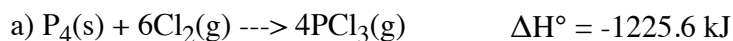
[Back to the Thermochemistry menu](#)

Downloaded from <http://www.chemteam.info/Thermochem/HessLawIntro1b.html>; accessed on August 15, 2014.

Problem #1: Calculate the value of ΔH° for the following reaction:



using the following four equations:

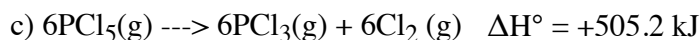


Solution:

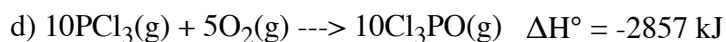
1) We know that P_4O_{10} **MUST** be on the left-hand side in the answer, so let's reverse (b):



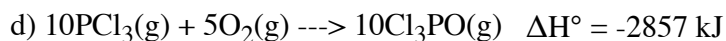
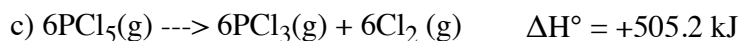
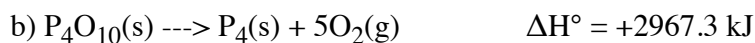
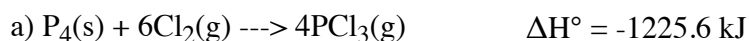
2) We know that PCl_5 **MUST** be on the left-hand side in the answer, so let's reverse (c) and multiply it by 6:



3) We know that Cl_3PO **MUST** have a 10 in front of it:



4) Now, write all four equations, but incorporate the revisions:



5) Now, we will add all four equations as well as the ΔH° values. Notice the following:

- a) $P_4(s)$ cancels out (see equations a and b)
- b) Cl_2 cancels out (see equations a and c)
- c) O_2 cancels out (see equations b and d)
- d) PCl_3 cancels out (see equations a+c and d)

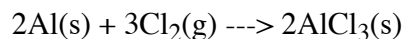
The ΔH° values added together:

$$-1225.6 \text{ kJ} + (+2967.3 \text{ kJ}) + (+505.2 \text{ kJ}) + (-2857 \text{ kJ}) = -610.1 \text{ kJ}$$

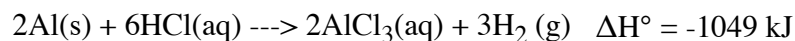
6) The answer:



Problem #2: Calculate the reaction enthalpy for the formation of anhydrous aluminum chloride:



from the following data:



Solution:

1) Let's examine each of the four equations in light of what needs to happen to it (in order to produce the target equation):

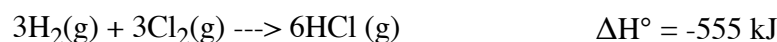
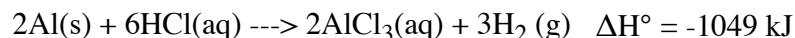
eq. 1 \Rightarrow this one remains unchanged. It gives us $2Al(s)$, which is what we want. The other substances will cancel out, as described below.

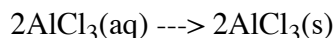
eq. 2 \Rightarrow this one will get multiplied by six in order to cancel the $6HCl(aq)$.

eq. 3 \Rightarrow this one gets multiplied by three. This gives us $3Cl_2(g)$, which is what we want, and cancels out the six $HCl(g)$ that was in eq. 2. It also cancels the $3H_2(g)$ from eq. 1.

eq. 4 \Rightarrow this one gets flipped (to put $AlCl_3(s)$ on the right) and it gets multiplied by two. It also cancels the $AlCl_3(aq)$ from eq. 1.

2) Rewrite the four equations with all applied changes:





$$\Delta H^\circ = +646 \text{ kJ}$$

3) Add the four enthalpies for the answer:

$$(-1049) + (-448.8) + (-555) + (+646) = -1406.8 \text{ kJ}$$



Comments:

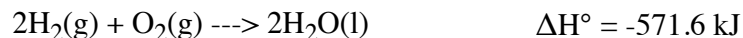
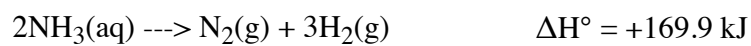
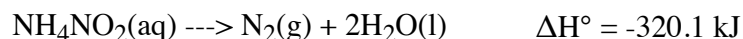
(1) This is not the enthalpy of formation for $\text{AlCl}_3(\text{s})$. Remember that an enthalpy of formation equation is always for **ONE** mole of the target substance. In other words, this:



The book value, by the way, is -705.63 kJ/mol .

(2) [This question was asked and answered on Yahoo Answers](#). The style of the answer is different than the way I answered the problem above. You may wish to take a look.

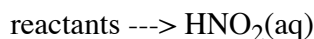
Problem #3: Using only the equations below, calculate the molar heat of formation of nitrous acid $\text{HNO}_2(\text{aq})$.



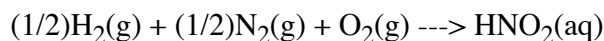
Solution:

1) Let's get the target equation:

a formation reaction is very specific. The reactants produce one mole of the product in its standard state:



the reactants must be elements in their standard states:



2) Let's examine each of the four equations in light of what needs to happen to it (in order to produce the target equation):

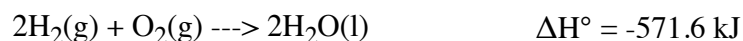
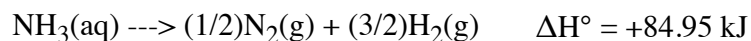
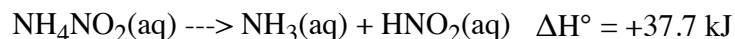
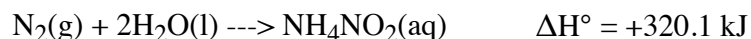
eq. 1 \Rightarrow this will be flipped because eq. 2 also gets flipped.

eq. 2 \Rightarrow this one gets flipped because we have to have $\text{HNO}_2(\text{aq})$ on the product side. This forces eq. 1 to also be flipped to cancel out the NH_4NO_2 .

eq. 3 \Rightarrow this one gets divided by 2. The most obvious reason is in order to cancel the NH_3 from eq. 2. The nitrogen and hydrogen will also cancel to give the final answer.

eq. 4 \Rightarrow this one is untouched. It will cancel the $2\text{H}_2\text{O}$ that is in eq. 1.

3) Rewrite the four equations with all applied changes:



4) Some comments on substances cancelling:

nitrogen: eq. 1 and eq. 3 cancel to leave $(1/2)\text{N}_2$ on the reactant side

hydrogen: eq. 3 and eq. 4 cancel to give $(1/2)\text{H}_2$ on the reactant side. Think of the 2H_2 in eq. 4 as $(4/2)\text{H}_2$

The only other substances that do not cancel are $\text{HNO}_2(\text{aq})$ (product side) and $\text{O}_2(\text{g})$ (reactant side), which is exactly what we want.

5) Add the 4 enthalpies:

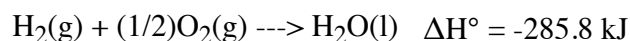
$$(+320.1) + (+37.7) + (+84.95) + (-571.6) = -128.85 \text{ kJ}$$

Do not write -128.85 kJ/mol, write this (rounded to three sig figs):

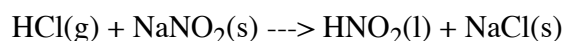
$$\Delta H^\circ_{\text{f, HNO}_2} = -129 \text{ kJ}$$

By the definition of formation, the amount is always for one mole of the target substance.

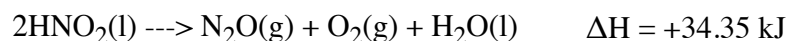
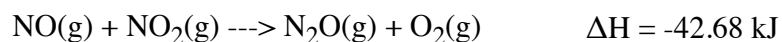
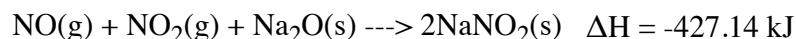
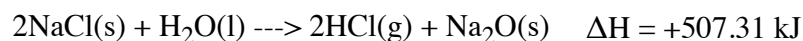
Note: for a variation on this question, use the fourth data equation like this:



Problem #4: Calculate the ΔH in kilojoules for the following reaction, the preparation of nitrous acid HNO_2 :



Use the following thermochemical equations:



Solution:

1) Let's examine each of the four equations in light of what needs to happen to it (in order to produce the target equation):

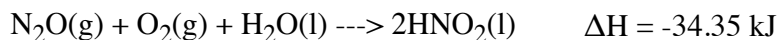
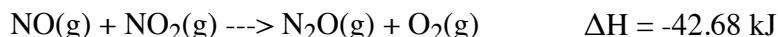
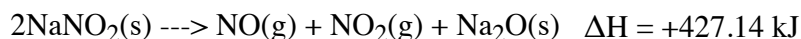
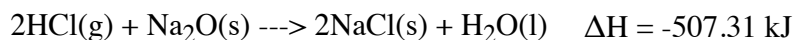
eq 1 \Rightarrow flip it (this puts NaCl on the right-hand side and HCl on the left-hand side)

eq 2 \Rightarrow flip it (this puts NaNO_2 on the left-hand side)

eq 3 \Rightarrow leave untouched

eq 4 \Rightarrow flip it (this puts HNO_2 on the right-hand side)

2) Rewrite all four equations with the above changes:



Note the sign changes on the enthalpies of the three flipped reactions. The substances that get eliminated are:

$\text{Na}_2\text{O(s)}$ (eq 1 & 3); $\text{H}_2\text{O(l)}$ (eq 1 & 4); NO(g) (eq 2 & 3); $\text{NO}_2\text{(g)}$ (eq 2 & 3); $\text{N}_2\text{O(g)}$ (eq 3 & 4); $\text{O}_2\text{(g)}$ (eq 3 & 4)

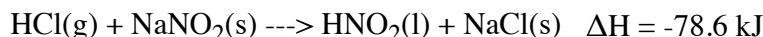
3) Add the four reactions to get this:



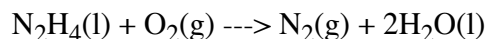
The ΔH value came from this:

$$(-507.31) + (+427.14) + (-42.68) + (-34.35)$$

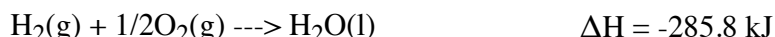
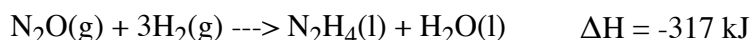
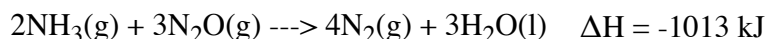
4) Divide everything by two for the final answer:



Problem #5: Determine the heat of reaction (in kJ) at 298 K for the reaction:



given the following equations and ΔH values:



Solution:

1) First, some discussion:

a) Equation 1 stays untouched. The main reason is because that's the only reaction that has N_2 on the product side, which is where we need it. The 4 in front of the N_2 is going to play a role. Suppose I divided

through by 4 to get the one N_2 in the final answer. That means I would wind up with $3/4$ in front of the N_2O and also in front of the H_2O . Way too complicated. Keeping the 4 in front of the N_2 means two things: (i) we will only deal with fractions that have a 2 in the denominator and (ii) the very least step will be to divide by 4.

b) Equation 2 needs to be flipped, so the N_2O can be on the product side (to cancel with the $3\text{N}_2\text{O}$ in the first equation). I also have to multiply this reaction by 3, to give me my $3\text{N}_2\text{O}$ for cancelling purposes.

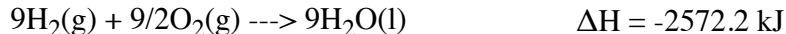
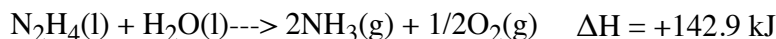
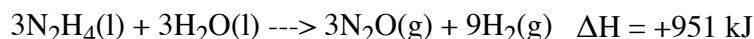
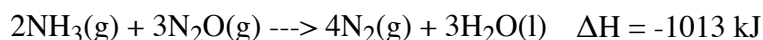
c) This reaction needs to be flipped too. I must have the 2NH_3 be on the product side to cancel with the 2NH_3 in equation 1.

d) Notice that I have two equations (#2 and #3) that have N_2H_4 . When I add everything up, I'll have $4\text{N}_2\text{H}_4$. Remember: my very last step will be to divide everything by 4.

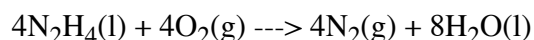
e) Equation 4 gets multiplied by 9. Look at the oxygens. I know I need 4O_2 (remember I will divide by 4 at the end), so I used 9 since I knew that would make $9/2\text{O}_2$ and the $1/2\text{O}_2$ in equation 3 would cancel, giving me $8/2\text{O}_2$ which is 4O_2 .

f) I will not discuss the H_2O , so that you may ponder how it works out.

2) Here's the result of everything I described:



3) When we add the four chemical reactions together, here is what results:



The 2NH_3 , the $3\text{N}_2\text{O}$ and the 9H_2 cancel completely.

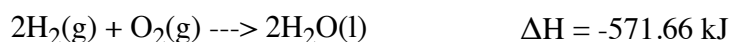
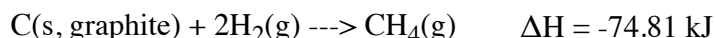
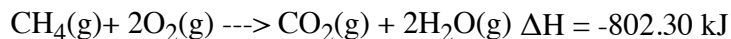
$1/2\text{O}_2$ cancels and four of the 12 H_2O on the right cancel.

4) Calculating the enthalpy:

a) add the four enthalpies: $-1013 \text{ kJ} + +951 \text{ kJ} + +142.9 \text{ kJ} + -2572.2 \text{ kJ} = -2491.3 \text{ kJ}$

b) divide by 4 for the final answer: -623 kJ (to three sig figs)

Problem #6: Calculate the standard enthalpy change for $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ at 298.15 K, given the following reaction enthalpies:



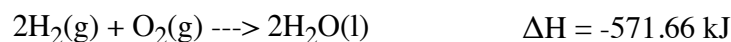
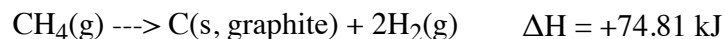
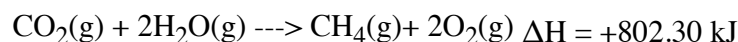
Solution:

1) Do these:

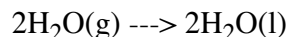
- a) flip first equation (puts $\text{H}_2\text{O}(\text{g})$ on the reactant side)
- b) leave second equation alone (need to cancel the CO_2 from the first equation)
- c) flip third equation (to cancel the CH_4 in the first equation)
- d) leave fourth equation alone ($\text{H}_2\text{O}(\text{l})$ is on the product side, which is where we want it)

I ignored the other items which will, if I did it right, take care of themselves.

2) The result:

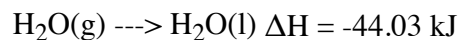


3) When the four modified equations are added together, we get this:

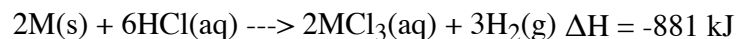


4) Add up the four enthalpies above and then divide that answer by 2 for the final answer.

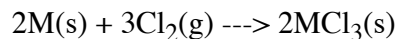
$$[+802.30 + (-393.51) + (+74.81) + (-571.66)] / 2 = -44.03 \text{ kJ}$$



Problem #7: Using these reactions, where M represents a generic metal:



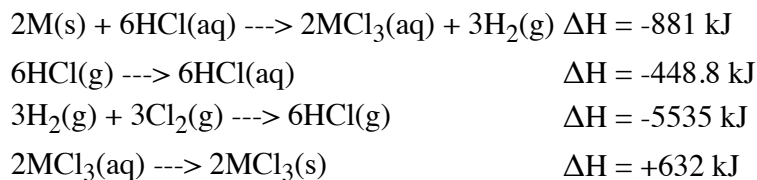
Determine the enthalpy of:

**Solution:**

1) These changes to the four data equations:

- 1) untouched (because it has 2M on the reactant side, where we want it)
- 2) mult by 6 (to cancel the $6\text{HCl}(\text{aq})$ in equation 1)
- 3) mult by 3 (to cancel the H_2 in eq 1, to cancel $6\text{HCl}(\text{g})$, to get 3Cl_2 in the final answer)
- 4) flip and mult by 2 (put $2\text{MCl}_3(\text{s})$ on the product side)

2) Result:



3) Add the four enthalpies for the answer:

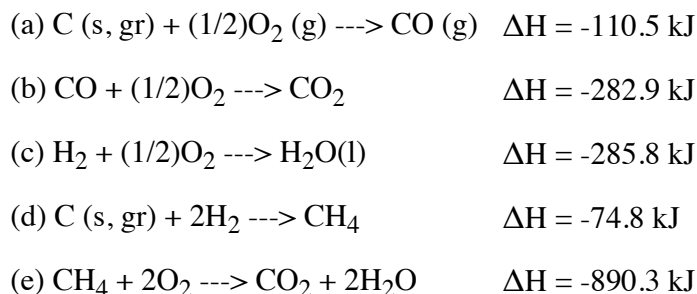


The following three problems use more than four data equations.

Problem #8: Determine ΔH for the reaction:



given the following data:



Solution:

When I solved this problem, in early August 2011, I went through several combinations of flip/don't flip and what factor to use before getting the right answer. That's because, due to how the equations interweave (each substance in the final equation is in two data equations), there is lots of trial-and-error involved.

As best as I can, I'm going to describe some of my thinking that led to the correct solution below, but you might want to avoid the explanation and try this one on your own first. It's a very, very good problem and no, I did not write this problem!

The solution is described starting in step five of the explanation, if you want to stop your scrolling before seeing the solution.

1) The two equations with carbon monoxide in them:

Equation (a) is connected to equation (d) and one of them must be flipped. Also, whatever factor I choose to use must be applied to both equations.

Equation (b) is connected to equation (e) with respect to the CO_2 . Notice that only one CO_2 will be required. That means that either equation (b) or (e) will wind up with a factor.

2) The two equations with methane in them:

If equation (d) gets flipped, then (e) must also be flipped.

If equation (d) gets flipped, then that means a possible factor of 4 for equation (e), since we required three CH_4 in the final answer.

If (e) gets flipped, then that means we will need a pretty big factor in equation (c), in order to generate enough H_2 and enough H_2O for the final equation.

3) The two equations with water in them:

One of them must be flipped. However, notice that we require eight H_2 , so flipping either one has consequences. For example, if I flip (d), then I must (e) to get methane on the right.

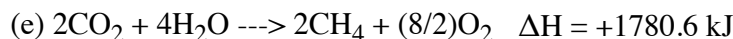
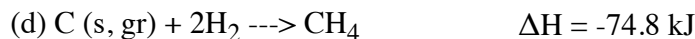
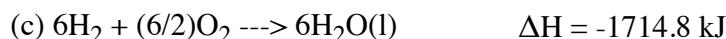
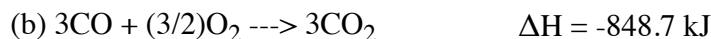
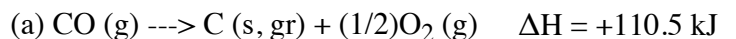
4) The four equations with O_2 in them:

You might think it wise to ignore the oxygen, but that can also be a mistake if you carry it too far. In this problem, I realized a relatively large factor needed to be used in equation (c). This was to get sufficient H_2 on the left and also to get sufficient O_2 on the left so as to cancel O_2 on the right.

5) Here is the solution to this problem:

- (a) flip, multiply by 1
- (b) do not flip, x3
- (c) do not flip, x6
- (d) do not flip, x1
- (e) flip, x2

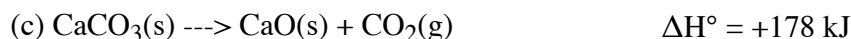
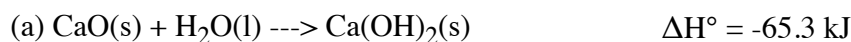
6) Let's rewrite according to the above instructions:



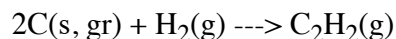
7) The enthalpy is:

$$(+110.5) + (-848.7) + (-1714.8) + (-74.8) + (+1780.6) = -747.2 \text{ kJ}$$

Problem #9: Acetylene, C_2H_2 , is a gas commonly used in welding. It is formed in the reaction of calcium carbide, CaC_2 , with water. Given the thermochemical equations below, calculate the value of ΔH°_f for acetylene in units of kilojoules per mole:



Here is the target equation:



Comment #1: the technique is to ignore simple things like CO_2 and H_2O . If we do the others right, they will take care of themselves.

Comment #2: what evolves during the solution is that the answer is the above target equation, but with the coefficients of 4, 2 \rightarrow 2. This means we will then divide by two in the final step. It turns out to be a bit of a hassle to try and go directly to the target equation. (However, I am certainly not going to stop you from trying on your own. Your life, not mine!)

Solution:

1) Let's analyse the six equations above:

- (a) flip and multiply by 2, this gets 2 for the calcium hydroxide and cancels the CaO
- (b) unchanged, this equation gets rid of the CaC_2 on the reactant side of equation (d)
- (c) not needed, the evil question writer put it there to confuse you.
- (d) this one has the C_2H_2 on the product side. This is where we want it, but we have to get rid of everything else. We have to multiply it by two.
- (e) flip, we need 4C because we have to multiply equation (d) by 2. We did that to (d) to be able to cancel the 2CaC_2
- (f) flip, notice that it has 2H_2 , which is what we need.

2) rewrite all the equations, with all changes applied:

- (a) $2\text{Ca(OH)}_2(\text{s}) \rightarrow 2\text{CaO}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = +130.6 \text{ kJ}$
- (b) $2\text{CaO}(\text{s}) + 5\text{C(s, gr)} \rightarrow 2\text{CaC}_2(\text{s}) + \text{CO}_2(\text{g}) \quad \Delta H^\circ = +753 \text{ kJ}$
- (c) not needed
- (d) $2\text{CaC}_2(\text{s}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Ca(OH)}_2(\text{s}) + 2\text{C}_2\text{H}_2(\text{g}) \quad \Delta H^\circ = -252 \text{ kJ}$
- (e) $\text{CO}_2(\text{g}) \rightarrow \text{C(s, gr)} + \text{O}_2(\text{g}) \quad \Delta H^\circ = +393.5 \text{ kJ}$
- (f) $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -572 \text{ kJ}$

3) What cancels and where:

$2\text{Ca(OH)}_2(\text{s}) \Rightarrow$ equations a and d

$2\text{CaO}(\text{s}) \Rightarrow$ equations a and b

$4\text{H}_2\text{O}(\text{l}) \Rightarrow$ equations d with a and f

$5\text{C(s)} \Rightarrow$ cancels with C(s) in equation e to give 4C

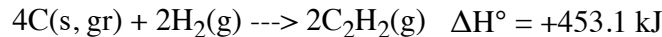
$2\text{CaC}_2(\text{s}) \Rightarrow$ equations b and d

$\text{CO}_2(\text{g}) \Rightarrow$ equations b and e

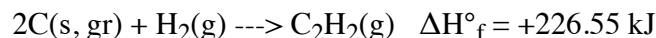
$\text{O}_2(\text{g}) \Rightarrow$ equations e and f

4) Add up all the ΔH values:

$$+130.6 + (+753) + (-252) + (+393.5) + (-572) = +453.1$$

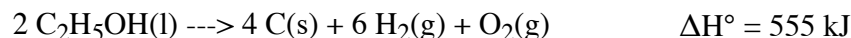
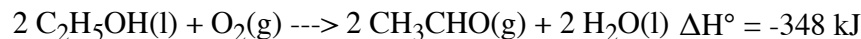
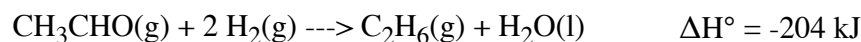


5) Divide by 2:



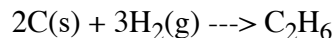
Note the addition of the subscripted f since we now have the correct formation reaction for $\text{C}_2\text{H}_2(\text{g})$.

Problem #10: From a consideration of the following reactions, calculate ΔH°_f for ethane, $\text{C}_2\text{H}_6(\text{g})$.



Solution:

1) The formation reaction for ethane is this:



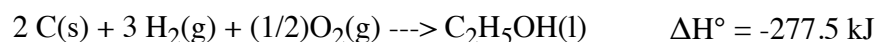
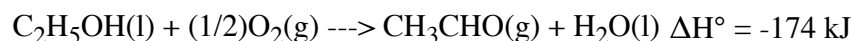
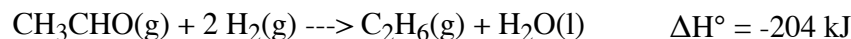
2) We will need to manipulate the 5 data equation to get what we want.

a) equation 1 of the 5 has C_2H_6 as the product. That's where we want it, so leave eq 1 untouched.

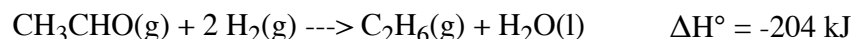
b) equation 3 must be divided by 2. This is to get one CH_3CHO on the product side, so it will cancel the CH_3CHO in eq 1.

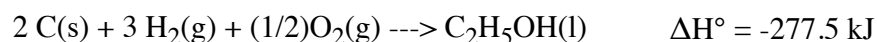
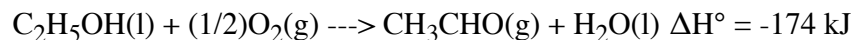
c) equation 5 must be flipped and divided by 2. This will put 2C on the reactant side and give us one $\text{C}_2\text{H}_5\text{OH}$ to cancel the one in eq 3.

3) Let's apply the above changes and then look at equations 2 and 4.



4) Flip equation 2 and multiply equation 4 by 2. This will cancel all of the $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2\text{O}(\text{l})$:





There are 5H_2 on the reactant side and 2H_2 on the product side, leaving 3H_2 on the reactant side, which is what we want. The one O_2 on each side will cancel.

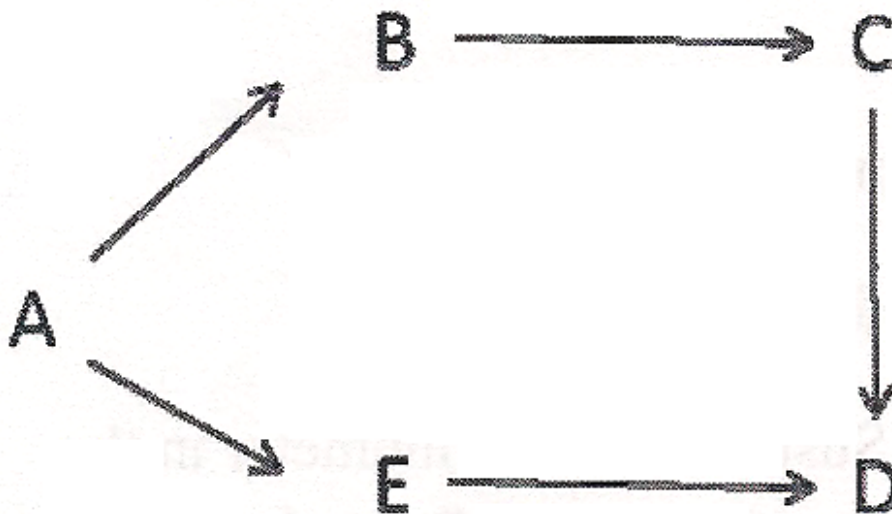
5) Adding up the five enthalpies gives

$$\Delta H^\circ = -83.5 \text{ kJ}$$

[Compare that to the data given here.](#)

Problem #11:

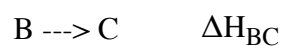
In the following cycle, the enthalpies can be measured for all of the following reactions: ΔH_{AB} , ΔH_{BC} , ΔH_{AE} , and ΔH_{ED} . Show that the molar enthalpy of reaction ΔH_{CD} , step $\text{C} \rightarrow \text{D}$, can be expressed in terms of the other steps.



Solution:

1) Let us write the chemical equations associated with the four enthalpies given:

Reaction Enthalpy Value





2) Rearrange the four data equations as follows:

first \Rightarrow flip, in order to cancel the B in the second equation

second \Rightarrow flip, because this puts C as the reactant

third \Rightarrow leave untouched, A will cancel with the A in the first equation

fourth \Rightarrow leave untouched, E cancels with the third equation and D is the product (which is what we want)

3) The results of the above-described modifications:

Reaction	Enthalpy Value
B \rightarrow A	$-\Delta H_{AB}$
C \rightarrow B	$-\Delta H_{BC}$
A \rightarrow E	ΔH_{AE}
E \rightarrow D	ΔH_{ED}



Note how the signs for the first two enthalpies have changed.

4) ΔH_{CD} is arrived at by adding the four data enthalpies:

$$(-\Delta H_{AB}) + (-\Delta H_{BC}) + \Delta H_{AE} + \Delta H_{ED}$$

[Go to Hess' Law - using two equations and their enthalpies](#)

[Go to Hess' Law - using three equations and their enthalpies](#)

[Go to Hess' Law - using standard enthalpies of formation](#)

[Go to Hess' Law - using bond enthalpies](#)

[Back to the Thermochemistry menu](#)