# Hess' Law of Constant Heat Summation
# Using three equations and their enthalpies

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Germain Henri Hess, in 1840, discovered a very useful principle which is named for him:

> **The enthalpy of a given chemical reaction is constant, regardless of the reaction happening in one step or many steps.**

Another way to state Hess' Law is:

> **If a chemical equation can be written as the sum of several other chemical equations, the enthalpy change of the first chemical equation equals the sum of the enthalpy changes of the other chemical equations.**

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**Problem #1:** Calculate the enthalpy for this reaction:

$2C(s) + H_2(g) \text{ ---> } C_2H_2(g) \quad \Delta H° = ???\ kJ$

Given the following thermochemical equations:

$C_2H_2(g) + (5/2)O_2(g) \text{ ---> } 2CO_2(g) + H_2O(l) \quad \Delta H° = -1299.5\ kJ$

$C(s) + O_2(g) \text{ ---> } CO_2(g) \quad \Delta H° = -393.5\ kJ$

$H_2(g) + (1/2)O_2(g) \text{ ---> } H_2O(l) \quad \Delta H° = -285.8\ kJ$

**Solution:**

1) Determine what we must do to the three given equations to get our target equation:

a) first eq: flip it so as to put $C_2H_2$ on the product side
b) second eq: multiply it by two to get 2C
c) third eq: do nothing. We need one $H_2$ on the reactant side and that's what we have.

2) Rewrite all three equations with changes applied:

$2CO_2(g) + H_2O(l) \text{ ---> } C_2H_2(g) + (5/2)O_2(g) \quad \Delta H° = +1299.5\ kJ$

$2C(s) + 2O_2(g) \text{ ---> } 2CO_2(g)$ $\Delta H° = -787$ kJ

$H_2(g) + (1/2)O_2(g) \text{ ---> } H_2O(l)$ $\Delta H° = -285.8$ kJ

Notice that the ΔH values changed as well.

3) Examine what cancels:

$2CO_2 \Rightarrow$ first & second equation
$H_2O \Rightarrow$ first & third equation
$(5/2)O_2 \Rightarrow$ first & sum of second and third equation

4) Add up ΔH values for our answer:

+1299.5 kJ + (-787 kJ) + (-285.8 kJ) = +226.7 kJ

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**Problem #2:** The standard molar enthalpy of formation, $\Delta H_f°$ , of diborane cannot be determined directly because the compound cannot be prepared by reaction of boron and hydrogen. However, the value can be calculated. Calculate the standard enthalpy of formation of gaseous diborane ($B_2H_6$) using the following thermochemical information:

a) $4\ B(s) + 3\ O_2(g) \text{ ---> } 2\ B_2O_3(s)$ $\Delta H° = -2509.1$ kJ

b) $2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(l)$ $\Delta H° = -571.7$ kJ

c) $B_2H_6(g) + 3\ O_2(g) \text{ ----> } B_2O_3(s) + 3\ H_2O(l)$ $\Delta H° = -2147.5$ kJ

**Solution:**

1) An important key is to know what equation we are aiming for. The answer is in the word 'formation:'

$2B + 3H_2 \text{ ---> } B_2H_6$

Remember that formation means forming one mole of our target substance. This means that a one MUST be in front of the $B_2H_6$

2) In order to get to our formation reaction, the following must happen to equations (a), (b) and (c):

equation (a) - divide through by two
equation (b) - multiply through by 3/2
equations (c) - flip

Why?

equation (a) - this gives us 2B (from 4B) for our final equation
equation (b) - this gives us $3H_2$ for our final equation
equations (c) - this puts $B_2H_6$ on the right-hand side of the final equation

3) The above manipulations have consequences for the coefficients AND the ΔH° values. Rewrite equations

(a), (b) and (c):

a) $2\ B(s) + (3/2)\ O_2(g) \text{ ---> } B_2O_3(s)$ $\Delta H° = -1254.55$ kJ

b) $3\ H_2(g) + (3/2)\ O_2(g) \text{ ---> } 3\ H_2O(l)$ $\Delta H° = -857.55$ kJ

c) $B_2O_3(s) + 3\ H_2O(l) \text{ ---> } B_2H_6(g) + 3\ O_2(g)$ $\Delta H° = +2147.5$ kJ

Add the three equations and the ΔH° values:

$2B + 3H_2 \text{ ---> } B_2H_6$ $\Delta H° = +35.4$ kJ

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Here is the same diborane question, with slightly different numbers:

a) $4\ B(s) + 3\ O_2(g) \text{ ---> } 2\ B_2O_3(s)$ $\Delta H° = -2543.8$ kJ

b) $2\ H_2(g) + O_2(g) \text{ ---> } 2\ H_2O(g)$ $\Delta H° = -484.0$ kJ

c) $B_2H_6(g) + 3\ O_2(g) \text{ ----> } B_2O_3(s) + 3\ H_2O(l)$ $\Delta H° = -2032.9$ kJ

Calculate the standard enthalpy of formation of gaseous diborane ($B_2H_6$).

Just remember:

With all Hess's Law (of heat summation) problems, the chemical reactions given must add up to the final chemical equation. The key to these problems is that whatever you do to the reaction equation, you must do to the ΔH value. So, for example, if you reverse the equation, you must reverse the sign of ΔH. If you multiply the equation by 2, then you must multiply the ΔH value by 2.

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**Problem #3:** Given the following data:

$SrO(s) + CO_2(g) \text{ ---> } SrCO_3(s)$ $\Delta H = -234$ kJ

$2SrO(s) \text{ ---> } 2Sr(s) + O_2(g)$ $\Delta H = +1184$ kJ

$2SrCO_3(s) \text{ ---> } 2Sr(s) + 2C(s, gr) + 3O_2(g)$ $\Delta H = +2440$ kJ

Find the ΔH of the following reaction:

$C(s, gr) + O_2(g) \text{ ---> } CO_2(g)$

**Solution:**

1) Analyze what must happen to each equation:

a) first eq ⇒ flip it (this put the $CO_2$ on the right-hand side, where we want it)

b) second eq ⇒ do not flip it, divide through by two (no flip because we need to cancel the SrO, divide by two because we only need to cancel one SrO)

c) third equation ⇒ flip it (to put the $SrCO_3$ on the other side so we can cancel it), divide by two (since we need to cancel only one $SrCO_3$)

Notice that what we did to the third equation also sets up the Sr to be cancelled. Why not also multiply first equation by two (to get 2SrO for canceling)? Because we only want one $CO_2$ in the final answer, not two. Notice also that I ignored the oxygen. If everything is right, the oxygen will take care of itself.

2) Apply all the above changes (notice what happens to the ΔH values):

$SrCO_3(s) \text{ ---> } SrO(s) + CO_2(g)$ $\Delta H = +234$ kJ

$SrO(s) \text{ ---> } Sr(s) + (1/2)O_2(g)$ $\Delta H = +592$ kJ

$Sr(s) + C(s, gr) + (3/2)O_2(g) \text{ ---> } SrCO_3(s)$ $\Delta H = -1220$ kJ

3) Here is a list of what gets eliminated when everything is added:

$SrCO_3$, SrO, Sr, $(1/2)O_2$

The last one comes from $(3/2)O_2$ on the left in the third equation and $(1/2)O_2$ on the right in the second equation.

4) Add the equations and the ΔH values:

+234 + (+592) + (-1220) = -394

$C(s, gr) + O_2(g) \text{ ---> } CO_2(g)$ $\Delta H°_f = -394$ kJ

Notice the subscripted f. This is the formation reaction for $CO_2$ and its value can be looked up, either in your textbook or online.

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**Problem #4:** Given the following information:

$2NO(g) + O_2(g) \text{ ---> } 2NO_2(g)$ $\Delta H = -116$ kJ

$2N_2(g) + 5O_2(g) + 2H_2O(l) \text{ ---> } 4HNO_3(aq)$ $\Delta H = -256$ kJ

$N_2(g) + O_2(g) \text{ ---> } 2NO(g)$ $\Delta H = +183$ kJ

Calculate the enthalpy change for the reaction below:

$3NO_2(g) + H_2O(l) \text{ ---> } 2HNO_3(aq) + NO(g)$ $\Delta H = ???$

**Solution:**

1) Analyze what must happen to each equation:

a) first eq ⇒ flip; multiply by 3/2 (this gives me $3NO_2$ as well as the 3NO which will be necessary to get one NO in the final answer)

b) second eq ⇒ divide by 2 (give me my two nitric acid in the final answer)

c) third eq ⇒ flip (cancels 2NO as well as nitrogen)

2) Comment on the oxygens:

a) 1a above puts $(3/2)O_2$ on the right
b) 1b puts $(5/2)O_2$ on the left
c) 1c puts $(2/2)O_2$ on the right

a and c give $(5/2)O_2$ on the right to cancel out the $(5/2)O_2$ on the left

3) Apply all the changes listed above:

$3NO_2(g) \text{ ---> } 3NO(g) + (3/2)O_2(g)$ $\Delta H = +174$ kJ

$N_2(g) + (5/2)O_2(g) + H_2O(l) \text{ ---> } 2HNO_3(aq)$ $\Delta H = -128$ kJ

$2NO(g) \text{ ---> } N_2(g) + O_2(g)$ $\Delta H = -183$ kJ

4) Add the equations and the $\Delta H$ values:

+174 + (-128) + (-183) = -137

$3NO_2(g) + H_2O(l) \text{ ---> } 2HNO_3(aq) + NO(g)$ $\Delta H = -137$ kJ

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**Problem #5:** Calculate $\Delta H$ for this reaction: $CH_4(g) + NH_3(g) \text{ --> } HCN(g) + 3H_2(g)$

given:

$N_2(g) + 3\ H_2(g) \text{ ---> } 2\ NH_3(g)$ $\Delta H = -91.8$ kJ

$C(s) + 2\ H_2(g) \text{ ---> } CH_4(g)$ $\Delta H = -74.9$ kJ

$H_2(g) + 2\ C(s) + N_2(g) \text{ ---> } 2\ HCN(g)$ $\Delta H = +270.3$ kJ

**Solution:**

1) Analyze what must happen to each equation:

a) first eq ⇒ flip and divide by 2 (puts one $NH_3$ on the reactant side)

b) second eq ⇒ flip (puts one $CH_4$ on the reactant side)
c) third eq ⇒ divide by 2 (puts one HCN on the product side)

2) rewite all equations with the changes:

$NH_3(g)$ ---> $(1/2)N_2(g) + (3/2)H_2(g)$ $\Delta H = +45.9$ kJ

$CH_4(g)$ ---> $C(s) + 2\ H_2(g)$ $\Delta H = +74.9$ kJ

$(1/2)H_2(g) + C(s) + (1/2)N_2(g)$ ---> $HCN(g)$ $\Delta H = +135.15$ kJ

3) What cancels when you add the equations:

$(1/2)N_2(g)$ ⇒ first and third equations
$C(s)$ ⇒ second and third equations
$(1/2)H_2(g)$ on the left side of the third equation cancels out $(1/2)H_2(g)$ on the right, leaving a total of $3H_2(g)$ on the right (which is what we want)

4) Calculate the ΔH for our reaction:

+45.9 kJ plus +74.9 kJ plus +135.15 = 255.95 kJ = 260. kJ (to three sig figs)

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**Problem #6:** Given the following thermochemical equations:

$2H_2(g) + O_2(g)$ ---> $2H_2O(l)$ $\Delta H = -571.6$ kJ
$N_2O_5(g) + H_2O(l)$ ---> $2HNO_3(l)$ $\Delta H = -73.7$ kJ
$(1/2)N_2(g) + (3/2)O_2(g) + (1/2)H_2(g)$ ---> $HNO_3(l)$ $\Delta H = -174.1$ kJ

Calculate ΔH for the formation of one mole of dinitrogen pentoxide from its elements in their stable state at 25 °C and 1 atm.

**Solution:**

1) Here's the target equation:

$N_2 + (5/2)O_2$ ---> $N_2O_5$

2) Here's what you need to do:

1) divide equation by 2 and flip
2) flip second eq
3) multiply equation by 2

3) Here's the result:

$H_2O(l)$ ---> $H_2(g) + (1/2)O_2(g)$ $\Delta H = +285.8$ kJ
$2HNO_3$ ---> $N_2O_5(g) + H_2O(l)$ $\Delta H = +73.7$ kJ

$N_2(g) + 3O_2(g) + H_2(g) \text{ ---> } 2HNO_3(l)\ \Delta H = -348.2$ kJ

4) What cancels?

$H_2O$ - equation 1 and 2
$H_2$ - equation 1 and 3
$2HNO_3$ - equation 2 and 3
$(1/2)O_2$ - equation 1 and 3

This last cancel will reduce the $O_2$ from 6/2 to 5/2, which is what we want.

5) Add up the enthalpies:

+285.8 +73.7 -348.2 = +11.3 kJ

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**Problem #7:** The heats of combustion of C, $H_2$ and $CH_4$ at 298 K and 1 atm are respectively -393 kJ/mol, -286 kJ/mol and -892 kJ/mol. What is the enthalpy of formation for $CH_4$?

**Solution:**

1) The three combustion reactions are:

| | |
|---|---|
| $C + O_2 \text{ ---> } CO_2$ | $\Delta H = -393$ kJ |
| $H_2 + (1/2)O_2 \text{ ---> } H_2O$ | $\Delta H = -286$ kJ |
| $CH_4 + 2O_2 \text{ ---> } CO_2 + 2H_2O$ | $\Delta H = -892$ kJ |

2) The reaction we're looking for is:

$C + 2H_2 \text{ ---> } CH_4$

3) This is what the answerer on Yahoo Answers wrote:

This is a Hess's Law problem. If you multiply the first reaction by 1, the second by 2, and the third by negative 1 (write it backwards) they add together to give the reaction you're looking for. So, the enthalpy of the reaction you're solving for is equal to 1(-393) + 2(-286) + (-1)(-892). I'll let you finish it, the critical thing is understanding where the 1, 2, and -1 came from.

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**Problem #8:** What is the standard enthalpy of reaction for the reduction of iron (II) oxide by carbon monoxide?

$FeO(s) + CO(g) \text{ ---> } Fe(s) + CO_2(g)$

given the following information:

| | |
|---|---|
| $3Fe_2O_3(s) + CO(g) \text{ ---> } 2Fe_3O_4(s) + CO_2(g)$ | $\Delta H = -48.26$ kJ |
| $Fe_2O_3(s) + 3CO(g) \text{ ---> } 2Fe(s) + 3CO_2(g)$ | $\Delta H = -23.44$ kJ |

$$Fe_3O_4(s) + CO(g) \text{ ---> } 3FeO(s) + CO_2(g) \quad \Delta H = +21.79 \text{ kJ}$$

**Solution:**

1) Changes to be made to the data equations:

a) reverse equation 3 and multiply it by two (this puts FeO on the reactant side and gives us $2Fe_3O_4$ to cancel)
b) reverse equation 1 (this puts $Fe_3O_4$ on opposite side to compensate for switching equation 3)
c) multiply equation 2 by 3 (this will give $3Fe_2O_3$, allowing it to cancel)

Please note that no attention was paid to CO and $CO_2$. If everything else is done correctly, they should fall into line.

2) The three data equations with the changes applied:

$$2Fe_3O_4(s) + CO_2(g) \text{ ---> } 3Fe_2O_3(s) + CO(g) \quad \Delta H = +48.26 \text{ kJ}$$
$$3Fe_2O_3(s) + 9CO(g) \text{ ---> } 6Fe(s) + 9CO_2(g) \quad \Delta H = -70.32 \text{ kJ}$$
$$6FeO(s) + 2CO_2(g) \text{ ---> } 2Fe_3O_4(s) + 2CO(g) \quad \Delta H = -43.58 \text{ kJ}$$

3) Adding the three equations together gives:

$$6FeO(s) + 6CO(g) \text{ ---> } 6Fe(s) + 6CO_2(g)$$

and the enthalpy for the above reaction:

$$+48.26 + (-70.32) + (-43.58) = -65.64 \text{ kJ}$$

4) Dividing through by six gives the final answer:

$$FeO(s) + CO(g) \text{ ---> } Fe(s) + CO_2(g) \; \Delta H = -10.94 \text{ kJ}$$

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**Problem #9:** Determine the enthalpy of the following reaction:

$$3Fe_2O_3(s) + CO(g) \text{ ---> } 2Fe_3O_4(s) + CO_2(g)$$

given the folowing data:

$$Fe_2O_3(s) + 3CO(g) \text{ ---> } 2Fe(s) + 3CO_2(g) \; \Delta H = -23.44 \text{ kJ}$$
$$Fe_3O_4 + CO(g) \text{ ---> } 3FeO(s) + CO_2(g) \quad \Delta H = +21.79 \text{ kJ}$$
$$Fe(s) + CO_2(g) \text{ ---> } FeO(s) + CO(g) \quad \Delta H = -10.94 \text{ kJ}$$

**Solution:**

1) Apply the following changes to the data equations:

a) multiply first equation by 3 (to give us $3Fe_2O_3$)

b) flip second equation and multiply by 2 (to put $2Fe_3O_4$ on the product side)
c) multiply third equation by 6 (to cancel Fe and FeO)

Note that I have ignored the CO and $CO_2$. If everything works out, the right amounts will be there.

2) The result:

$3Fe_2O_3(s) + 9CO(g) \text{ ---> } 6Fe(s) + 9CO_2(g)$ $\Delta H = -70.32$ kJ
$6FeO(s) + 2CO_2(g) \text{ ---> } 2Fe_3O_4 + 2CO(g)$ $\Delta H = -43.58$ kJ
$6Fe(s) + 6CO_2(g) \text{ ---> } 6FeO(s) + 6CO(g)$ $\Delta H = -65.64$ kJ

3) Add the three equations and their enthalpies to obtain:

$3Fe_2O_3(s) + CO(g) \text{ ---> } 2Fe_3O_4(s) + CO_2(g)$ $\Delta H = -179.54$ kJ

Comment: I saw this problem on Yahoo Answers, but it had enthalpy values which were not the correct values (which are the values I used). Be aware of this practice (one with which I disagree). It is done to guard against someone finding the solved problem on the Internet with the correct values and just copying out the answer.

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**Problem #10:** Iron metal can be produced in a blast furnace through a complex series of reactions involving reduction of iron(III) oxide with carbon monoxide. The overall reacton is this:

iron(III)oxide + carbon monoxide ---> iron + carbon dioxide

Use the equations below to calculate ΔH for the overall equation.

(a) $3Fe_2O_3(s) + CO(g) \text{ ---> } 2Fe_3O_4(s) + CO_2(g)$ $\Delta H = -48.26$ kJ
(b) $Fe(s) + CO_2(g) \text{ ---> } FeO(s) + CO(g)$ $\Delta H = +10.94$ kJ
(c) $Fe_3O_4(s) + CO(g) \text{ ---> } 3FeO(s) + CO_2(g)$ $\Delta H = +21.79$ kJ

**Solution:**

1) Let's get a balanced equation for our target equation:

$Fe_2O_3 + 3CO \text{ ---> } 2Fe + 3CO_2$

2) Rearrange the three data equations so that, when added, they give the target equation:

a) leave untouched
b) flip, multiply by 6
c) multiply by 2

3) This results in:

(a) $3Fe_2O_3(s) + CO(g) \text{ ---> } 2Fe_3O_4(s) + CO_2(g)$ $\Delta H = -48.26$ kJ

(b) $6FeO(s) + 6CO(g) \dashrightarrow 6Fe(s) + 6CO_2(g)$ $\Delta H = -65.64$ kJ

(c) $2Fe_3O_4(s) + 2CO(g) \dashrightarrow 6FeO(s) + 2CO_2(g)$ $\Delta H = +43.58$ kJ

4) When the three equations are added together, this results in:

$3Fe_2O_3(s) + 9CO(g) \dashrightarrow 6Fe(s) + 9CO_2(g)$

and the $\Delta H$ is

$-48.26 + (-65.64) + 43.58 = -70.32$ kJ

5) To get the final answer, divide everything by 3:

$Fe_2O_3(s) + 3CO(g) \dashrightarrow 2Fe(s) + 3CO_2(g)$ $\Delta H = -23.44$ kJ

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