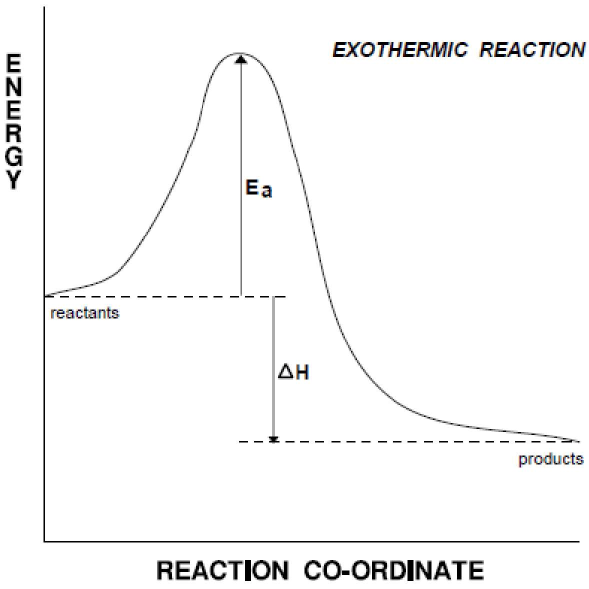
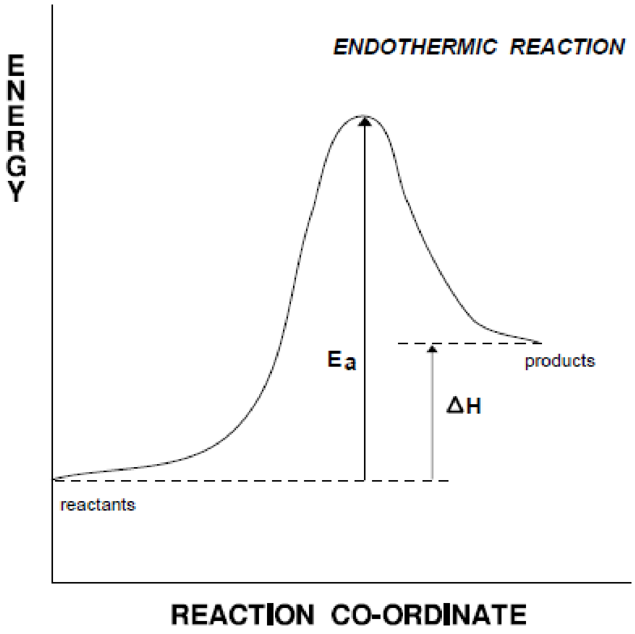
Chemical Energetics

First Law of thermodynamics: 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.





Enthalpy of reactants > products

ΔH = -ve

Heat energy is given out

Increase in temperature

Examples

1. **combustion** of fuels
2. **respiration**

Enthalpy of reactants < products

ΔH = +ve

Heat energy is absorbed

Decrease in temperature

Examples

1. **photosynthesis**
2. **thermal decomposition**

Standard Enthalpy Changes

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^o**. During these chemical changes, the pressure should be kept constant.

Enthalpy Change **Standard Enthalpy Change (at 298K)**

ΔH $\Delta H^{\ominus}_{298}$

Standard Enthalpy change of Reaction $\Delta H^{\ominus}_{r}$

Definition: ***It is the energy change when the molar quantities of reactants as stated in the equation react together under standard conditions***

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.

Experiment to determine ΔH°_{r}

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

$$\boxed{Q = mc\Delta T}$$

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 $Jg^{-1}K^{-1}$.

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

Questions

In all the following questions, assume that the densities and specific heat capacities of the solutions are the same as pure water i.e. $\rho = 1.0\ gcm^{-3}$ and $c = 4.18\ Jg^{-1}K^{-1}$

1. ***Zinc will displace copper from copper (II) sulphate solution according to the following equation:***

   $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$

   If an excess of zinc powder is added to 50 cm^3 of 1.0 $moldm^{-3}$ copper(II) sulphate, the temperature increases by 6.3 ^oC. Calculate the enthalpy change for the reaction.

2. ***Magnesium will also displace copper from copper (II) sulphate solution. If an excess of magnesium is added to 100 cm^3 of 1.0 $moldm^{-3}$ copper(II) sulphate, the temperature increases by 46.3 ^oC.***

   a) ***Calculate the molar enthalpy change for the reaction***

b) ***Calculate the minimum quantity of magnesium required to ensure it is in excess.***

c) ***Calculate the temperature change if only 0.8 g of magnesium is added.***

3. ***When 5.73 g of sodium chloride (NaCl) dissolves in 100 cm^3 of water, the temperature of the water fell from 22.4 ^{o}C to 19.8 ^{o}C. Calculate the enthalpy change of the reaction.***

4. ***When 2.3 g of magnesium chloride dissolves in 200 cm^3 of water, the temperature rose by 3.4 ^{o}C. Calculate the enthalpy change for the reaction.***

5. ***If 50 cm^3 of 0.1 moldm^{-3} HCl and 50 cm^3 of 0.1 moldm^{-3} NaOH are mixed, the temperature of the solution rises by 0.68 ^{o}C. Calculate the enthalpy change of the reaction in kJmol^{-1}.***

6. ***If 50 cm^3 of 1.0 moldm^{-3} NaOH is added to 25 cm^3 of 2.0 moldm^{-3} CH_3COOH, the temperature rose by 8.3 ^{o}C. Calculate the molar enthalpy change for the reaction.***

Standard Enthalpy of Combustion (ΔH°c)

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.***

Values **Always exothermic**

Example(s)

$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$H_{2(g)} + ½\, O_{2(g)} \rightarrow H_2O_{(l)}$,□ΔH = -285.8 kJmol^{-1}
The standard enthalpy of combustion of hydrogen is -285.8 kJmol^{-1}.

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$,□ ΔH = -890.3 kJmol^{-1}
The standard enthalpy of combustion of methane is -890.3 kJmol^{-1}.

$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$,□ ΔH = -1367.3 kJmol^{-1}
The standard enthalpy of combustion of ethanol is -1367.3 kJmol^{-1}.

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

Write out equations representing the standard enthalpies of combustion of...
methanol
cyclohexane

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

Experiment to determine enthalpy of combustion

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 calculated using...

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

where
q = heat energy J
m = mass g
c = Specific Heat Capacity J K -1 g -1 [water is 4.18]
ΔT = change in temperature K

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

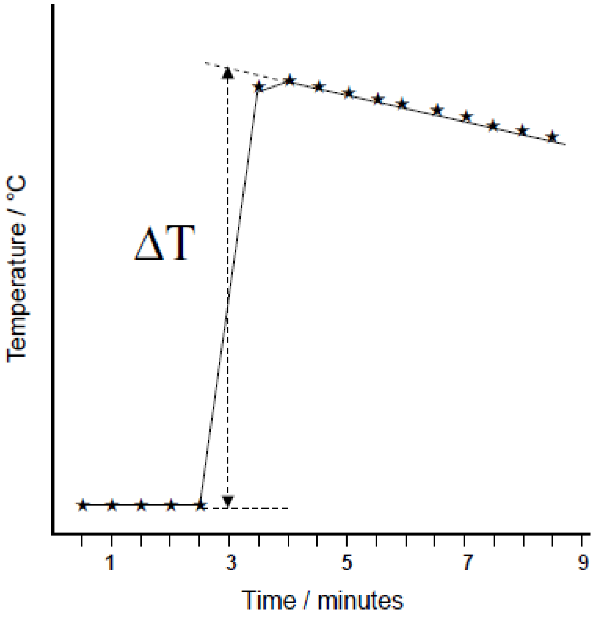
Graphical method

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

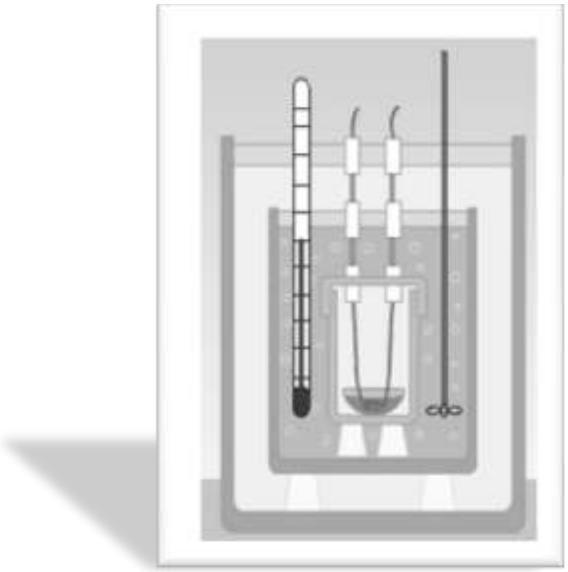
Reactants are mixed after three minutes.

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

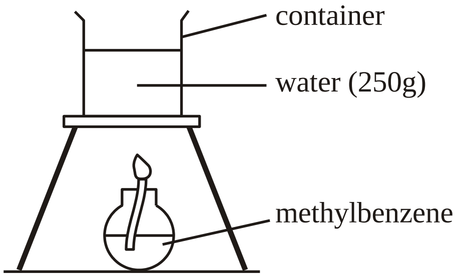
Extrapolate the lines as shown and calculate the value of DT.



The Bomb Calorimeter:



An experiment was carried out to determine a value for the enthalpy of combustion of liquid methylbenzene using the apparatus shown in the diagram.



Burning 2.5 g of methylbenzene caused the temperature of 250 g of water to rise by 60°C. Use this information to calculate a value for the enthalpy of combustion of methylbenzene, C_7H_8 (The specific heat capacity of water is 4.18 J K^{-1} g^{-1}. Ignore the heat capacity of the container.)