

2.3.1 Enthalpy Changes

Enthalpy changes: ΔH of reaction, formation and combustion

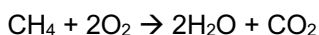
Enthalpy (chemical energy), symbol **H** is the total energy content of the reacting materials. During a reaction, an enthalpy change ΔH usually occurs. Conservation of energy applies to reactions, energy is not created or destroyed but is converted from one form into another. Heat energy, a form of kinetic energy, is often observed in reactions. Sound and light are less important.

Exothermic reactions occur when the temperature increases. Enthalpy is reduced. ΔH is **negative as chemical energy is converted into heat energy**, e.g.

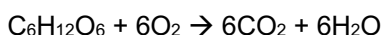
Oxidation is an important exothermic process in:

- a. Combustion of fuels

e.g. methane



- b. Oxidation of carbohydrates such as Glucose in respiration

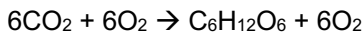


Endothermic reactions occur when the temperature falls. They require an input of energy. Enthalpy is increased. ΔH is **positive as heat energy has been converted into chemical energy**, e.g.

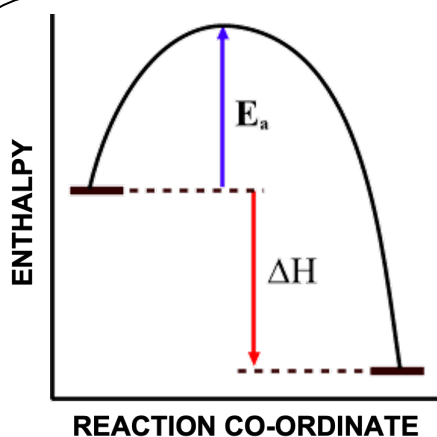
Thermal decomposition, e.g. of calcium carbonate



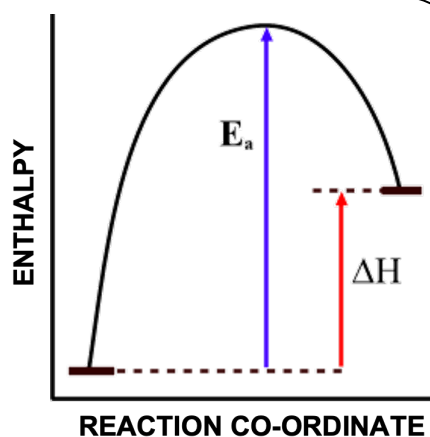
Photosynthesis (here energy is absorbed from light)



Energy (enthalpy) profiles show enthalpy changes as the reaction proceeds:



Enthalpy of reactants > products
 $\Delta H = -$ ive
EXOTHERMIC Heat given out



Enthalpy of reactants < products
 $\Delta H = +$ ive
ENDOTHERMIC Heat absorbed

E_a is the Activation Energy this is the minimum amount of energy needed for particles to react- if less energy is available the reaction cannot happen - the collisions will not be effective.

Units of Enthalpy The kilojoule kJ is commonly used.

Enthalpy Changes are normally quoted in kJ mol^{-1} (kilojoules per mole)

Standard conditions are used when comparing energy changes. The conditions are:

Pressure 100 kPa

Temperature 298K

Concentration 1.0M for any solutions

Standard Enthalpy Change of Reaction, ΔH^{\ominus}_r is the enthalpy change when the amounts of reactants shown in the equation react together under standard conditions to give the products in their standard states.

Standard Enthalpy Change of Combustion, ΔH^{\ominus}_c is the enthalpy change when one mole of substance is burned in an excess of oxygen under standard conditions.

Standard Enthalpy Change of Formation, ΔH^{\ominus}_f is the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.

Determining Energy Changes by direct practical measurement.

The enthalpy change is transferred to water, which heats up or cools down. $\Delta H = mc\Delta T$ is used to work out the amount of energy transferred.

To find ΔH_c of propan-1-ol, $\text{C}_3\text{H}_7\text{OH}$.

When 0.28g of propan-1-ol was burned, the temp of 100g water increased by 21.5°C . Assume the specific heat capacity of water is $4.2\text{Jg}^{-1}\text{K}^{-1}$

a) Calculate ΔH when 0.28g of propan-1-ol was burned : $100 \times 4.2 \times 21.5 = 9030\text{J}$ or 9.030kJ

b) Calculate the number of moles of propan-1-ol in 0.28g: $0.28 / 60 = 0.00466$

c) Calculate ΔH_c in kJmol^{-1} of propan-1-ol: $9.030 / 0.004666 = \underline{\underline{-1935 \text{ kJmol}^{-1}}}$

N.B. Sign is negative because reaction is exothermic.

N.B. The actual value is more exothermic than the experimental value because some energy released heats the container and surroundings, not the water, combustion is incomplete and some fuel evaporates.

Bond Enthalpies

Enthalpy changes are linked to the making and breaking of bonds.

Bond breaking is endothermic because energy must be added to overcome the attractive forces in the bond.

Bond making is exothermic because it is the exact opposite of bond breaking so the same amount of energy must be transferred but in the opposite direction.

Average Bond Enthalpy is the energy required to break one mole of bonds in the substance in the gaseous state.

An average value is used because the same bonds in different chemicals will not be identical. (e.g. the C—H bonds in methane do not have exactly the same bond enthalpy as the C—H bonds in ethane)

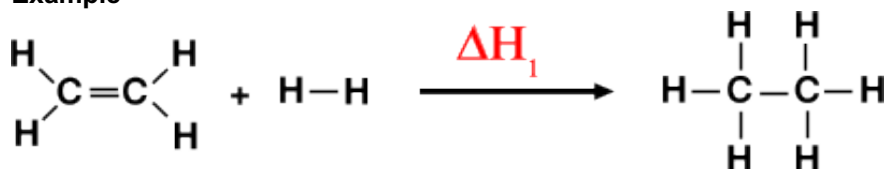
Determining Energy Changes by estimation from bond enthalpies. By studying the structures of reactants and products it is possible to work out which bonds have been broken and which have been made.

Step 1 Energy is put in to break bonds to form separate, gaseous atoms.

Step 2 Gaseous atoms then combine to form bonds and energy is released; its value will be equal and opposite to that of breaking the bonds

$$\Delta H_r = \text{Step 1} - \text{Step 2}$$

Example



Breaking bonds:

1 x C=C bond	@	611	=	611 kJ mol ⁻¹
4 x C-H bonds	@	413	=	1652 kJ mol ⁻¹
1 x H-H bond	@	436	=	436 kJ mol ⁻¹

Total energy to break bonds of reactants = 2699 kJ mol⁻¹

Making Bonds:

1 x C-C bond	@	346	=	346 kJ mol ⁻¹
6 x C-H bonds	@	413	=	2478 kJ mol ⁻¹

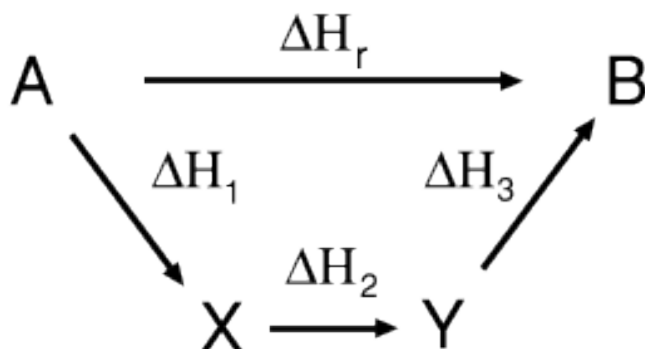
Total energy to break bonds of products = 2824 kJ mol⁻¹

$\Delta H = \text{Bonds broken} - \text{bonds made}$

$$= 2699 - 2824 = -125 \text{ kJ mol}^{-1}$$

Hess' Law and enthalpy cycles

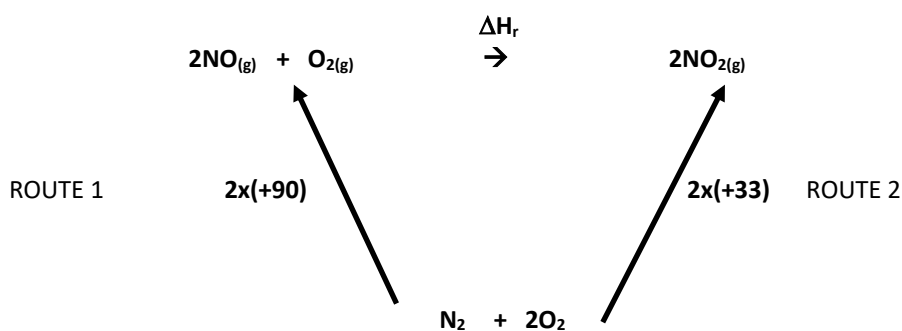
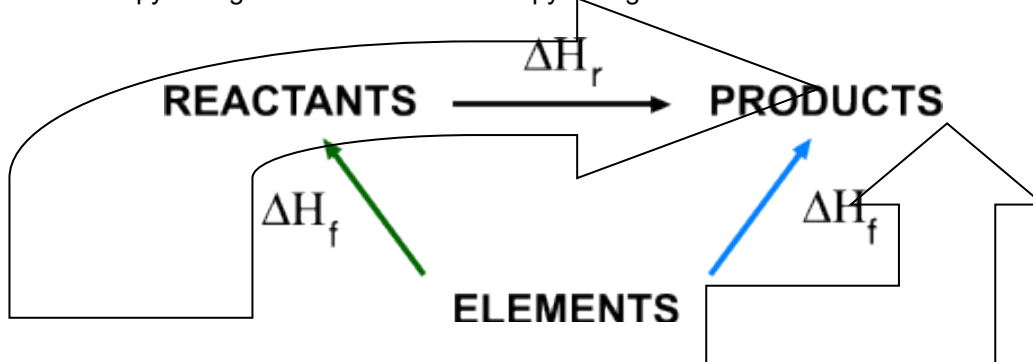
Hess's Law states that the enthalpy change of a reaction depends only on the initial and final conditions and not on the route of the reaction.



$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Determining Energy Changes using Hess' cycle

1. Enthalpy change of reaction from enthalpy changes of formation

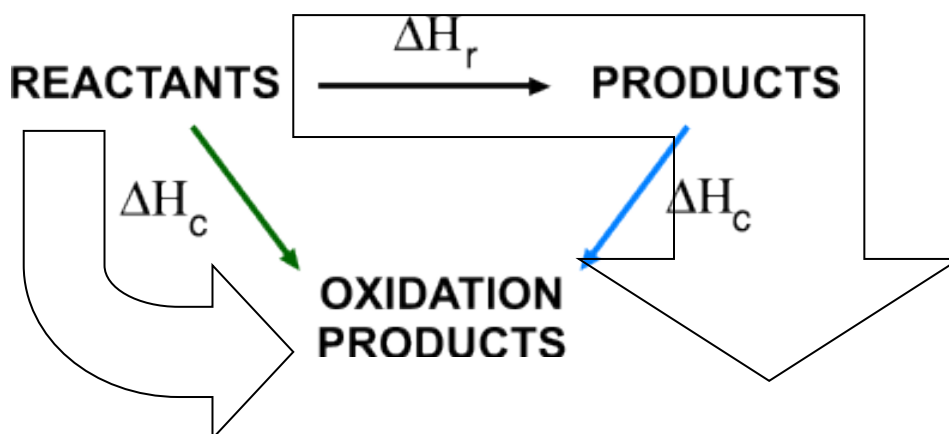


$$\Delta H_r + 2x(+90) = 2x(+33)$$

$$\Delta H_r = 66 - 180 = -114 \text{ kJmol}^{-1}$$

2. Enthalpy change of reaction from enthalpy changes of combustion

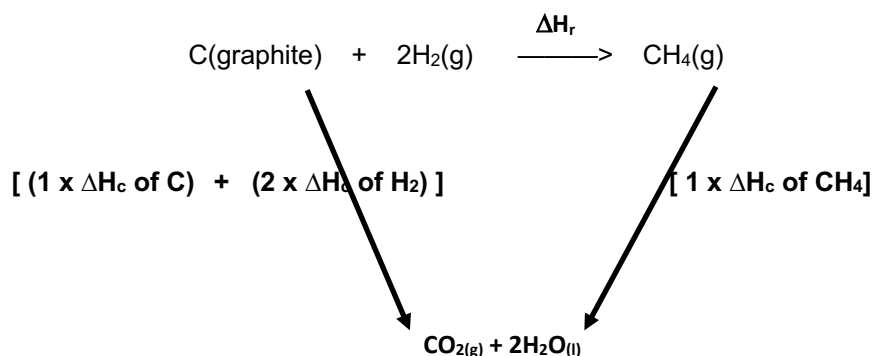
If you burned all the products you should get the same amounts of oxidation products such as CO_2 and H_2O as if you burned the reactants.



$$\Delta H_r + \Sigma \Delta H_c (\text{products}) = \Sigma \Delta H_c (\text{reactants})$$

Sample calculation

Calculate the standard enthalpy of formation of methane; the standard enthalpies of combustion of carbon, hydrogen and methane are -394, -286 and -890 kJ mol⁻¹.



The Standard Enthalpy of Reaction ΔH_r° will be...

$$\Delta H_r + \Sigma \Delta H_c (\text{products}) = \Sigma \Delta H_c (\text{reactants})$$

$$\Delta H_r + [1 \times \Delta H_c \text{ of CH}_4] = [(1 \times \Delta H_c \text{ of C}) + (2 \times \Delta H_c \text{ of H}_2)]$$

$$\Delta H_r + 1 \times (-890) = 1 \times (-394) + 2 \times (-286)$$

$$\Delta H_r - 890 = -966$$

$$\Delta H_r = -966 + 890$$

$$\text{ANSWER} = -76 \text{ kJ mol}^{-1}$$