

Topic 2.1

ENERGETICS

Measuring and Calculating Enthalpy Changes

Mean Bond Dissociation Enthalpies

Hess' Law

ENTHALPY CHANGES

1. Exothermic and endothermic reactions

When a chemical reaction takes place, the products and reactants have different stabilities and thus there is a change in potential energy. However since total energy is always conserved, any change in potential energy must be balanced by an equal and opposite change in kinetic energy.

The lower the chemical potential energy of a given chemical species, the more stable it is. This means that stable species have a lower potential energy than unstable species.

In some reactions, the products are more stable than the reactants. The products therefore have less potential energy than the reactants, and the potential energy of the reacting species decreases.

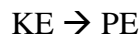
Since the total energy is always conserved, it follows that the kinetic energy of the species must increase. The particles thus move faster and the temperature increases. Reactions in which the products are more stable than the reactants thus involve a transfer of energy from potential to kinetic and an increase in temperature.



Such reactions give out heat and are thus said to be **EXOTHERMIC**.

In other reactions, the reactants are more stable than the products. The products therefore have more potential energy than the reactants, and the potential energy of the reacting species increases.

Since the total energy is always conserved, it follows that the kinetic energy of the species must decrease. The temperature of the system thus decreases. Reactions in which the reactants are more stable than the products thus involve a transfer of energy from kinetic to potential and a decrease in temperature.



Such reactions absorb heat and are said to be **ENDOTHERMIC**.

2. Standard enthalpy changes

The change in chemical potential energy during a chemical reaction is known as the **enthalpy change** for that reaction. It is given the symbol ΔH .

By convention, if the reaction is exothermic (ie heat is given out) the enthalpy change is said to be negative: $\Delta H = -ve$. If the reaction is endothermic (ie heat is absorbed) the enthalpy change is said to be positive: $\Delta H = +ve$.

The enthalpy change of a reaction depends on the reaction conditions. It is therefore necessary to specify standard conditions for the measurement of enthalpy changes. These are taken to be atmospheric pressure (1 atm) and room temperature (298K). Enthalpy changes measured under standard conditions are known as **standard enthalpy changes** and are given the symbol ΔH^\ominus . During these chemical changes, the pressure should be kept constant.

The enthalpy change for a reaction is the heat energy change measured under conditions of constant pressure.

The standard enthalpy change for a reaction is the heat energy change measured under standard conditions: 100 kPa and a stated temperature (usually 298K).

The enthalpy change also depends on the amount of substance used. It is therefore necessary to specify the amount of reactants used. Enthalpy changes are conventionally measured in kJmol^{-1} .

So $\Delta H = \text{heat energy change/no. of moles}$

Given a reaction: $A + 3B \rightarrow 2C + 4D$

The standard enthalpy change for this reaction is taken to be the enthalpy change under standard conditions when one mole of A reacts with three moles of B to give two moles of C and four moles of D.

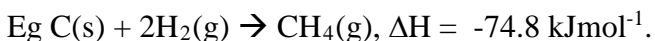
Eg If 0.2 moles of A react with 0.6 moles of B and 200 kJ of energy are released, the enthalpy change is $-200/0.2 = -2000 \text{ kJmol}^{-1}$
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3. Standard enthalpies of formation and combustion

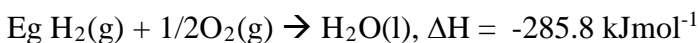
The term "standard enthalpy of reaction" can be used to describe any chemical reaction, but there are some important reactions which have special names:

The **standard enthalpy of formation** of a substance is the enthalpy change when one mole of that substance is formed from the most stable allotropes of its elements in their standard states under standard conditions.

It is given the symbol ΔH°_f .



The standard enthalpy of formation of methane is -74.8 kJmol^{-1} .



The standard enthalpy of formation of water is $-285.8 \text{ kJmol}^{-1}$.



The standard enthalpy of formation of ammonium nitrate is $-365.6 \text{ kJmol}^{-1}$.

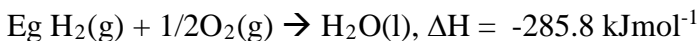


The standard enthalpy of formation of nitrogen monoxide is $+82.0 \text{ kJmol}^{-1}$.

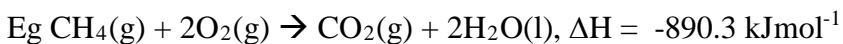
The standard enthalpy of formation of all elements in their standard states is zero.

The **standard enthalpy of combustion** of a substance is the enthalpy change when one mole of that substance is burned in an excess of oxygen under standard conditions.

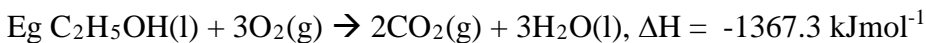
It is given the symbol ΔH°_c .



The standard enthalpy of combustion of hydrogen is $-285.8 \text{ kJmol}^{-1}$.



The standard enthalpy of combustion of methane is $-890.3 \text{ kJmol}^{-1}$.



The standard enthalpy of combustion of ethanol is $-1367.3 \text{ kJmol}^{-1}$.

Burning a substance in oxygen is almost always exothermic, so standard enthalpies of combustion almost always have negative values.

Substances which do not support combustion, like water, carbon dioxide and most other oxides, have zero enthalpy of combustion.

4. Calculating enthalpy changes from temperature changes

Enthalpy changes are generally measured by carrying out a reaction under controlled conditions in a laboratory and measuring the temperature change.

The amount of heat required to change the temperature of a system by 1K is known as the heat capacity of a system (H_c). It is measured in JK^{-1} .

The heat energy change for a given reaction can therefore be calculated from the equation:

$$q = \Delta T \times H_c.$$

The **specific heat capacity (c)** is the amount of heat required to heat 1g of a substance by 1K. So: heat capacity = specific heat capacity x mass

Mass = volume x density

So: heat capacity = specific heat capacity x volume x density

$q = V\rho c\Delta T$ $\text{or } q = mc\Delta T$

If a reaction is taking place in solution (and therefore water is the main species present) it is reasonable to assume that the solution behaves as if it were pure water.

The density of water is 1.0 gcm^{-3} and the specific heat capacity of water is $4.18 \text{ Jg}^{-1}\text{K}^{-1}$.

So the calculation is $q = (\text{volume of solution}) \times 4.18 \times \Delta T$. The enthalpy change can then be calculated by dividing the energy change by the number of moles of reactants.

If the temperature goes up the enthalpy change is negative. If the temperature goes down the enthalpy change is positive.

MEAN BOND ENTHALPIES

During a chemical reaction, the bonds in the reactants are broken. This is an endothermic process; energy is required to do this. After the bonds have been broken, however, the bonds in the products are formed. This is an exothermic process; energy is released when this happens.

The enthalpy change for a chemical reaction can be deduced from consideration of the energy required to break bonds in the reactants and the energy released when the bonds in the products are formed. It can be calculated from the following equation:

$\Delta H = \text{Energy required to break bonds in reactants} - \text{Energy required to break bonds in products}$.

This method can be used to calculate the enthalpy changes for any reaction which does not involve ionic bonds. The breaking and making of ionic bonds involves a more complicated sequence of energetic processes and thus cannot be considered in this way.

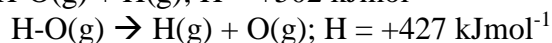
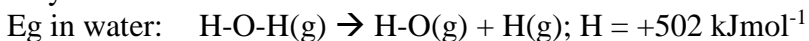
a) Molecules in the gaseous state

In gas phase reactions, the bonds which are broken and formed are covalent bonds. The energy required to separate completely the atoms in one mole of covalent bonds is known as the **bond dissociation enthalpy** of that bond (ΔH_b).



Bond	$\Delta H / \text{kJmol}^{-1}$
C-H	+413
O-H	+464
C-C	+347
C=C	+612
C=O	+805
H-F	+568
H-Cl	+432
Cl-Cl	+243
Br-Br	+193
O=O	+498

These bond enthalpies are mean values; the exact strength of a bond depends on its environment. Even the strengths of the same type of bond in the same molecule may vary:



It is necessary therefore to take an **average** = ie $(502 + 427)/2 = +465 \text{ kJmol}^{-1}$.

Thus bond enthalpies calculated from different reactions may vary slightly. They also do not take intermolecular forces into account. **Mean bond enthalpies thus only give you approximate values for enthalpy changes.**

b) Solids and liquids

In giant covalent substances, all the covalent bonds have to be broken before free gaseous atoms can be formed.

In either case, the energy required to separate completely the atoms in one mole of the substance is known as the **atomisation energy** (ΔH_{at}).

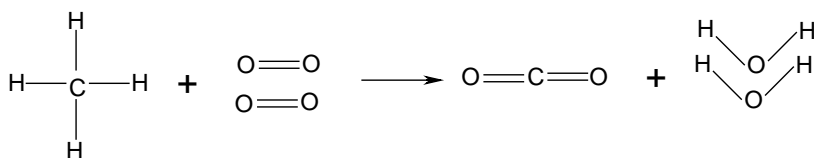
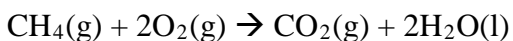


Substance	$\Delta H_{at}/\text{kJmol}^{-1}$
$C(s) \rightarrow C(g)$	+717
$Si(s) \rightarrow Si(g)$	+377
$SiO(s) \rightarrow Si(g) + 2O(g)$	+1864

Using mean bond enthalpies to calculate approximate enthalpy changes:

The approximate enthalpy change can be calculated by considering the mean bond enthalpies of the bonds broken and bonds formed

Eg Consider the combustion of methane:



$$\begin{aligned} \text{Broken: 4 C-H bonds, 2 O=O bonds: total energy} &= (4 \times 413) + (2 \times 498) \\ &= +2648 \text{ kJmol}^{-1} \end{aligned}$$

$$\text{Formed: 2 C=O bonds, 4 O-H bonds: total energy} = (2 \times 805) + (4 \times 464)$$

$$= +3466 \text{ kJmol}^{-1}$$

$$\text{So approximate } \Delta H = 2648 - 3466 = -818 \text{ kJmol}^{-1}$$

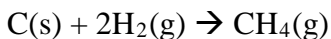
This answer is only approximate because it is using mean bond enthalpies, not molecule-specific ones, and because it is ignoring changes in intermolecular forces. The correct value of ΔH for the reaction is -890 kJmol^{-1} .

Determining mean bond enthalpies from given data:

If the enthalpy change for a reaction is known, and most of the bond enthalpies are known, it is possible to calculate the mean bond enthalpy of a particular bond:

Eg The enthalpy of formation of methane is known to be -76 kJmol^{-1} . The bond enthalpy of a H-H bond is $+436 \text{ kJmol}^{-1}$, and the enthalpy of atomization of carbon ($\text{C(s)} \rightarrow \text{C(g)}$) is $+713 \text{ kJmol}^{-1}$.

Using this information, the mean bond enthalpy of a C-H bond can be calculated.



The bonds broken are the bonds in carbon ($\text{C(s)} \rightarrow \text{C(g)}$) and 2 H-H bonds:

$$\text{Total energy} = 713 + 2(436) = 1585$$

The bonds formed are four C-H bonds:

$$\text{Total energy} = 4x \text{ (x = mean C-H bond enthalpy)}$$

$$\text{So } 1585 - 4x = -76$$

$$\text{So } 4x = 1585 + 76 = 1661 \text{ kJmol}^{-1}$$

$$\text{So } x = 415 \text{ kJmol}^{-1} = \text{mean bond enthalpy of C-H}$$

HESS' LAW

Hess' Law states that "the enthalpy change for a chemical reaction depends only on the initial and final states and is independent of the path followed".

In other words whichever route, however direct or indirect, by which the reaction proceeds, the overall enthalpy change for the reaction will be same. It is an application of the principle of conservation of energy.

Hess' Law can be used to calculate many enthalpy changes which cannot be measured directly.

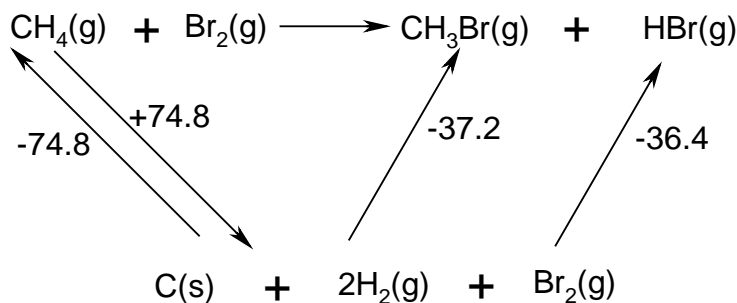
Many enthalpy changes can be calculated simply by using enthalpies of formation and combustion and applying Hess' Law.

1. Calculations using enthalpies of formation

Consider the reaction $\text{CH}_4(\text{g}) + \text{Br}_2(\text{l}) \rightarrow \text{CH}_3\text{Br}(\text{g}) + \text{HBr}(\text{g})$

One way by which this reaction could proceed would be to convert all the reactants into their constituent elements in their standard states and then to convert the elements into products.

Since the enthalpy of formation of CH_4 is -74.8 kJmol^{-1} then the enthalpy change when one mole of CH_4 is converted into its elements will be $+74.8 \text{ kJmol}^{-1}$. Given that the enthalpies of formation of CH_3Br and HBr are -37.2 kJmol^{-1} and -36.4 kJmol^{-1} respectively, then the enthalpy change for the reaction by this route can be calculated:



An energetic cycle such as this is known as a Hess' Law cycle.

$$\Delta H = -(-74.8) + (-37.2) + (-36.4) = +1.2 \text{ kJmol}^{-1}$$

The enthalpy change of any reaction can be calculated if the enthalpies of formation of all the reactants and products are known. The enthalpy of formation of elements in their standard states is always zero.

The calculation can be condensed into a simple formula:

$$\Delta H = \Sigma[\Delta H_f(\text{products})] - \Sigma[\Delta H_f(\text{reactants})]$$

2. Calculations using enthalpies of combustion

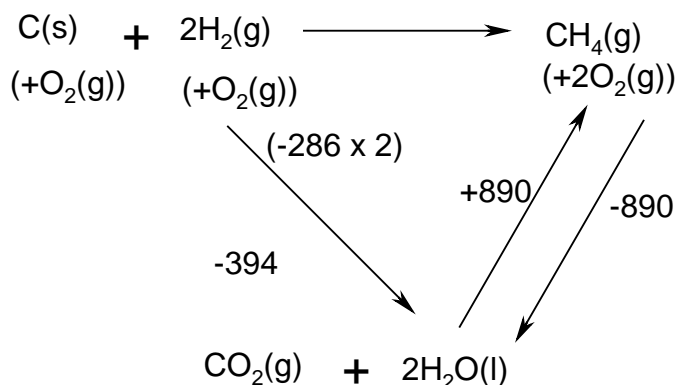
All organic compounds burn in air to give carbon dioxide and water.

Consider the reaction $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$

One way by which this reaction could proceed is to convert the reactants to carbon dioxide and water by combustion, and to convert carbon dioxide and water to methane and oxygen (ie the reverse of combustion).

If the enthalpy of combustion of methane is -890 kJmol^{-1} , then the reverse must be $+890 \text{ kJmol}^{-1}$. The enthalpy of combustion of hydrogen needs to be doubled because there are two moles of hydrogen in the equation.

If all the relevant enthalpies of combustion are known, the enthalpy change of the reaction by this route can be deduced.



$$\Delta H = -394 + (2 \times -286) - (-890) = -76 \text{ kJmol}^{-1}$$

The enthalpy change for a reaction can always be calculated if the enthalpy of combustion of reactants and products are known.

The calculation can be condensed into a simple formula:

$$\Delta H = \Sigma[\Delta H_c(\text{reactants})] - \Sigma[\Delta H_c(\text{products})]$$