UNIT 5 - CHEMICAL ENERGETICS

Enthalpy Changes

Every chemical reaction involves the exchange of energy between what we call the system and its surroundings. For example, when magnesium and sulphuric acid react in a test tube:

1) The **system** consists of the chemical bonds and other forces of attraction and repulsion between the atoms of reactants and of the products formed.
2) The **surroundings** include:
    a) The test tube
    b) The air around the test tube
    c) The thermometer dipped into the reaction mixture

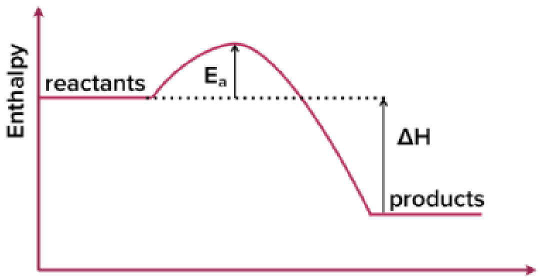
The total heat energy content of any substance at constant pressure is called its enthalpy. Because of how difficult it is to observe things at the atomic and sub-atomic levels, it is not possible to measure the total enthalpy of a substance.

We can easily measure the enthalpy change that accompanies reactions. This is written as ΔH and pronounced 'delta H'. ΔH can either have a positive or negative value, depending on the nature of energy exchange in the reaction.

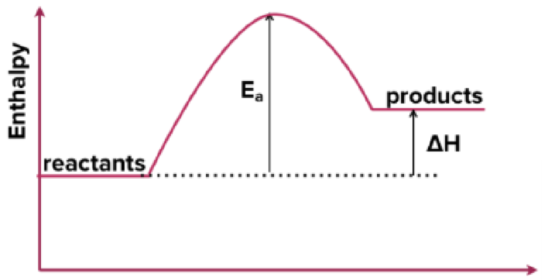
When energy flows from the system to the surroundings, the temperature of the surroundings increases. This indicates that heat was given out as a result of the reaction, and so the products of the reaction are at a lower energy level than the reactants were. These types of reactions are called exothermic reactions. **The value for ΔH is *negative* for exothermic reactions.**

When energy flows from the surroundings to the system, the temperature of the surroundings decreases. This indicates that heat was taken in as a result of the reaction, and so the products of the reaction are at a higher energy level than the reactants were. These types of reactions are called endothermic reactions. **The value for ΔH is *positive* for endothermic reactions.**

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



Enthalpy of reactants > products,ΔH = —ve
EXOTHERMIC: Heat given out



Enthalpy of reactants < products, ΔH = +ve
ENDOTHERMIC: Heat absorbed

Standard Enthalpy Changes

The energy change that accompanies a reaction depends on:

1) The amount of reactants (moles)
2) The physical state of the reactants and products
3) The temperature of the reactants and products

As reactants can exist at various energy levels at different physical states, temperatures, and pressures, there was a need to standardize conditions under which these values were measured. These are now known as <u>standard conditions</u>. They are a *pressure* of 10^5 Pa (100 kPa), a *temperature* of 298K (25°C) and each substance involved in the reaction is in its normal state at these values of temperature and pressure.

Enthalpy changes are described depending on what type of reaction is taking place. The following are some of the most commonly used enthalpy changes:

1) Standard enthalpy change of formation
2) Standard enthalpy change of combustion
3) Standard enthalpy change of neutralization

<u>Standard Enthalpy Change of Formation</u>

"The enthalpy change when one mole of a compound is formed in its standard state from its elements in their standard states under standard conditions."

Symbol: ΔH°_f
Values: Usually, but not exclusively, exothermic
Example:
$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$

Standard Enthalpy Change of Combustion

"The enthalpy change when one mole of a substance undergoes complete combustion under standard conditions. All reactants and products are in their standard states."

Symbol: ΔH^{O}_{c}

Values: Always exothermic

Example:

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$

Standard Enthalpy Change of Neutralization

"The enthalpy change when an acid and a base react to form one mole of water under standard conditions."

Symbol: $\Delta H^{O}_{neu.}$

Values: Exothermic

Example:

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

Measuring Enthalpy Changes

Calorimetry is used to measure enthalpy changes.

It usually involves heating)or cooling) known amounts of water.

Many reactions occur in aqueous solution – reactants and/or products dissolved in water – so water is the natural choice to measure various enthalpy changes. The enthalpy change of reaction causes the temperature of the water to change:

- **Endothermic reactions** take in energy, thus the temperature of water falls
- **Exothermic reactions** give energy out, thus the temperature of water rises

The energy required to change the temperature of a substance can be calculated using:

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

Q = heat energy, measured in Joules (J)
m = mass, measured in grams (g)
c = Specific Heat Capacity of water, measured in $JK^{-1}g^{-1}$ or $J^{O}C^{-1}g^{-1}$
ΔT = change in temperature, measured in Kelvin (K) or degrees Celsius (^{O}C)

25cm³ of 1 moldm⁻³ HCl (aq) was neutralized by 25 cm³ of 1 moldm⁻³ NaOH (aq). The temperature was increased by 5°C. Calculate the enthalpy change of neutralisation.

$NaOH + HCl \rightarrow NaCl + H_2O.$

$q = mc\Delta T.$

$= 50 \times 4.18 \times 5$

$= 1045\,J.$

$\hookrightarrow 1.045\,kJ.$

$n(NaOH) = \frac{1 \times 25}{1000} = 0.0250\,mol$

$\Delta H^{\theta}_{neu} = \frac{-1.045}{0.0250} = -41.8\,kJmol^{-1}$

C_6H_{14}

On complete combustion, 0.18g of hexane raised the temperature of 100g water from 22°C to 47°C. Calculate its enthalpy of combustion.

1. 100g.
2. 25°C.
3. 4.18

$m = 0.18g.$

$Mr = 86.$

$nC_6H_{14} = \frac{0.18}{86}$

$= 2.09 \times 10^{-3}\,mol$

$q = mc\Delta T.$

$= 100 \times 4.18 \times 25$

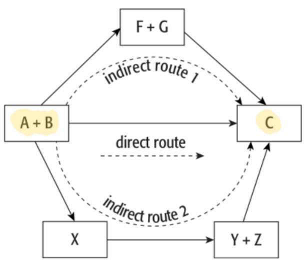
$= 10450\,J$

$\hookrightarrow \frac{10450}{1000}$

$\Delta H^{\theta}_{c} = \frac{-q}{n} = \frac{-10.45}{2.09 \times 10^{-3}}$

$= -5000\,kJmol^{-1}$

Hess' Law



ΔH(direct) = ΔH(indirect 1) = ΔH(indirect 2)

Hess' law is an application of the first law of thermodynamics, which in its simplest form is the law of conservation of energy. Since energy cannot be destroyed or created the energy change in a chemical process should be the same as long as the initial and final states are the same. It states that:

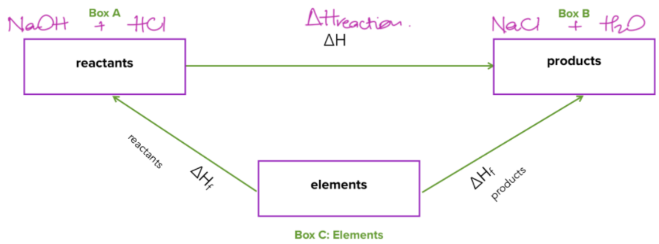
> "The total enthalpy change in a chemical reaction is independent of the route by which the chemical reaction takes place as long as the initial and final conditions are the same."

How to solve questions using Hess' Law:

1) Write out the balanced equations for all energy changes mentioned in the question
2) Choose the most complicated (or populated) equation
3) Fill the first two boxes with it
4) Put everything else in the third box
5) Balance each box to ensure the number of atoms in each box is the same
6) The box with which your cycle begins is the start box and the one where the cycle ends is the stop box
7) Construct an equation and solve it

Note: the enthalpies given are per mole therefore as the number of moles changes, the energies have to be multiplied by the same number.

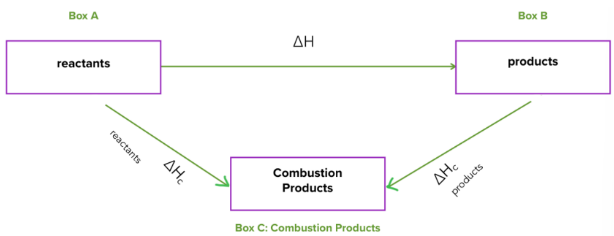
<u>Formation Reactions</u>



Start box: C **End box: B**

C ➜ A + A ➜ B = C ➜ B

<u>Combustion Reactions</u>



Start box: A **End box: C**

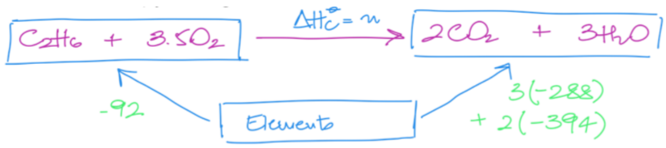
A ➜ B + B ➜ C = A ➜ C

Question: Calculate the standard enthalpy change of combustion of ethane from the following data:

Standard enthalpy change formation of carbon dioxide = -394 kJ mol^{-1}

Standard enthalpy change of formation water = -288 kJ mol^{-1}

Standard enthalpy change of formation of ethane = -92 kJ mol^{-1}



$-92 + \Delta H_c = 2(-394) + 3(-288)$

- ★ Standard enthalpy change of atomization - of an element; when 1 mole of a gaseous atom is formed from its elements in their standard state, under standard conditions. For example:
  - $\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}$
  - $Na_{(s)} \rightarrow Na_{(g)}$

Bond Enthalpy

Bond enthalpy is the energy required to break one mole of a particular type of bond in gaseous molecules under standard conditions. Bond enthalpy values are all positive, showing that bond enthalpies are endothermic (breaking bonds takes in energy).

The values found in the data booklet (now the data section) are average values for each type of bond. The same bond may have very slightly different bond enthalpies in different compounds.

The O–H bond has a slightly different enthalpy value in each compound.

- ★ The amount of energy needed to break or form the same type of bond is the same.