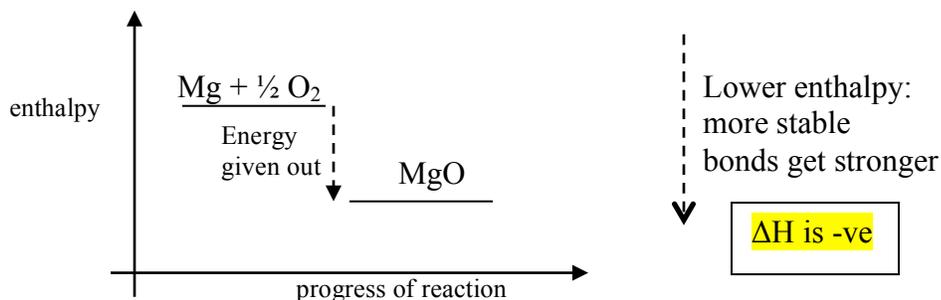# Enthalpy Changes

Enthalpy is chemical energy, given the symbol **H**. We are interested in enthalpy changes – resulting from the transfer of energy between chemical substances (the system) and the surroundings as a result of reactions, in accordance with the law of conservation of energy.

The **enthalpy change of reaction, ΔH**, is the enthalpy change when the number of moles of reactants, as specified in a balanced equation, react together.
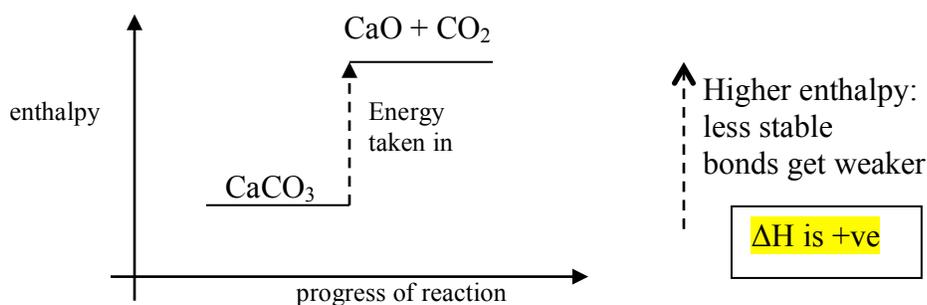
An **exothermic reaction** is a reaction in which energy is transferred from the chemical system to the surroundings. There is a decrease of internal energy (enthalpy), so the value of ΔH is negative. There is a corresponding increase in heat energy in the surroundings, according to the law of mass conservation, which results in an increase in temperature.

Consider Mg + ½ O_2 → MgO - the magnesium burns with a white flame, lots of heat is given out.

enthalpy | Mg + ½ O_2
Energy given out | MgO
progress of reaction

Lower enthalpy:
more stable
bonds get stronger

ΔH is -ve

The products are lower in enthalpy than the reactants which is what we mean by the reaction is exothermic. We would say that the products are (thermodynamically) more stable than the reactants – an idea associated with the bonds in MgO being stronger than those in Mg and O_2. The lower the enthalpy of a substance, the more stable is its bonding and the more energy is required to break those bonds.

Endothermic reactions are characterised by the transfer of energy from the surroundings to the chemical system, resulting in an increase in enthalpy so that ΔH is positive. There is a corresponding decrease in heat energy in the surroundings.

enthalpy | CaO + CO_2
Energy taken in
$CaCO_3$
progress of reaction

Higher enthalpy:
less stable
bonds get weaker

ΔH is +ve

Most endothermic reactions are therefore carried out at a high temperatures. The high temperature gives the energy needed to break bonds (i.e. to exceed the activation energy for the reaction).
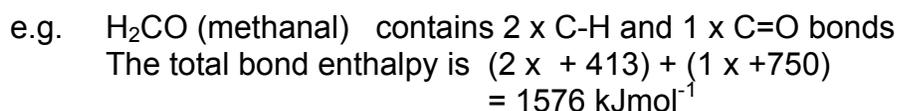
Bond breaking

Energy must be supplied to break bonds. This energy is called the **bond enthalpy**. Bond enthalpies are positive values because energy has to be supplied to break the bonds, so bond breaking is an endothermic process.

e.g. $H_2(g) \rightarrow H(g) + H(g)$ $\Delta H = +436$ kJ mol^{-1}
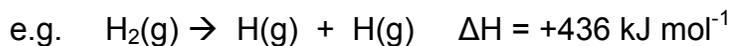
Definition: The bond enthalpy is the energy required to break one mole of a specific bond in a substance, in the gaseous state. (i.e. free from the influences of intermolecular forces from other substances nearby).
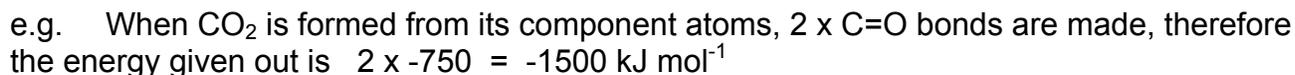
The values published in tables are usually **average** bond enthalpies. They are the average value of the bond enthalpy for the same bond in different molecules. The individual values vary a little because of the varying chemical environment. **Note: Average bond enthalpies are valid to use for the bonds in gaseous substances only**.

We can add up the average bond enthalpies to determine the energy required to break the all the bonds in a substance into its component atoms.

e.g. H_2CO (methanal)   contains 2 x C-H and 1 x C=O bonds
       The total bond enthalpy is (2 x + 413) + (1 x +750)
                                 = 1576 kJmol^{-1}

Bond making

Energy is given out when bonds are formed. The amount given out is equal and opposite to the bond enthalpy (i.e. the same value, but negative). Bond formation is therefore an exothermic process.

e.g.   When CO_2 is formed from its component atoms, 2 x C=O bonds are made, therefore the energy given out is   2 x -750 = -1500 kJ mol^{-1}

Calculated values of ΔH for a reaction

First of all, the necessary bonds in the reactants need to be broken – an endothermic step with a positive enthalpy change – then the new bonds in the products need to be made – an exothermic step with a negative enthalpy change. We can therefore use the published (average) bond enthalpies for each bond broken or made to work out the overall enthalpy change for a reaction:

ΔH = Σ(bonds broken) + Σ(bonds made)

Application:
For example: $CH_4 + 2O_2$ → $CO_2 + 2H_2O$
Bonds broken: 4 x C-H   = 4 x +413   Bonds made: 2 x C=O = 2 x -750
                  2 x O=O   = 2 x+498   4 x H-O   = 4 x -464
                  Total = +2648 kJ mol^{-1} Total = -3356 kJ mol^{-1}

ΔH = +2648 + (– 3356) = -708 kJmol^{-1} so the reaction is exothermic (ΔH –ve)

Activation Energy, E_A

The process of breaking the necessary bonds in the reactants requires an total amount of energy called the **Activation Energy**. In an exothermic reaction, the heat given out continues to provide the E_A as the reaction continues. Endothermic reactions need to be heated (or an alternative energy supplied e.g. light) to keep providing the E_A.

We show enthalpy changes using an **enthalpy profile diagram**;, enthalpy on the y-axis against "progress of the reaction" along the x-axis (a sort of time axis).
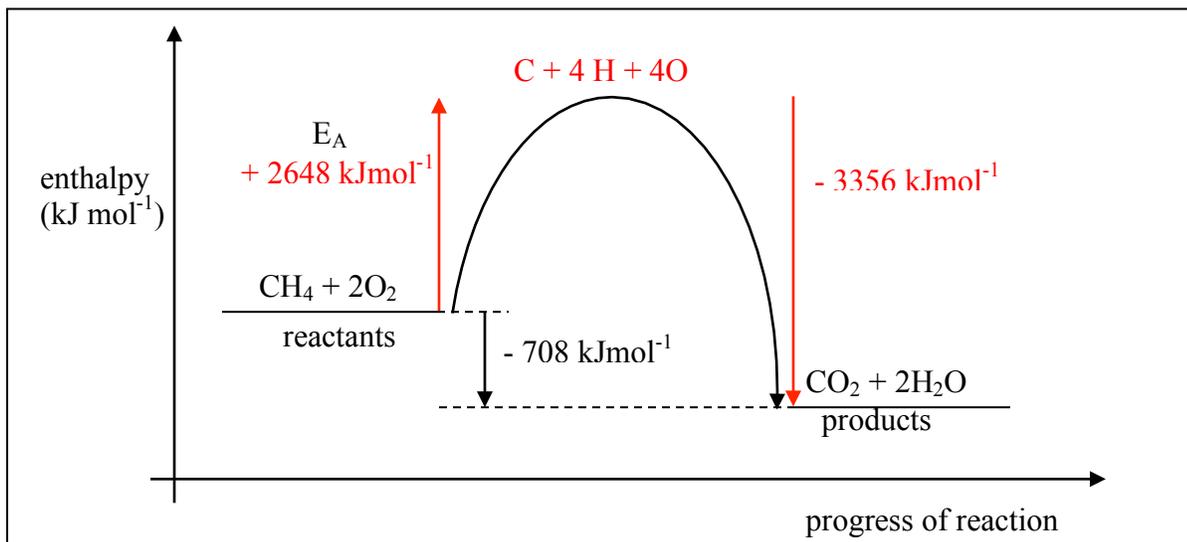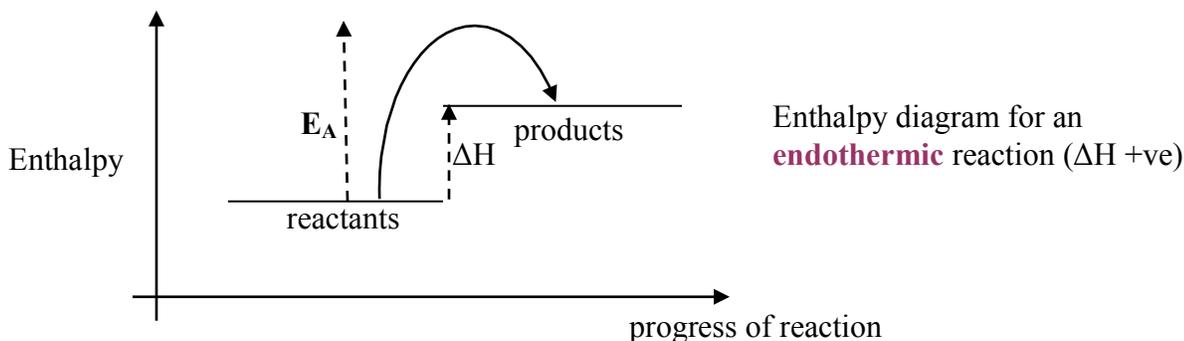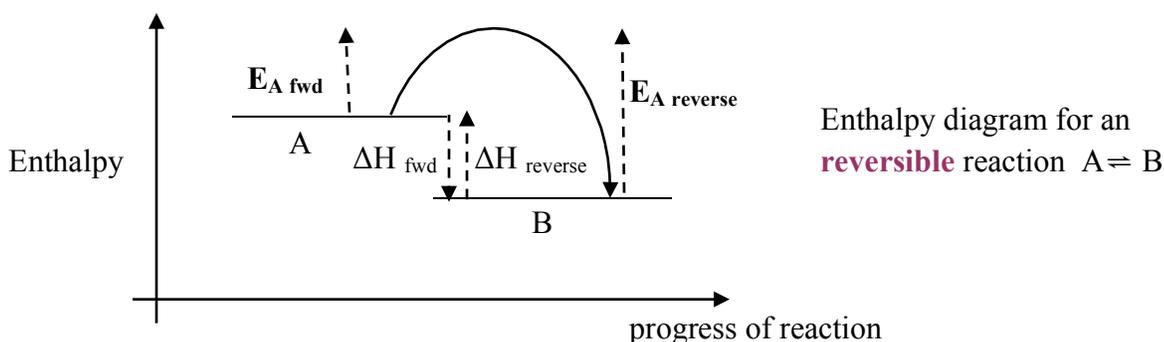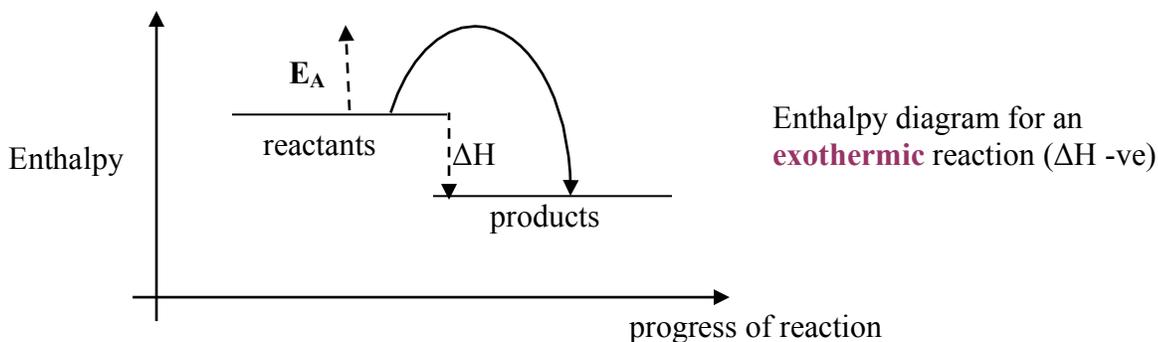

It is easy to see from an enthalpy profile diagram whether a reaction is exothermic or endothermic, and we can also show the Activation Energy (E_A) –the energy required to break the necessary bonds in the reactants (which is the same as minimum energy the reactant need to collide with in order for a reaction to be successful).

Link between E_A and rate of reaction

The rate of a reaction is directly affected by E_A, the activation energy. The activation energy represents the energy with which the reactants need to collide in order to break the necessary bonds in the reactants, so the lower E_A is, the more likely it is that each collision will be successful, and the faster the rate will be (or the more likely that the reaction will take place).

Endothermic reactions typically have larger E_A than exothermic reactions. These reactions are slower, or less likely to take place NOT because they are endothermic but because of the high activation energy.


Enthalpy diagram for an **endothermic** reaction (ΔH +ve)

Enthalpy diagram for an **exothermic** reaction (ΔH -ve)

Enthalpy diagram for an **reversible** reaction $A \rightleftharpoons B$

Standard enthalpy changes

Standard conditions, denoted with a $^\ominus$ symbol, are needed in order to compare enthalpy changes between different reactions. Standard conditions are: temperature of 298K (which is close to room temperature, being 25°C) and pressure of 100kPa (which is close to atmospheric pressure as 1 atmosphere = 101kPa), and substances in their **standard states** which means they are in the physical state they would be in at 25°C and 1 atmosphere pressure.

The enthalpy changes of reactions carried out under standard conditions, are referred to as **standard enthalpy changes** of reaction. We define these for a number of specific types of reaction:

The **standard enthalpy change of formation**, **$\Delta_f H^\ominus$**, is the enthalpy change when one mole of a substance is formed from its elements under standard conditions with reactants and products in their standard states.

We may be asked to write an equation to illustrate this, e.g. the standard enthalpy change of formation of calcium oxide would be represented as:

$$\text{Ca(s)} + \tfrac{1}{2}\,\text{O}_2\text{(g)} \quad \rightarrow \quad \text{CaO(s)}$$
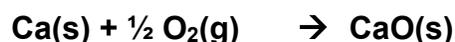
… because calcium is a solid metal at 25°C and oxygen is a gas at 25°C and 1 atm, and the calcium oxide formed is a solid under these conditions. The equation is balanced to show just 1 mole of CaO being made, using fractions on the left hand side as necessary.

i) Write an equation to show the standard enthalpy change of formation of ethanol, C_2H_5OH

ii) All elements have the same enthalpy change of formation. Explain this statement.

The **standard enthalpy change of combustion, $\Delta_cH^\ominus$**, is the enthalpy change when one mole of a substance is completely burned (i.e. in an excess of oxygen) under standard conditions, and with reactants and products in their standard states.
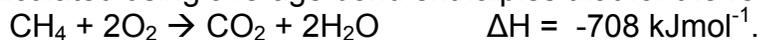
We may be asked to write an equation to illustrate this, e.g. the standard enthalpy change of combustion of ethane should be shown as:

$$C_2H_{6(g)} + 3\tfrac{1}{2}\,O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$
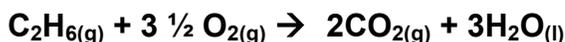
… because ethane, oxygen and carbon dioxide are gases at 25°C and 1 atm, and water is a liquid, and because the equation has been balanced to show exactly one mole of ethane being burnt (despite needing to use a fractional number of moles of oxygen).

Limitation of using average bond enthalpies
We earlier calculated using average bond enthalpies that for the reaction
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H = -708 \text{ kJmol}^{-1}.$$
The published value for $\Delta_cH^\ominus$ for this reaction is -890 kJmol^{-1}. The discrepancy arises because ΔH calculated with bond enthalpies assumes all reactants and products are gases (because that's how bond enthalpies are defined). Standard conditions requires the states to be correct at room temp and pressure, and under these conditions water is a liquid, not a gas.
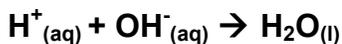
Check your understanding:
iii) Write an equation to show the standard enthalpy change of combustion of ethanol.

The **standard enthalpy change of neutralisation, $\Delta_{neut}H^\ominus$** is the enthalpy change when an acid and a base react to form one mole of water, under standard conditions and with reactants and products in their standard states.

We may be asked to write an equation to illustrate this, e.g. the standard enthalpy change of neutralisation of phosphoric acid by sodium hydroxide should be shown as:

$$\tfrac{1}{3}H_3PO_{4(aq)} + NaOH_{(aq)} \rightarrow \tfrac{1}{3}Na_3PO_{4(aq)} + H_2O_{(l)}$$
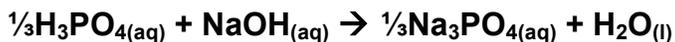
… because phosphoric and and sodium hydroxide were solutions at 25°C and 1 atm, and because water is a liquid, and because the equation has been balanced to show exactly one mole of water being produced (despite needing to use a fractional number of moles of phosphoric acid and sodium phosphate). Note that this will reduce to the ionic equation:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Check your understanding:
iv) Write an equation to show the standard enthalpy change of neutralisation of dilute nitric acid by solid calcium hydroxide.

v) The enthalpy change of neutralisation of dilute sulphuric acid, of dilute nitric acid and of dilute hydrochloric acid by any alkali has the same value. Explain this statement.

Using standard enthalpy changes
We use standard enthalpies for making fair comparisons – an example might be comparing different fuels to determine how much energy each produces per mole of CO_2 released into the atmosphere.
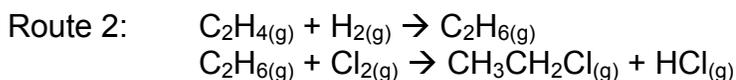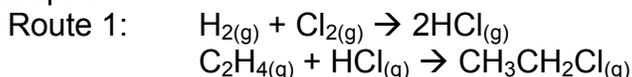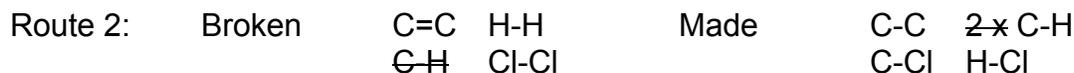
Application

$CH_4 + 2O_2 \rightarrow CO_2 + 2 H_2O$ $\qquad\qquad$ $\Delta_cH^\ominus = $ -890 kJ mol^{-1}

$C_8H_{18} + 12½ O_2 \rightarrow 8CO_2 + 9H_2O$ $\qquad$ $\Delta_cH^\ominus = $ -5472 kJ mol^{-1}

Therefore octane produces 5472 ÷ 8 = 684 kJ per mole of CO_2 produced. Methane produces 890 kJ of energy per mole of CO_2 produced, showing that methane is a more environmentally friendly fuel than octane.

Hess's Law
We can often turn one substance into another by a variety of different reaction sequences. For example:

Route 1: $\quad$ $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$
$\qquad\qquad$ $C_2H_{4(g)} + HCl_{(g)} \rightarrow CH_3CH_2Cl_{(g)}$

Route 2: $\quad$ $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$
$\qquad\qquad$ $C_2H_{6(g)} + Cl_{2(g)} \rightarrow CH_3CH_2Cl_{(g)} + HCl_{(g)}$

By considering bonds broken and made we can calculate the enthalpy changes for each of these reactions.

Route 1: $\quad$ Broken $\qquad$ H-H $\quad$ Cl-Cl $\qquad$ Made $\qquad$ ~~2 x~~ H-Cl
$\qquad\qquad\qquad\qquad\qquad$ C=C $\quad$ ~~H-Cl~~ $\qquad\qquad\qquad$ C-C $\quad$ C-Cl $\quad$ C-H

Route 2: $\quad$ Broken $\qquad$ C=C $\quad$ H-H $\qquad\quad$ Made $\qquad$ C-C $\quad$ ~~2 x~~ C-H
$\qquad\qquad\qquad\qquad\qquad$ ~~C-H~~ $\quad$ Cl-Cl $\qquad\qquad\qquad\quad$ C-Cl $\quad$ H-Cl

Without doing the calculations, we can see that in either route the same bonds are broken and made, just in a different sequence. We can therefore conclude that the <u>overall</u> enthalpy change will be the same regardless of the route taken. This is **Hess's Law**.

<mark>The total enthalpy change for a reaction is the same no matter which route the reaction takes, provided the initial and final conditions are the same.</mark>
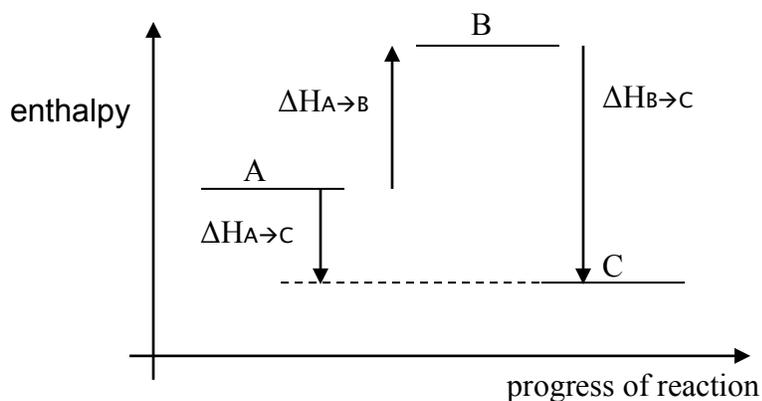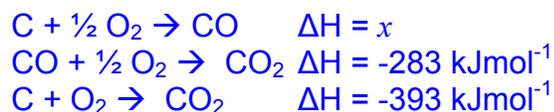
In practice, Hess's Law means that $\Delta H_{A \to C} = \Delta H_{A \to B} + \Delta H_{B \to C}$
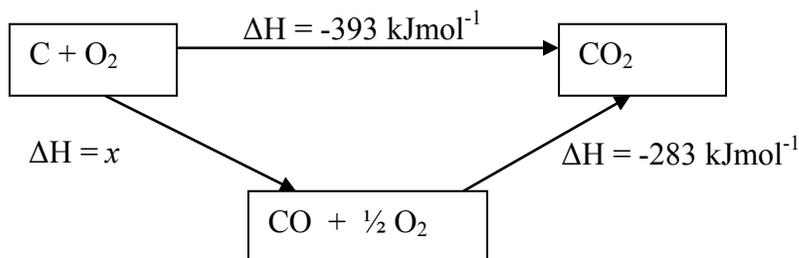
We can use this to help calculate the enthalpy change during a reaction if we know other enthalpy changes and can form a **cycle**. We would want to do this for any reaction where we couldn't measure the enthalpy change directly e.g. because the reaction doesn't work at all, or only happens inside a complex system such as photosynthesis.

Application:
When we burn carbon, it is very difficult to get only CO as the product and no CO_2 formed, so we can't measure the enthalpy change of formation of CO directly. We can burn carbon to form only CO_2, however, and we can also burn CO to form only CO_2 so the enthalpy changes for these reactions could be measured directly.

$$C + \tfrac{1}{2} O_2 \to CO \qquad \Delta H = x$$
$$CO + \tfrac{1}{2} O_2 \to CO_2 \quad \Delta H = -283 \text{ kJmol}^{-1}$$
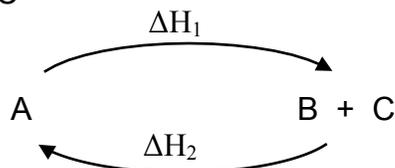$$C + O_2 \to CO_2 \qquad \Delta H = -393 \text{ kJmol}^{-1}$$

We can draw a **Hess Cycle** for this:

Using Hess's law, $x + (-283) = -393$ therefore $x = -393 - (-283) = -110$
So $C + \tfrac{1}{2} O_2 \to CO \qquad \Delta H = -110 \text{ kJmol}^{-1}$

Reversible reactions

We can also see why the enthalpy change in a reversible reaction is equal and opposite.
Consider $A \rightleftharpoons B + C$

$$\Delta H_1$$

A   B + C

$$\Delta H_2$$

We can either leave A alone, in which case the enthalpy change is zero, or we can turn A into B + C, then turn B + C back into A. Hess's law says the enthalpy change for doing this must be the same, i.e. 0, so $\Delta H_1 = -\Delta H_2$. You should be able to see that Hess's Law is a consequence of the law of conservation of energy.

Check your understanding

Given that for $CH_{4(g)} + O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta_c H = -708 \text{ kJmol}^{-1}$
And the following average bond enthalpies: H-H   436 kJmol^{-1}
                                                O=O   498 kJmol^{-1}
                                                C=O   750 kJmol^{-1}
                                                O-H   464 kJmol^{-1}

vi) Use the bond enthalpies to calculate ΔH for $C_{(g)} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

vii) Use the Hess Cycle below to calculate ΔH for the reaction $C_{(g)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ which cannot be measured directly as carbon does not react with hydrogen in this way, and if it did, methane would not be the only product formed.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2\,H_2O$$

$$C + 2H_2 + 2O_2$$
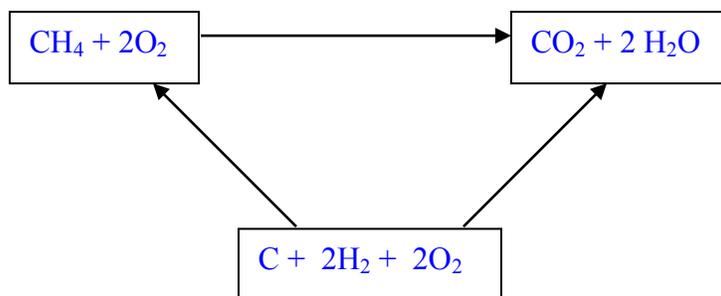
viii) The published value for the standard enthalpy change of formation, $\Delta_f H^{\ominus}$, of methane is -76 kJmol^{-1}. Explain the difference between this value and the one you calculated in vii).

Using enthalpies of combustion in Hess Cycles

Enthalpies of combustion are comparatively easy to measure experimentally, and so are used to calculate the enthalpy changes for other reactions which would not be so easy to do directly.

We can work out any kind of enthalpy change (reaction, combustion, formation) this way – doesn't matter. What is key is what kind of data we are given in the question. We recognise this type of question because we are given $\Delta_c H$ values to work with.

The layout is always the same:
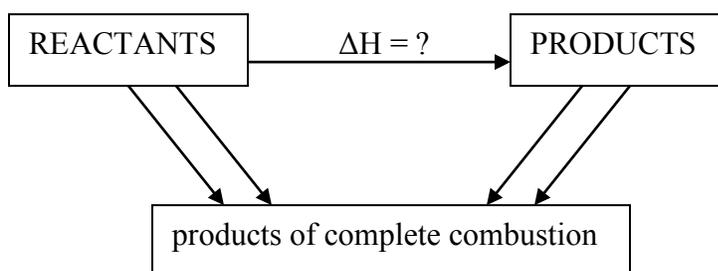
In general, if we prefer to use maths rather than the diagrammatic approach, we can use the equation below when we are given enthalpies of combustion, so long as we remember to multiply the $\Delta H^\circ c$ values by the appropriate number of moles :
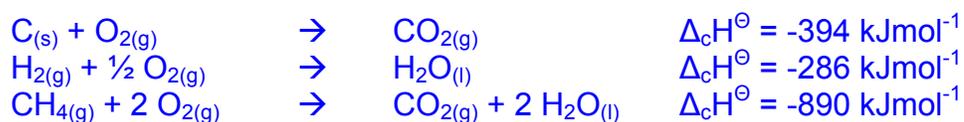
$$\Delta_r H^\ominus = \Sigma \Delta_c H^\ominus \text{ reactants } - \Sigma \Delta_c H^\ominus \text{ products}$$
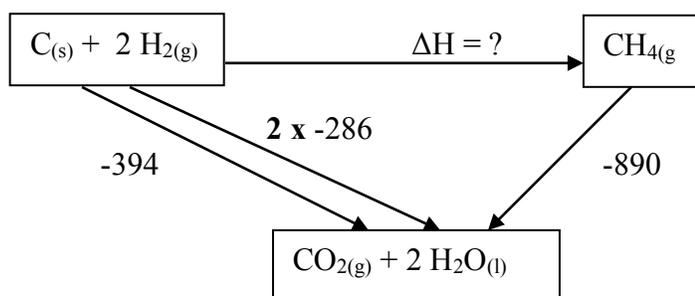
Application:
Carbon and hydrogen don't react to form methane when directly mixed, but if they <u>did</u> react, would the reaction be exothermic or endothermic ? What we are working out here is actually the enthalpy change of formation of methane:

$$C(s) + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \Delta_f H^\ominus = ?$$

We can use the standard enthalpies of combustion for carbon, hydrogen, and methane. All will burn readily and the energy released can be measured.

$C_{(s)} + O_{2(g)}$	$\rightarrow$	$CO_{2(g)}$	$\Delta_c H^\ominus = -394 \text{ kJmol}^{-1}$
$H_{2(g)} + \frac{1}{2} O_{2(g)}$	$\rightarrow$	$H_2O_{(l)}$	$\Delta_c H^\ominus = -286 \text{ kJmol}^{-1}$
$CH_{4(g)} + 2 O_{2(g)}$	$\rightarrow$	$CO_{2(g)} + 2 H_2O_{(l)}$	$\Delta_c H^\ominus = -890 \text{ kJmol}^{-1}$

Now we can draw the Hess Cycle:

And calculate $\Delta H = -394 + (2 \times -286) + 890 = -76 \text{ kJmol}^{-1}$
So the reaction would be exothermic if it happened.

CHECKING A HESS CYCLE – MASK CHECK

M – moles correctly multiplied up on arrows depending on balanced equation
A – arrows in correct direction depending on type of Hess cycle
S – signs correctly transferred from arrows into the calculation
K – knowledge (does the answer fit with your experience ?)

Check your understanding:
ix) Calculate $\Delta H^{\ominus}$ for the cracking of decane to give octane and ethene using the standard enthalpy changes of combustions given in an appropriate Hess Cycle:

decane, $\Delta_c H^{\ominus}$ = -6777.9 kJmol-1
octane, $\Delta_c H^{\ominus}$ = -5470.2 kJmol-1
ethene $\Delta_c H^{\ominus}$ = -1410.8 kJmol-1

Using enthalpies of formation in Hess Cycles
Enthalpies of formation are also available in the data books, and are also very useful for calculating enthalpy changes for "inaccessible" reactions.

We can work out any kind of enthalpy change (reaction, combustion, formation) this way. What is key is what kind of data we are given in the question. For these we'll be given $\Delta_f H^{\ominus}$ values to work with.

The layout is always the same: Note the different direction of the arrows !
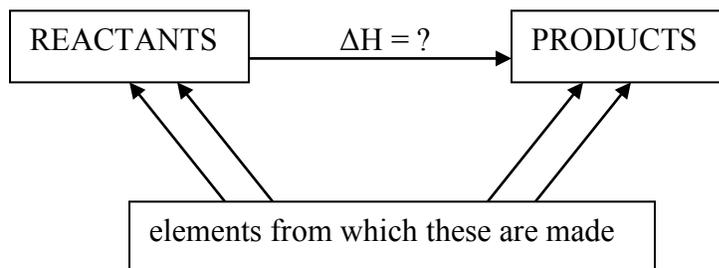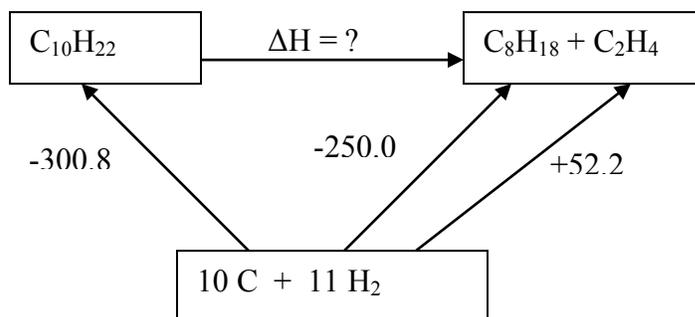

We can write a general mathematical formula in the same way as before if we prefer:

$\Delta_r H^{\ominus}$ = Σ $\Delta_f H^{\ominus}$ products - Σ $\Delta_f H^{\ominus}$ reactants

Application:
We can consider the cracking of decane as before and prove that we can get the same answer regardless of what type of enthalpy changes we use in the Hess cycle. We'll need the enthalpies of formation of decane, octane and ethene:

decane	$\Delta_f H^{\ominus}$	= -300.8 kJmol^{-1}
octane	$\Delta_f H^{\ominus}$	= -250.0 kJmol^{-1}
ethene	$\Delta_f H^{\ominus}$	= +52.2 kJmol^{-1}

$$C_{10}H_{22} \xrightarrow{\Delta H = ?} C_8H_{18} + C_2H_4$$

-300.8   -250.0   +52.2

$$10\ C\ +\ 11\ H_2$$

So ΔH = +300.8 – 250.0 + 52.2 = +103.0 kJmol^{-1} (which should be the same as you got with the previous "Check your Understanding" question !)

Check your understanding:
x) A reaction to manufacture hydrogen for use in the Haber process is carried out at high temperature, using natural gas and steam: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3\ H_{2(g)}$
Use the given enthalpies of formation to work out the enthalpy change for this reaction.

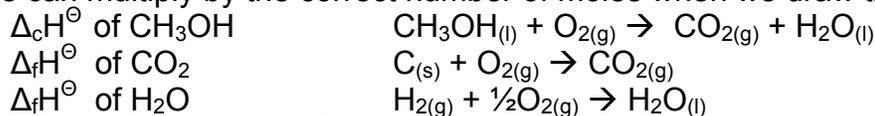| Δ_fH values (kJmol^{-1})		Equation for the enthalpy change of formation
$CH_{4(g)}$	-75	$C + 2\ H_2 \rightarrow CH_4$
$H_2O_{(g)}$	-242	$H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$
$CO_{(g)}$	-110	$C + \frac{1}{2}\ O_2 \rightarrow CO$

Finding missing data
We may be given some Δ_cH or Δ_fH values and the ΔH for a reaction and be required to work out a missing enthalpy change. The Hess Cycle is used in exactly the same way.

Example: The standard enthalpy change of combustion of methanol, $\Delta_cH^\ominus$ = -726.0 kJmol^{-1}. Construct a Hess Cycle to calculate the standard enthalpy change of formation of methanol, $\Delta_fH^\ominus$, given the following data: $\Delta_fH^\ominus\ CO_2$ = -393.5 kJmol^{-1}
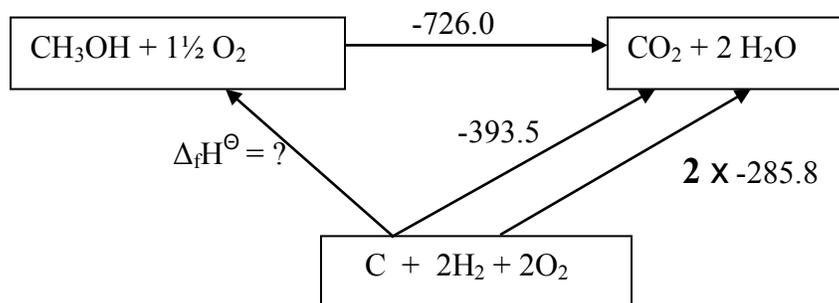 $\Delta_fH^\ominus\ H_2O$ = -285.8 kJmol^{-1}

The first thing to do is write the equations corresponding to the given enthalpy changes, so that we can multiply by the correct number of moles when we draw the Hess cycle:
      $\Delta_cH^\ominus$ of CH_3OH $CH_3OH_{(l)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(l)}$
      $\Delta_fH^\ominus$ of CO_2 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$
      $\Delta_fH^\ominus$ of H_2O $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$
And we want to work out $\Delta_fH^\ominus$ of CH_3OH: $C_{(s)} + 2H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(l)}$

$$CH_3OH + 1\frac{1}{2}\ O_2 \xrightarrow{-726.0} CO_2 + 2\ H_2O$$

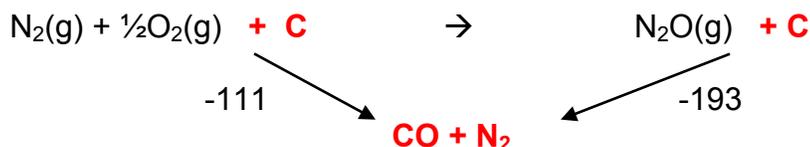$\Delta_fH^\ominus = ?$ -393.5   **2 x** -285.8

$$C\ +\ 2H_2 + 2O_2$$

So $\Delta_fH^\ominus$ for methanol = -393.5 + (2 x -285.8) + 726.0 = -239.1 kJ mol^{-1}

Note:
Some Hess Cycle problems are not based on combustion or formation data, but on ΔH values for other reactions. You have to look at the given reactions and piece together how to form a Hess Cycle with them, given the reaction you want to find ΔH for.

e.g. Calculate $\Delta_f H$ for $N_2O_{(g)}$, given that for $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H = -111$ kJmol^{-1} and for $C_{(s)} + N_2O_{(g)} \rightarrow CO_{(g)} + N_{2(g)}$ $\Delta H = -193$kJmol^{-1}

$$N_2(g) + \frac{1}{2}O_2(g) \;\; \textbf{+ C} \qquad\qquad \rightarrow \qquad\qquad N_2O(g) \;\; \textbf{+ C}$$

-111 $\qquad\qquad\qquad$ -193

CO + N$_2$

So ΔH = -111 + 193 = +82 kJmol^{-1}

Calorimetry – measurement of enthalpy changes
When the temperature of a substance is changed, the amount of energy needed to cause this can be calculated:

Heat energy required is given by the equation $\;\;$ <mark>q = m c ΔT</mark>

Where q = energy required (J)
$\qquad$ m = mass of stuff getting heated (g)
$\qquad$ c = specific heat capacity $\;(Jg^{-1}K^{-1})$
$\qquad\qquad\qquad$ *usually 4.18 or 4.2, given in question*
$\qquad$ ΔT = change in temperature (K)
$\qquad\quad$ = final temp – initial temp $\qquad$ *remember to show the sign too !*

The source of this heat may be a chemical reaction, in which case the heat energy was produced by a change in chemical energy – an enthalpy change. The enthalpy change is given by:

<mark>ΔH = -q / (moles of reactant)</mark>

Where ΔH is in Jmol^{-1} $\qquad$ - you need to ÷ 1000 to get it in kJmol^{-1}
moles = moles of whichever reactant in <u>NOT</u> in excess

We must also check that the sign of ΔH is correct ! If the temperature increased, the reaction was exothermic and ΔH must have a – sign. If the temperature decreased, the reaction was endothermic and ΔH has a + sign. SHOW + SIGNS !

For liquids/solutions which get heated, we may know the volume rather than the mass. We need to convert volume to mass. This is done using density:
<mark>*mass (g) = volume (cm^3) x density (g cm^{-3})*</mark>

The density of pure water is 1.00 g cm^{-1}, so essentially the mass of the liquid will be the same as the volume. You will be given the actual density to use if a calculation is needed.

Application:
50.0cm^3 each of two solutions A and B with density 1.00 g cm^{-1} at 18.0ºC were reacted together. The resulting temperature rose to 31.9ºC. Calculate the heat energy produced in this reaction: [specific heat capacity of A and B solutions = 4.18 Jg^{-1}K^{-1}]

$$q = mass \times 4.18 \times (31.9 - 18)$$
$$mass = (50 + 50) \times 1.00 \text{ so mass = 100g}$$
$$q = 100 \times 4.18 \times 13.9 = \textbf{+5810 Joules}$$

During the reaction 0.1 moles of B reacted with an excess of A. Calculate the enthalpy change of the reaction:

$$\Delta H = -q / (moles)$$
$$= -5810 / (0.1)$$
$$= \textbf{-58100 J mol}^{-1} \qquad = \qquad \textbf{-58.1 kJ mol}^{-1}$$

Check: The reaction was exothermic – temperature INCREASED so ΔH is negative

A common mistake is to use the mass of the reactants rather than the mass of the substance whose temperature is being measured – these are not always the same !

Consider the following three examples of different experiments to measure enthalpy changes, and for each decide what value of mass to use in order to calculate Q and what number of moles to use to calculate ΔH.
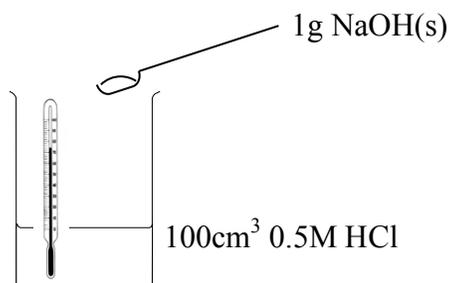
Example 1:

$100cm^3$ 0.1M HCl$_{(aq)}$

$50cm^3$ 0.1M NaHCO$_{3(aq)}$
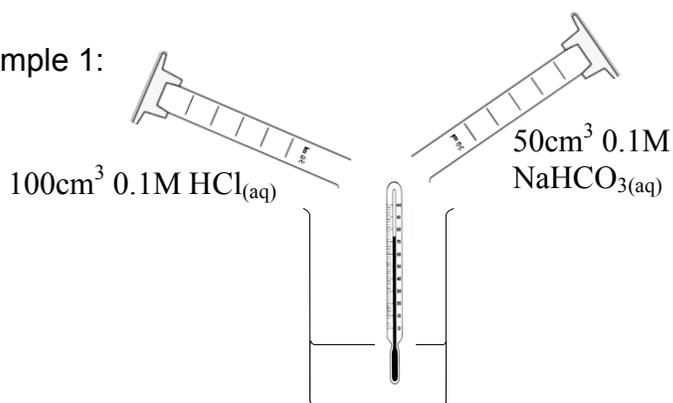
density of HCl and NaOH solutions, and of water = 1.00 g cm^{-3}

Mass to use = 150g since 150cm^3 of solution after mixing.
Moles to use = 0.1 x 50/1000 = 0.005 moles (based on NaHCO$_3$ since HCl was in excess, 1:1 mole ratio)
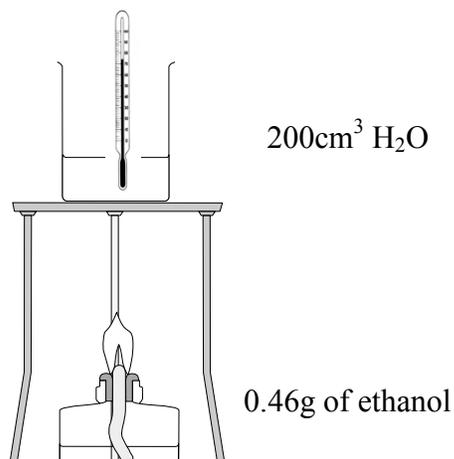
Example 2:

1g NaOH(s)

$100cm^3$ 0.5M HCl

Mass to use = 100g since we used 100cm^3 of solution with density of 1.00 g cm^{-3} (we can ignore the mass of the solid, since its specific heat capacity will be very low)

Moles to use depends on which is in excess.
    Moles NaOH = 1 / (23 + 16 + 1) = <u>0.025 moles</u>
    Moles HCl = 0.5 x (100/1000) = 0.050 moles (excess, so we use moles of NaOH)

Example 3:

200cm^3 H$_2$O

0.46g of ethanol

Mass is 200g since 200cm^3 of water gets heated
Moles = mass/M$_r$ = 0.46/46 = 0.01 moles of ethanol burnt (oxygen was in excess).

Check your understanding: *use c = 4.2 Jg^{-1}K^{-1}*
xi) Calculate Q and hence ΔH for example 1 if the temperature on reaction dropped from 20.0°C to 2.5°C

xii) Calculate Q and hence ΔH for example 2 if the temperature on reaction increased from 15.0°C to 21.2°C

xiii) Calculate the temperature change expected in example 3 given that Δ$_c$H$^⊖$ of ethanol is -1367 kJ mol^{-1}

Answers to Check your Understanding questions:

i)   Write an equation to show the standard enthalpy change of formation of ethanol, C_2H_5OH

$$C_{(s)} + 3\ H_{2(g)} + \tfrac{1}{2}\ O_{2(g)} \rightarrow C_2H_5OH_{(l)}$$

ii)   The definition of enthalpy change of formation is making a mole of a substance from its elements. Making an element from its elements requires nothing to be done, so the enthalpy change is zero in all cases.

iii)   Write an equation to show the standard enthalpy change of combustion of ethanol

$$C_2H_5OH_{(l)} + 3\ O_{2(g)} \rightarrow 2\ CO_{2(g)} + 3\ H_2O_{(l)}$$

iv)   Standard enthalpy change of neutralisation of nitric acid by solid calcium hydroxide:

$$HNO_{3(aq)} + \tfrac{1}{2}Ca(OH)_{2(s)} \rightarrow \tfrac{1}{2}Ca(NO_3)_{2(aq)} + H_2O_{(l)}$$
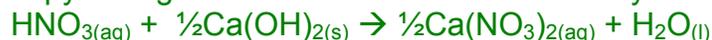
v)   In each case, the actual reaction taking place is shown by the ionic equation
$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)}$ so we expect the same enthalpy change of neutralisation. All the other ions present are spectator ions.

vi) Use the bond enthalpies to calculate ΔH for the reaction $C + 2H_2 + 2O_2 \rightarrow CO_2 + 2H_2O$

Broken		Made	
2 x H-H	2 x 436	2 x C=O	2 x -750
2 x O=O	2 x 498	4 x H-O	4 x -464
Total	+1868 kJmol^{-1}		-3365kJmol^{-1}

$$\Delta H = +1868 + (-3365) = -1488 \text{kJmol-1}$$

vii) Use the Hess Cycle below to calculate ΔH for the reaction $C + 2H_2 \rightarrow CH_4$ which cannot be measured directly as carbon does not react with hydrogen in this way, and if it did, methane would not be the only product formed.
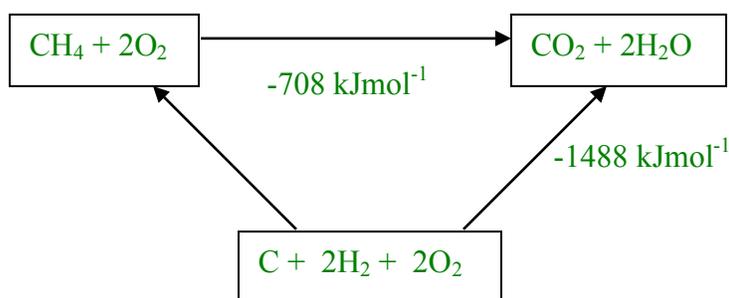
$$\Delta H \text{ for the reaction } C + 2H_2 \rightarrow CH_4 = -1488 + 708 = -780 \text{kJmol}^{-1}$$

viii)   The difference can be seen if we look at the equations for the two reactions:
$C_{(s)} + 2\ H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta_f H^{\ominus} = -76$ kJmol^{-1}
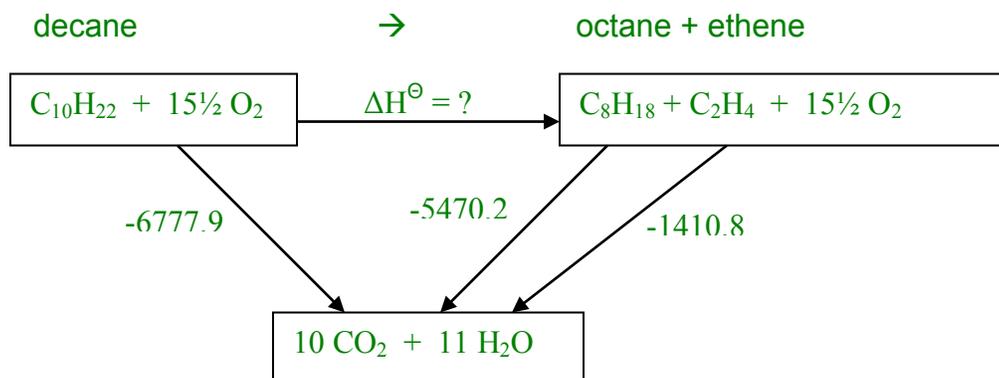$C_{(g)} + 2\ H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = -780$ kJmol^{-1}

The $C_{(s)} \rightarrow C_{(g)}$ step requires a lot of energy to vaporise the carbon (i.e. to break all the C-C bonds in the solid carbon lattice), so the energy released when the carbon has to be vapourised as well is much lower.

ix) Calculate $\Delta H^{\ominus}$ for the cracking of decane to give octane and ethene using the standard enthalpy changes of combustions given in an appropriate Hess Cycle:

decane, $\Delta_c H^{\ominus}$ = -6777.9 kJmol-1
octane, $\Delta_c H^{\ominus}$ = -5470.2 kJmol-1
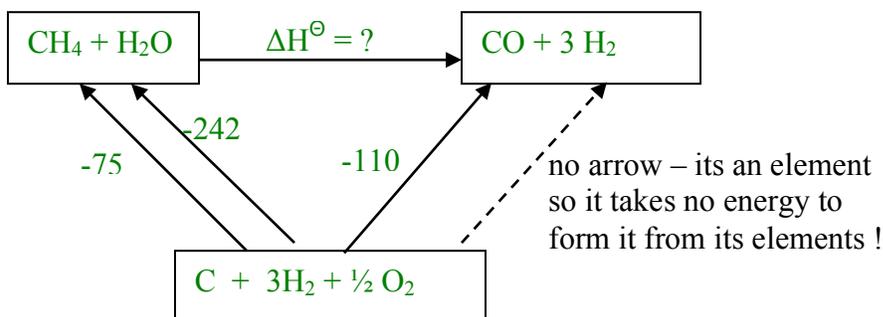ethene $\Delta_c H^{\ominus}$ = -1410.8 kJmol-1

decane $\rightarrow$ octane + ethene

| $C_{10}H_{22}$ + 15½ O_2 | $\Delta H^{\ominus}$ = ? → | C_8H_{18} + C_2H_4 + 15½ O_2 |

-6777.9   -5470.2   -1410.8

$10\ CO_2$ + $11\ H_2O$

So $\Delta H^{\ominus}$ = -6777.9 + 5470.2 + 1410.8 = +103.1 kJmol^{-1} (endothermic, as expected for a thermal decomposition)

x) A reaction to manufacture hydrogen for use in the Haber process is carried out at high temperature, using natural gas and steam: $CH_{4(g)}$ + $H_2O_{(g)}$ → $CO_{(g)}$ + 3 $H_{2(g)}$
Use the given enthalpies of formation to work out the enthalpy change for this reaction.

$\Delta_f H^{\ominus}$ values (kJmol^{-1})   Equation for the enthalpy change of formation
$CH_{4(g)}$ -75   C + 2 H_2 → CH_4
$H_2O_{(g)}$ -242 H_2 + ½ O_2 → H_2O
$CO_{(g)}$ -110   C + ½ O_2 → CO

| CH_4 + H_2O | $\Delta H^{\ominus}$ = ? → | CO + 3 H_2 |

-242
-75   -110   no arrow – its an element
so it takes no energy to
form it from its elements !

C + $3H_2$ + ½ O_2

$\Delta H^{\ominus}$ = +75 + 242 – 110 = +207kJ mol^{-1} which is endothermic (hence the need for high temp).

xi) Calculate q and hence ΔH for example 1 if the temperature on reaction dropped from 20°C to 2.5°C

q = mcΔT = 150 x 4.2 x (2.5 - 20.0)   = 150 x 4.2 x -17.5   = -1102.5 Joules

ΔH = +1102.5 / (0.005 x 1000)   **= + 220.5 kJ mol^{-1}**
Sign of ΔH is positive since temperature decreased in reaction

xii) Calculate q and hence ΔH for example 2 if the temperature on reaction increased from 15°C to 21.2°C

q = mcΔT   = 100 x 4.2 x (21.2 – 15.0) = 100 x 4.2 x 6.2   = +2604 Joules

ΔH = -2604 / (0.025 x 1000)   = **-104.16 kJ mol-1**
Sign of ΔH is negative since temperature increased in reaction

xiii) Calculate the temperature change expected in example 3 given that $\Delta_c H^{\ominus}$ of ethanol is -1367 kJ mol^{-1}

Using ΔH =   -q / (moles x 1000)   -1367 = -q / (0.01 x 1000)
So q = 13670 Joules

Using q = mcΔT   13670 = 200 x 4.2 x ΔT
So ΔT **= +16.3°C**