Hess's Law

Knowing how much heat is transferred as a chemical process occurs is very important. First of all, the direction of heat transfer is an important clue that helps predict in which direction a chemical reaction will go because, *at room temperature, most exothermic reactions are product-favored.* Second, we can use ΔH to calculate the heat obtainable when a fuel is burned. Third, when reactions are carried out on a larger scale, as in a chemical plant that produces sulfuric acid or ethene as a raw material for plastics, the surroundings must have enough cooling capacity to prevent an exothermic reaction from overheating and possibly damaging the plant. We therefore want to know ΔH values for as many reactions as possible.

For many reactions direct experimental measurements can be made by using a device called a calorimeter, but for many other reactions this is not a simple task. Besides, it would be very time-consuming to measure values for every conceivable reaction, and it would take a great deal of space to tabulate so many values. Fortunately there is a better way. It is based on the fact that mass *and* energy are conserved in chemical reactions.

Energy conservation is the basis of **Hess's Law**, which states that, *if a reaction is the sum of two or more other reactions, then* ΔH *for the overall process must be the sum of the* ΔH *values of the constituent reactions.*

For example: What is the heat of reaction for the reaction: A → D

Given…

1.	D → C	ΔH = +200 kJ
2.	A → B	ΔH = -150 kJ
3.	C → B	ΔH = +280 kJ

To calculate ΔH for the reaction: A --------→ D

Reverse 1	C → D	ΔH = -200 kJ
"as is" 2	A → B	ΔH = -150 kJ
Reverse 3	B → C	ΔH = -280 kJ
Net Reaction	A → D	ΔH = - 630 kJ

Hess's Law is useful because it enables us to find the enthalpy change for a reaction or state change that cannot be measured directly by experiment or indirectly.
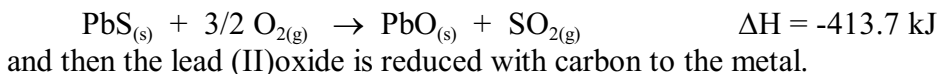
Using Hess's Law

Suppose we want to know the enthalpy change for the formation of methane, CH_4, from solid carbon (as graphite) and hydrogen gas: $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = ?$

The enthalpy change for the direct combination of the elements would be extremely difficult to measure in the laboratory. We can measure ΔH, however, when the elements and methane burn in oxygen

	Reaction	ΔH^0_f (kJ)
1.	$C_{(s)} + O_{2(g)} \quad \text{-------} \rightarrow \quad CO_{2(g)}$	-393.5
2.	$H_{2(g)} + O_{2(g)} \quad \text{-------} \rightarrow \quad H_2O_{(l)}$	-285.8
3.	$CH_{4(g)} + 2O_{2(g)} \quad \text{-------} \rightarrow \quad CO_{2(g)} + 2H_2O_{(l)}$	-890.3
	Net: $C_{(s)} + 2H_{2(g)} \quad \text{-------} \rightarrow \quad CH_{4(g)}$	-74.8

Hess's Law states that the enthalpy change for the direct reaction ($\Delta H net$) is the sum of the enthalpy changes along the alternative path [$\Delta H net = \Delta H_1 + 2\Delta H_2 - (-\Delta H_3]$
[Answer: - 74.8 kJ]

Lead has been known and used for centuries. To obtain the metal, lead (II) sulfide, (PbS: in the form of a common mineral called galena) is first roasted in air to form lead (II) oxide (PbO).

$PbS_{(s)} + 3/2\ O_{2(g)} \rightarrow PbO_{(s)} + SO_{2(g)}$ $\Delta H = -413.7$ kJ

and then the lead (II)oxide is reduced with carbon to the metal.

$PbO_{(s)} + C_{(s)} \rightarrow Pb_{(s)} + CO_{(g)}$ $\Delta H = +106.8$ kJ

What is the enthalpy change for the following reaction?

$PbS_{(s)} + C_{(s)} + 3/2\ O_{2(g)} \rightarrow Pb_{(s)} + CO_{(g)} + SO_{2(g)}$
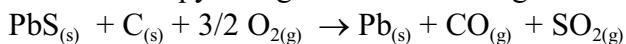
[Answer: $\Delta H = - 306.9$ kJ]

Is the reaction exothermic or endothermic? How much energy, in kilojoules, is required (or evolved) when 454 g of PbS is converted to lead?

[Answer: Exothermic, - 582.3 kJ]

STATE FUNCTIONS

Energy, pressure, volume and temperature are all said to be state functions. Properties that are determined by the state of the system regardless of how that condition was achieved, i.e. when the state of the system changes, then the magnitude of the change of any state of the system depends only on the initial and the final state of the system and not how that change is accomplished.

Hess's Law works because the enthalpy change for a reaction is a **state function**, a quantity whose value is determined only be the state of the system.

The enthalpy change for a chemical or physical change does not depend on the path you choose to go from the initial conditions to the final conditions.

The enthalpy of a system depends on the substances present and their physical states and temperatures and not on how the system was prepared.

No matter how you go from reactants to products in a reaction the net heat evolved or required (at constant pressure) is always the same.

This point is illustrated in the formation of methane. For the reaction:

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta H = -78.4 \text{ kJ}$$
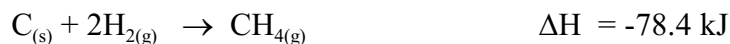
The enthalpy change for the direct reaction (ΔH direct = -74.8 kJ) is the same as the sum of the enthalpy changes along the indirect pathway that goes through carbon dioxide and water:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$
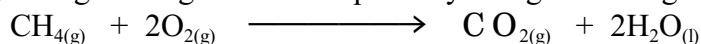
Many commonly measured quantities, such as the pressure of a gas, the volume of a gas or liquid, the temperature of a substance, and the size of your bank account, are state functions. You could have arrived at a current bank balance of $25 by having deposited $25, or you could have deposited $100 and then withdrawn $75.

The volume of a balloon is also a state function. You can blow up a balloon to a large volume and then let some air out to arrive at the desired volume. Alternatively, you can blow up the balloon in stages, adding tiny amounts of air at each stage. The final volume does not depend on how you got there.

For both bank accounts and balloons, an infinite number of ways exist for how to arrive at the final state, but the final value depends only on the size of the bank balance or the balloon, and not on the path taken from the initial to the final state.

Because enthalpy is a state function, in principle there is an absolute enthalpy for the reactants ($H_{initial} = H_{reactants}$) and for the products ($H_{final} = H_{products}$). The difference between these enthalpies is the change for the system:

$$\Delta H_{reaction} = H_{final} - H_{initial}$$
$$= H_{products} - H_{reactants}$$

Because the reaction starts and finishes at the same place no matter which pathway is chosen, $\Delta H_{reaction}$ must always be independent of pathway. Unlike volume, temperature, pressure, energy or a bank balance, however, the absolute enthalpy of a substance is not usually determined, only its change in a chemical or physical process. The thermal energy evolved or required in a chemical process, for example, is a reflection of the *difference* in enthalpy between the reactants and products. We determine only whether the enthalpy of the products is greater than or less than that of the reactants by some amount.

The **Equation** I below can be used to find the standard enthalpy change for a reaction, $\Delta H°_{rxn}$:

Enthalpy change for a reaction = $\Delta H°_{rxn}$ = Σ [$\Delta H°_f$ (products)] - Σ [$\Delta H°_f$ (reactants)]

    Standard enthalpy change = standard enthalpy of products - Standard enthalpy of reactants
    The standard enthalpy of a substance = its standard enthalpy of formation

In the above Equation I, the symbol Σ (the Greek letter *sigma*) means to "take the sum" Thus, to find $\Delta H°_{f\ rxn}$ you add up the molar enthalpies of formation of the products and subtract from this sum, the sum of the molar enthalpies of formation of the reactants.

Hess' Law and the Use of standard Enthalpy Changes of Formation $\Delta H°_f$

Equation I is a convenient way to apply Hess' law when the enthalpies of formation of all the reactants and products are known. Let us look again at the decomposition of calcium carbonate:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \qquad\qquad \Delta H°_{rxn} = ?$$

and think about an alternative route from the reactant to the products. We can imagine the reaction as occurring by first breaking $CaCO_3$ up into its elements, and then recombining the elements in a different way to produce CO_2 and CaO.
The enthalpy change for each step in this process is known …

Step 1, below, is the reverse of the equation for the formation of $CaCO_3$, so the enthalpy change is the negative of the enthalpy of formation of $CaCO_3$.
For the other two steps, $\Delta H°_{rxn}$ is the same as the enthalpy of formation.
Notice that the sum of reactions 1, 2 and 3 gives the equation for the net reaction.
Most importantly, notice that $\Delta H°_{rxn}$ for the net reaction is the sum of the enthalpy changes for each step. Here:

$$\Delta H°_{rxn} = [1mol\ \Delta H°_f CaO_{(s)} + 1mol\ \Delta H°_f\ CO_{2(g)}\ ] - [1mol\ \Delta H°_f\ CaCO_{3(s)}]$$

This is exactly the result given by applying Equation I above. The enthalpy change for the reaction is indeed the sum of the enthalpies of formation of the products minus that of the reactant.

Reaction		$\Delta H°_{rxn}$
Step 1	$CaCO_{3(s)} \longrightarrow Ca_{(s)} + C_{(s)} + 3/2\ O_{2(g)}$	$-\Delta H°_f$ [$CaCO_{3(s)}$] = -(-1206.9 kJ)
Step 2	$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$	$\Delta H°_f$ [$CO_{2(g)}$] = -393.5 kJ
Step 3	$Ca_{(s)} + 1/2O_{2(g)} \longrightarrow CaO_{(s)}$	$\Delta H°_f$ [$CaO_{(s)}$] = -635.1 kJ
Net	$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$	$\Delta H°_{rxn}$ = + 178.3 kJ

Using Enthalpies of Formation

Example 1

Nitroglycerin is a powerful explosive giving for different gases when detonated:

$$2C_3H_5(NO_3)_{3\,(l)} \rightarrow 3N_{2(g)} + 1/2O_{2(g)} + 6CO_{2(g)} + 5H_2O_{(g)}$$
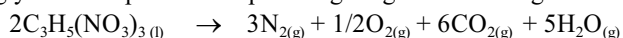
Given that the enthalpy of formation of nitroglycerin, $\Delta H°_f$, is -364 kJ/mol, and consulting your **Data Book** for the enthalpies for the other compounds, (i.e. for $6CO_{2(g)} + 5H_2O_{(g)}$, and standard enthalpy of elements is zero), calculate the energy (heat at constant pressure) liberated when 10.0 g of nitroglycerin is detonated.

Solution

$\Delta H°_{rxn} = $ -2845 kJ using Equation 1 above

Based on the enthalpy change for the explosion of 2 moles of nitroglycerin, we can calculated the heat liberated by this exothermic reaction when only 10.0 g of nitroglycerin is used. Molar mass of nitroglycerin = 227.1 g mol^{-1}, i.e 0.044 mol of nitroglycerin $\therefore \Delta H$ = -62.6 kJ

Example 2

Benzene, C_6H_6, is an important hydrocarbon. Calculate its enthalpy of combustion; that is, find the value of $\Delta H°$ for the following reaction using Equation I: $C_6H_{6(l)} + 15/2\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 3\ H_2O_{(l)}$

Solution

The enthalpy of formation of benzene, $\Delta H°_f[C_6H_{6(l)}] = +$ 49.0 kJ/mol. Use any other data, i.e for $CO_{2(g)}$ and $H_2O_{(g)}$, and enthalpy of formation for elements such as $O_{2\,(g)}$ is zero you many need from the Data Book. [Answer: - 3.17 x 10^3 kJ mol^{-1}]

Example 3

Calculate the enthalpy of combustion of ethanoic acid, $CH_3COOH_{(l)}$, the enthalpy of formation of ethanoic acid, $\Delta H_f^0 = $ - 2003 kJ mol^{-1}:

$$CH_3COOH_{(l)} + 3\ O_{2(g)} \longrightarrow 2CO_{2(g)} + 4H_2O_{(g)}$$
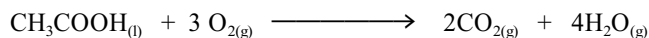
Example 4
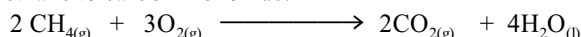
Standard enthalpies of combustion of graphite and diamond are - 393.5 kJ mol^{-1} are - 395.4 kJ mol^{-1}. Calculate the change in enthalpy for the change: graphite $\longrightarrow$ diamond
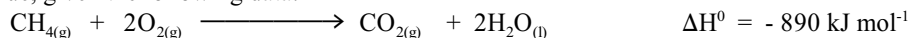
(Answer: $\Delta H^0 = +$ 1.9 kJ mol^{-1})

Example 5

a) Explain why it is difficult to obtain an experimental value for the standard enthalpy of reaction for the combustion of methane to carbon monoxide:

$$2\ CH_{4(g)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 4H_2O_{(l)}$$

b) Calculate a value, given the following data:

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H^0 = - 890\ kJ\ mol^{-1}$$
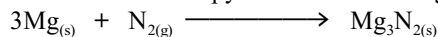$$CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} \qquad \Delta H^0 = - 566.0\ kJ\ mol^{-1}$$

Solution

a) Oxidation produces CO_2 as well as CO   b) $\Delta H^0 = $ - 1214 kJmol^{-1}

Example 6

When 2.00 g of magnesium reacts with nitrogen to form magnesium nitride, Mg_3N_2, the heat evolved is 12.7 kJ. Calculate the standard enthalpy of formation of magnesium nitride.

$$3Mg_{(s)} + N_{2(g)} \longrightarrow Mg_3N_{2(s)}$$

Solution: $\Delta H^0 = $ - 457 kJ mol^{-1}

Using Hess's Law Experimentally

1. What experiments would you do to find the standard enthalpy of formation of solid calcium hydroxide? $Ca_{(s)} + O_{2(g)} + H_{2(g)} \rightarrow Ca(OH)_{2\,(s)}$ $\Delta H°_f = ?$

We know from experience that the enthalpy change for the reaction cannot be measured directly in any convenient manner. It is therefore necessary to break down the formation of calcium hydroxide into a series of reactions that can be added together to give the equation for the formation of solid $Ca(OH)_2$ from the elements and whose enthalpy changes can be determined in a calorimeter.

2. How would you determine the enthalpy of hydration of magnesium sulphate, for the following reaction: $MgSO_{4(s)} + 7\ H_2O_{(l)} \longrightarrow MgSO_4.7H_2O_{(s)}$

[You will be provided with $MgSO_{4(s)}$, and $MgSO_4.7H_2O_{(s)}$]