

THERMODYNAMICS

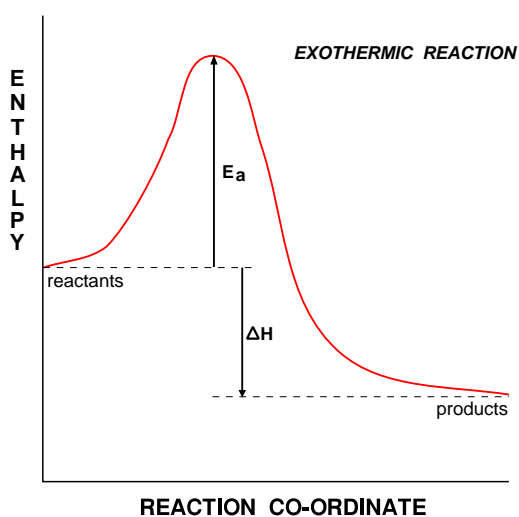
First Law Energy can be neither created nor destroyed but it can be converted from one form to another.

- all chemical reactions are accompanied by some form of energy change
- changes can be very obvious (*gas burning*) but in many cases it goes unnoticed

Enthalpy

- a measure of the heat content of a substance at constant pressure
- you cannot measure the actual enthalpy of a substance
- you can measure an ENTHALPY CHANGE at CONSTANT PRESSURE
- written as the symbol ΔH , "delta H"

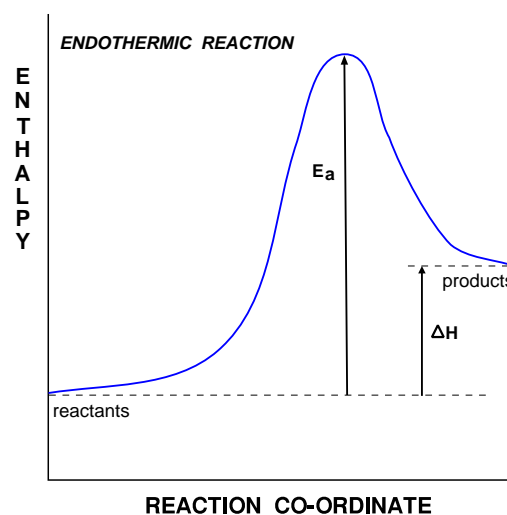
Enthalpy change (ΔH) = Enthalpy of products - Enthalpy of reactants



Enthalpy of reactants > products

$$\Delta H = - \text{ive}$$

EXOTHERMIC *Heat given out*



Enthalpy of reactants < products

$$\Delta H = + \text{ive}$$

ENDOTHERMIC *Heat absorbed*

Examples

EXOTHERMIC

- **combustion** of fuels $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- **respiration** $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$
(oxidation of carbohydrates such as glucose)

ENDOTHERMIC

- **photosynthesis** $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$
- **thermal decomposition** of calcium carbonate $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

Standard Enthalpy Changes

- enthalpy values vary with the conditions - so standard conditions are needed
- a substance will then be in its **standard state** ...

Pressure:- 100 kPa (1 atm) A stated temperature:- usually 298K (25°C)

- as a guide, just think of a substance under normal laboratory conditions
- assign the correct subscript [e.g. (g), (l) or (s)] to indicate which state it is in
- **any solutions are of concentration 1 mol dm⁻³**
- to tell if standard conditions are used we modify the symbol for ΔH .

Enthalpy Change



Standard Enthalpy Change (at 298K)



Enthalpy Change of Reaction (ΔH_r or $\Delta_r H$) (NO \ominus sign)

Definition The enthalpy change associated with a stated reaction.

Enthalpy Change of Combustion (ΔH_c or $\Delta_c H$) (NO \ominus sign)

Definition The enthalpy change when ONE MOLE of a substance undergoes complete combustion

Standard Enthalpy Change of Combustion (ΔH_c^{\ominus}) (there is a \ominus sign)

Definition The enthalpy change when ONE MOLE of a substance undergoes complete combustion under standard conditions. All reactants and products are in their standard states.

AQA

Values **Always exothermic**

Example(s) **$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$**

$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

Notes To aid balancing the equation, remember that you get one carbon dioxide molecule for every carbon atom in the original molecule and a water molecule for every two hydrogen atoms. Having done this, go back and balance the oxygen.

Q.1 Write equations representing the (standard) enthalpy change of combustion of...

methane

methanol

cyclohexane

hydrogen

carbon

Enthalpy Change of Formation (ΔH_f or $\Delta_f H$)

Definition The enthalpy change when ONE MOLE of a compound is formed from its elements.

Standard Enthalpy Change of Formation (ΔH_f^\ominus) (there is a \ominus sign)

Definition The enthalpy change when ONE MOLE of a substance is formed in its standard state from its elements in their standard states.

AQA

Values Usually, but not exclusively, **exothermic**

Example(s) $2\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$

Notes

- elements in their standard states have zero enthalpy of formation
- carbon is usually taken as the graphite allotrope.

Q.2 Construct equations representing the standard enthalpy change of formation of

methane

sulphuric acid

sodium chloride

water

carbon dioxide

Q.3 What do you notice about the equations for...

- the standard enthalpy change of combustion of hydrogen and the standard enthalpy change of formation of water?
- the standard enthalpy change of combustion of carbon and the standard enthalpy change of formation of carbon dioxide?

Enthalpy of Neutralisation (ΔH_{neut} or $\Delta_{\text{neut}} H$)

Definition Enthalpy change when ONE MOLE of water is formed from its ions in dilute soln.

Values **Exothermic**

Equation $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$

Notes A value of -57kJ mol^{-1} is obtained when strong acids react with strong alkalis.

Bond Dissociation Enthalpy (Energy)

Definition Energy required to break ONE MOLE of gaseous bonds to form gaseous atoms.

Values **Endothermic** Energy must be put in to break any chemical bond

Example $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g})$

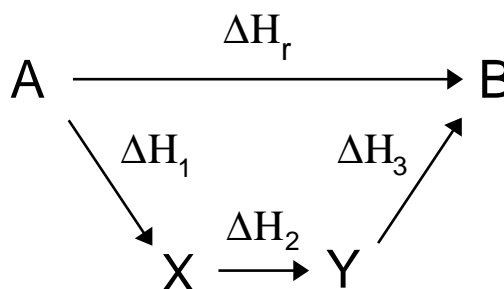
- Notes**
- the strength of a bond depends on its environment so MEAN values are quoted
 - making a bond is an exothermic process as it is the opposite of breaking a bond
 - for diatomic gases, the bond enthalpy is twice the enthalpy of atomisation
 - the smaller the bond enthalpy, the weaker the bond and the easier it is to break

Some mean bond enthalpies (in kJ mol^{-1}) (values may differ slightly in other texts)

H-H	436	H-F	562	N-N	163
C-C	346	H-Cl	431	N=N	409
C=C	611	H-Br	366	N≡N	944
C≡C	837	H-I	299	P-P	172
C-O	360	H-N	388	F-F	158
C=O	743	H-O	463	Cl-Cl	242
C-H	413	H-S	338	Br-Br	193
C-N	305	H-Si	318	I-I	151
C-F	484	P-H	322	S-S	264
C-Cl	338	O-O	146	Si-S	176
C-Br	276	O=O	496	Si-O	374

HESS'S LAW

“The enthalpy change is independent of the path taken”



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

- applying Hess's Law enables one to calculate enthalpy changes from other data
- used for calculating changes which can't be measured directly - *Lattice Enthalpy*
- used for calculating
 - enthalpy change of reaction from bond enthalpy
 - enthalpy change of reaction from ΔH°_c
 - enthalpy change of formation from ΔH°_f

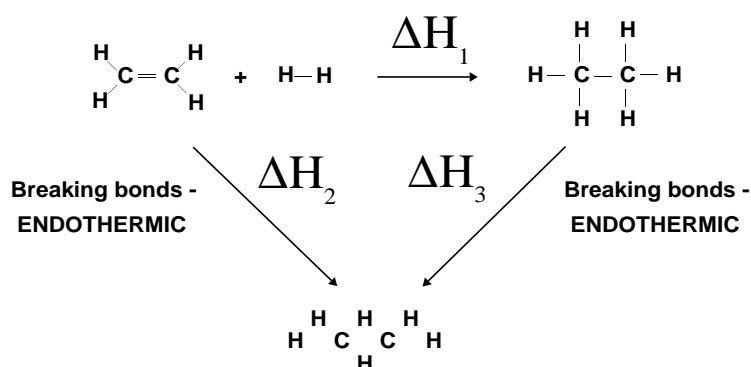
Enthalpy change of reaction from average bond enthalpies

Theory Imagine that, during a reaction, all the bonds of reacting species are broken and the individual atoms join up again but in the form of products. The overall energy change will depend on the difference between the energy required to break the bonds and that released as bonds are made.

energy released making bonds > energy used to break bonds ... **EXOTHERMIC**

energy used to break bonds > energy released making bonds ... **ENDOTHERMIC**

Example Calculate the enthalpy change for the hydrogenation of ethene



$$\Delta H_2 \quad \begin{array}{l} 1 \times \text{C}=\text{C} \text{ bond @ } 611 = 611 \\ 4 \times \text{C}-\text{H} \text{ bonds @ } 413 = 1652 \\ 1 \times \text{H}-\text{H} \text{ bond @ } 436 = 436 \end{array}$$

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

$$\Delta H_3 \quad \begin{array}{l} 1 \times \text{C}-\text{C} \text{ bond @ } 346 = 346 \\ 6 \times \text{C}-\text{H} \text{ bonds @ } 413 = 2478 \end{array}$$

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

$$\begin{aligned} \text{Applying HESS'S LAW} \quad \Delta H_1 &= \Delta H_2 - \Delta H_3 \\ &= 2699 - 2824 = -125\text{kJ} \end{aligned}$$

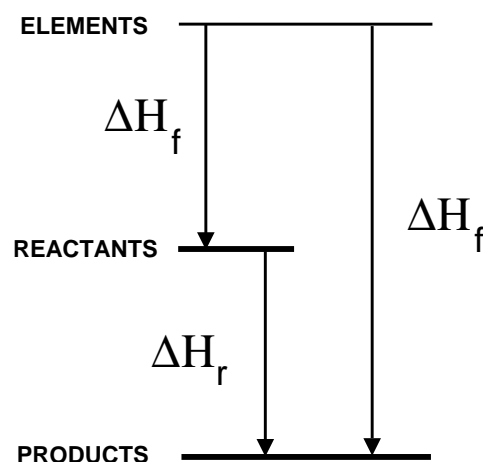
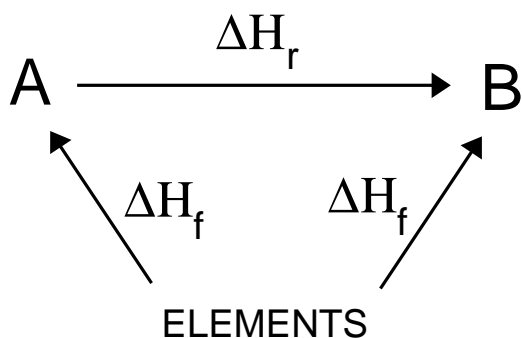
Q.4 Using the average bond enthalpies in your notes, calculate the standard enthalpy changes of reaction for the following reactions.

- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{HCl}(\text{g})$
- $\text{C}_2\text{H}_5\text{OH}(\text{g}) + \text{HBr}(\text{g}) \longrightarrow \text{C}_2\text{H}_5\text{Br}(\text{g}) + \text{H}_2\text{O}(\text{g})$

Enthalpy change of reaction from enthalpy changes of combustion and formation

Formation If you formed the products from their elements you should need the same amounts of every substance as if you formed the reactants from their elements.

By applying Hess's Law ...



$$\Delta H_r = \sum \Delta H_f (\text{PRODUCTS}) - \sum \Delta H_f (\text{REACTANTS})$$

example Calculate the standard enthalpy change for the following reaction, given that the standard enthalpies of formation of water, nitrogen dioxide and nitric acid are -286 , $+33$ and -173 kJ mol^{-1} respectively. [oxygen's value is ZERO as it is an element]

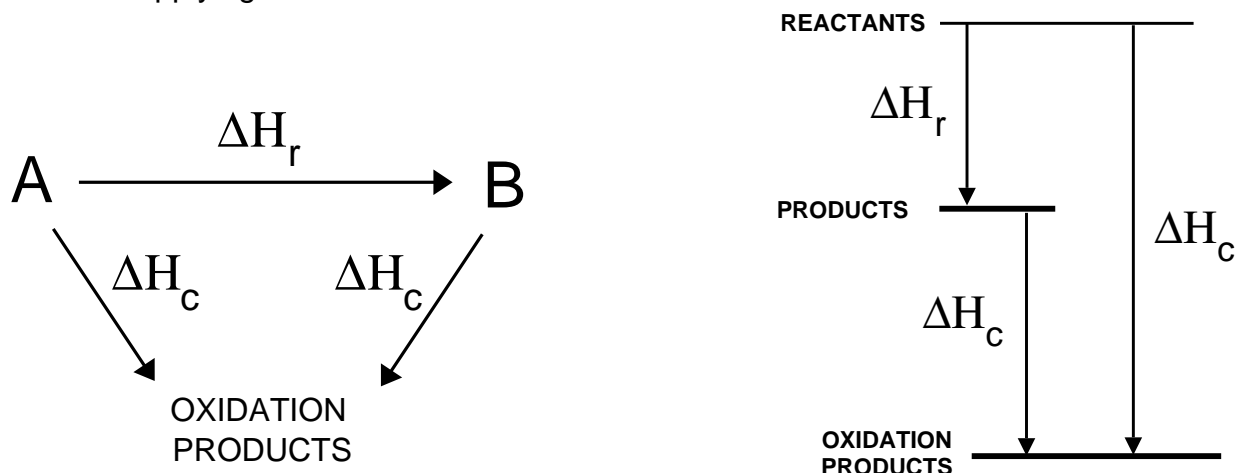


applying Hess's Law ... $\Delta H_r = [4(-173)] - [2(-286) + 4(+33) + 0] = -252 \text{ kJ}$

Q.5 If the standard enthalpy changes of formation of $\text{SO}_2(g)$ and $\text{SO}_3(g)$ are -296 and -395 kJ mol^{-1} respectively, calculate the enthalpy change of reaction of ... $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$

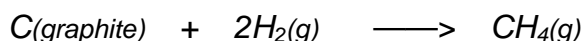
Combustion If you burned all the products you should get the same amounts of CO_2 and H_2O etc. as if you burned the reactants.

Applying Hess's Law ...



$$\Delta H_r = \sum \Delta H_{c(\text{REACTANTS})} - \sum \Delta H_{c(\text{PRODUCTS})}$$

example Calculate the standard enthalpy change of formation of methane, given that the standard enthalpies of combustion of carbon, hydrogen and methane are -394 , -286 and -890 kJ mol^{-1} respectively.



applying Hess's law ... $\Delta H_r = [(-394) + 2(-286)] - [(-890)] = -74 \text{ kJ mol}^{-1}$

Q.6 Calculate the enthalpy change of reaction for $\text{H}_2 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_2\text{H}_6$ given that the enthalpy changes of combustion of H_2 , C_2H_4 and C_2H_6 are -286 , -1409 and $-1560 \text{ kJ mol}^{-1}$ respectively.

Compare this value with that obtained using average bond enthalpies.

Measuring Enthalpy Changes

- Calorimetry**
- involves the practical determination of enthalpy changes
 - usually involves heating (or cooling) known amounts of water

water is heated up	reaction is EXOTHERMIC
water cools down	reaction is ENDOTHERMIC

Calculation The energy required to change the temperature of a substance can be found;

$$q = m \times c \times \Delta T$$

where	q = heat energy	kJ
	m = mass	kg
	c = Specific Heat Capacity	kJ K ⁻¹ kg ⁻¹ [water is 4.18]
	ΔT = change in temperature	K

ΔT The value of ΔT is usually calculated graphically by measuring the temperature changes before, during and after a reaction.

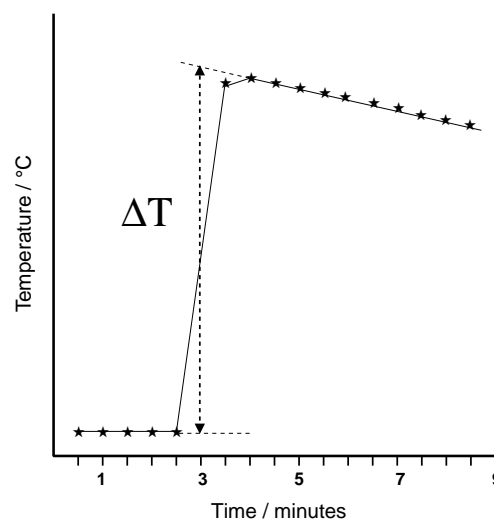
Graphical method

The temperature is taken every half minute before mixing the reactants.

Reactants are mixed after 3 minutes.

Further readings are taken every half minute as the reaction mixture cools.

Extrapolate the lines as shown and calculate the value of ΔT .



Example 1 When 0.18g of hexane underwent complete combustion, it raised the temperature of 100g (0.1kg) water from 22°C to 47°C. Calculate its enthalpy of combustion.

$$\text{Heat absorbed by the water (q)} = 0.1 \times 4.18 \times 25 = 10.45 \text{ kJ}$$

$$\begin{aligned} \text{Moles of hexane burned} &= \text{mass} / M_r = 0.18 / 86 \\ &= 0.00209 \end{aligned}$$

$$\text{Enthalpy change} = \text{heat energy} / \text{moles} = -10.45 / 0.00209$$

ANS **- 5000 kJ mol⁻¹**

Example 2 25cm³ of 2.0M HCl was added to 25cm³ of 2.0M NaOH in an insulated beaker. The initial temperature of both solutions was 20°C. The reaction mixture was stirred to ensure mixing and the highest temperature reached by the solution was 33°C. Calculate the Molar Enthalpy of Neutralisation.

$$\begin{array}{lll}
 \text{Temperature rise } (\Delta T) & = & 306\text{K} - 293\text{K} & = & 13\text{K} \\
 \text{Volume of resulting solution} & = & 50\text{cm}^3 & = & 0.05 \text{ dm}^3 \\
 \text{Equivalent mass of water} & = & 50\text{g} & = & 0.05 \text{ kg} \\
 \text{Heat absorbed by the water } (q) & = & 0.05 \times 4.18 \times 13 & = & 2.717 \text{ kJ}
 \end{array}$$

$$\begin{array}{lll}
 \text{Moles of HCl reacting} & = & 2 \times 25/1000 & = & 0.05 \text{ mol} \\
 \text{Moles of NaOH reacting} & = & 2 \times 25/1000 & = & 0.05 \text{ mol}
 \end{array}$$



$$\text{Moles of water produced} = 0.05 \text{ mol}$$

$$\begin{aligned}
 \text{Enthalpy change per mol } (\Delta H) & = - (\text{heat energy} / \text{moles of water}) \\
 & = - 2.717 / 0.05
 \end{aligned}$$

$$\text{ANS} \quad - 54.34 \text{ kJ mol}^{-1}$$

Q.7 What is the usual value for the Molar Enthalpy of Neutralisation ?

Why might the value calculated from the reaction between sodium hydroxide and ethanoic acid differ from the usual value?

Results from simple calorimetry experiments are seldom very accurate. Make a list of possible sources of error and suggests improvements to the experiment.

Enthalpy of Combustion of Alkanes

1. Write the equation representing the Standard Enthalpy Change of Combustion of heptane, C_7H_{16} .

.....

2. Using the data, plot a graph of Enthalpy of Combustion against number of carbon atoms.

Compound	Enthalpy of Combustion / kJ mol^{-1}
CH_4	- 890
C_2H_6	- 1560
C_3H_8	- 2220
C_4H_{10}	- 2877
C_5H_{12}	- 3509
C_6H_{14}	- 4194
C_8H_{18}	- 5512

3. Use your graph to calculate the following

a) the value of the Enthalpy Change of Combustion of heptane

b) an approximate value for the Enthalpy Change of Combustion of hydrogen

4. State, giving reasons, any advantages of using butane as a household fuel.

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.....
.....

5. State, giving reasons, any disadvantages of using butane as a household fuel.

.....
.....
.....

6. Calculate the amount of heat produced when 1kg of the following undergo complete combustion.

a) CH_4

b) C_4H_{10}