SALAAMA SECONDARY SCHOOLS

Chapter four

Enthalpy change

Common thermodynamic terms:

When we study a set of energy changes, we focus our attention on a limited and well defined part of the universe

- **System**: parts of the world of interest or everything involves in the reaction
  e.g water in beaker, reaction in vessel, solution in beaker, chemical cell and biological cell
- **Surrounding:** everything outside the system or everything that surrounds the system
  e.g : Beaker, test tube, person, air, thermometer
- **Boundary:** is a substance that separates system from its surrounding

Types of system:

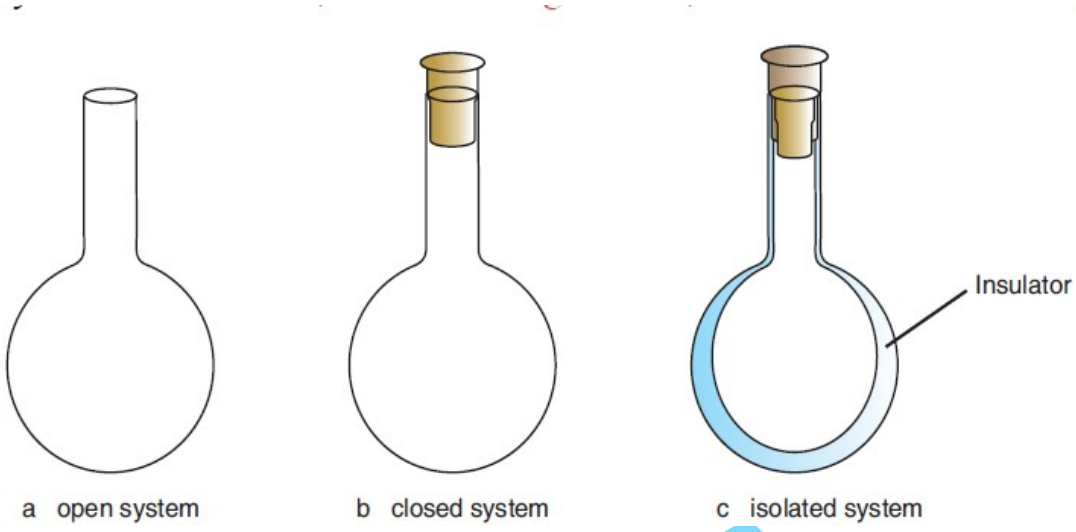
- **Open system**
- **Closed system**
- **Isolated system**

An open system – is a system that can exchange mass and energy, usually in the form of heat, with its surroundings. For example, an open system may consist of a quantity of water in an open container

A closed system – is a system which transfers energy, but not mass across its boundary
with its surroundings.
Example: If you close the flask, so that no water vapor can escape from or condense into the container, you create a closed system.

An isolated system – is a system in which neither the transfer of mass nor that of
energy takes place across its boundary with the surroundings. By placing the water in a
totally insulated container, as shown in we construct an isolated system.

SS BOYS



Thermochemistry:

- Thermochemistry is the study of heat changes during chemical reactions. When chemical reaction takes place bonds must be broken and others must be formed. Bond breaking is an endothermic process while bond formation is an exothermic process.

Most chemical reactions release or takes heat energy to the surrounding. These can be described by either exothermic or endothermic reactions.

Endothermic reactions:

Endothermic reactions absorb heat energy from the surrounding to the system.

- ➢ In endothermic reaction the temperature decrease
- These reactions require input of energy that may come from a flame, electricity, sunlight or other surrounding.
- In endothermic reactions the energy absorbed by the bond breaking is greater than the energy released by the bond formation.
- The total heat content of product is greater than the heat content of the reactant therefore more energy is absorbed from the surrounding

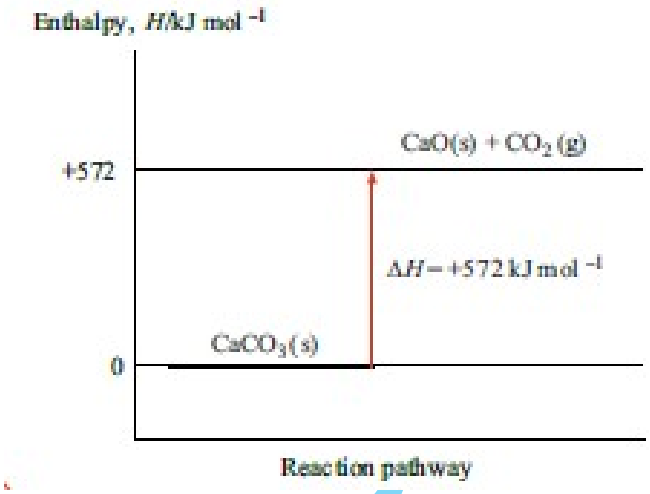
$$H_{product} > H_{reactant}$$

SSS BOYS

- It is always given a positive value (+ΔH)

Examples of endothermic reactions:

1) Photosynthesis occurs in plants
2) The reactions that occurs within food during cooking
3) Polymerization reactions
4) Electrolysis
5) The reduction of silver in ion to silver in photograph
6) Dissolving ammonium chloride in water. As water and ammonium chloride crystal mixes. Energy transferred from the surroundings cooling the injury.
7) Evaporation
8) Decomposition reactions
9) Making copper oxide from copper carbonate



Exothermic reactions:

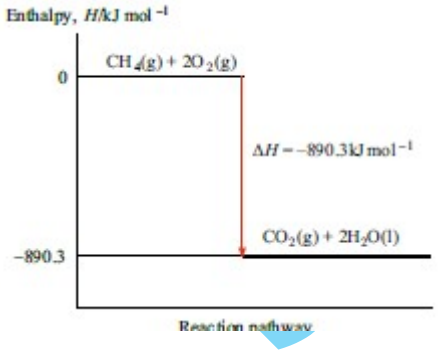
Exothermic reactions are reactions that release energy from the system to the surroundings.

- We can recognize exothermic reactions by detecting a rise in temperature of reacting materials and their surroundings. (the test tubes, beaker, the solvent or air).
- In exothermic reactions the energy released by the bond formation is greater than the energy absorbed by the bond breaking.

- The total heat content of reactant is larger than total heat content of product therefore the excess heat is released to the surroundings
- It is always Negative value (-ΔH)

Examples of exothermic reactions:

- ✓ Neutralization reactions
- ✓ All combustion reactions
- ✓ Respiration in plants and animals
- ✓ Reactions of acids with metals
- ✓ Water with quick lime
- ✓ Precipitation reactions
- ✓ Displacement reactions
- ✓ Also the reaction between iron and sulphur to form iron(ii)sulphide
- ✓ Crystallization reactions



Common fuels:

The term fuel refers to a combustible substance which on burning in air gives large amount of heat that can be used economically for domestic and industrial purpose. Fuels can be in different physical state.

- ❖ **Solids –** coal, fire wood, charcoal
- ❖ **Liquid –** petroleum fuels, such as fuel oil, kerosene, petrol and diesel

- **Gases –** liquefied petroleum gas(LPG),coal gas, natural gas, water gas and biogas.

Choice of fuel:

The value of a fuel depends on the quantity and intensity of heat produced per unit mass of the fuel.

Factors considering when choosing fuel are:

- Energy content
- Availability and affordability
- Easy and rate of combustion
- Easy of storage and transportation
- Effects on the environment
- Non- combustible material content
- Environmental pollution by fuels.

Enthalpy and enthalpy changes:

Measurements of energy transferred during chemical reactions must be made under controlled conditions. A special name is given to energy exchange with the surroundings when it takes place at constant pressure is called enthalpy change.

- Enthalpy: is the total energy content of the reacting materials at constant pressure. It is given the symbol.H enthalpy cannot be measured but it is possible to measure the enthalpy change, when energy is transferred to or from reacting system and changes from one enthalpy to another.

Enthalpy change is given the symbol. ΔH (Δ this is a Greek word delta which means a change)

$\Delta H = H_{product} - H_{reactant}$

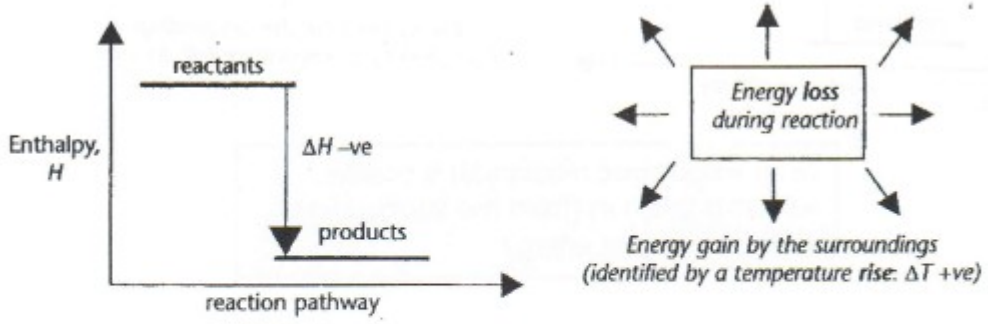
The unit for enthalpy change is Kj/Mol

- We illustrate enthalpy changes by enthalpy profiles.

SSS BOYS

a) An exothermic enthalpy changes: energy is lost from the system to the surroundings.

It is always given negative value. $\Delta H = -XKj/Mol$

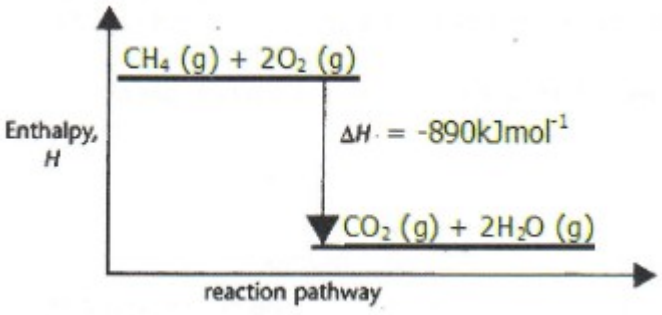


In an exothermic reaction, ΔH is negative:
- Heat is given out (to the surrounding)
- The reacting chemicals lose energy.

For example:

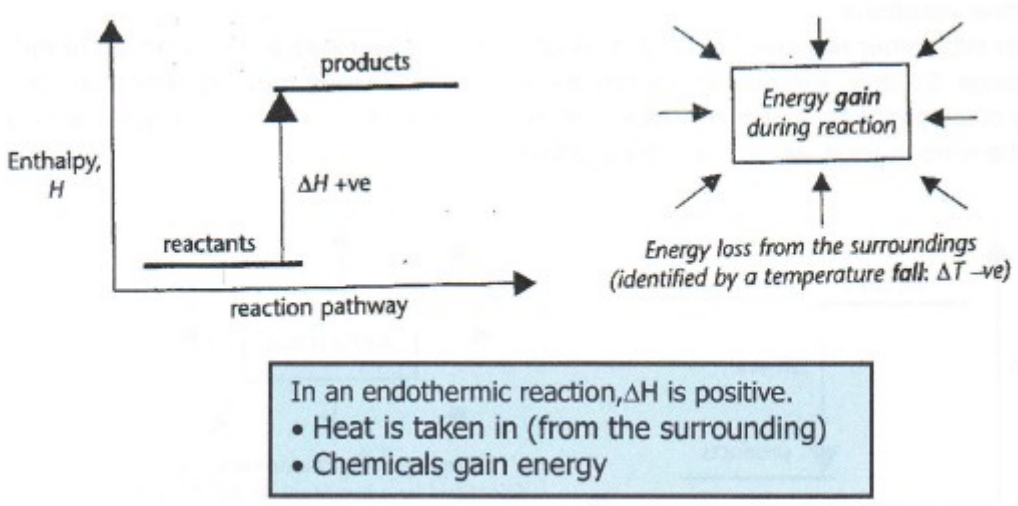
Draw an enthalpy profile for the reaction in which methane burns completely in oxygen to give carbon dioxide and water vapour. ΔH for the reaction is -890kJmol-1.

$CH_4 + (g) + 2O_2 (g) \longrightarrow CO_2 (g) + 2H_2O (9)$



b) **An endothermic:**
During an endothermic reaction, heat energy is taken in from the surroundings, which will fall in temperature. So, in an

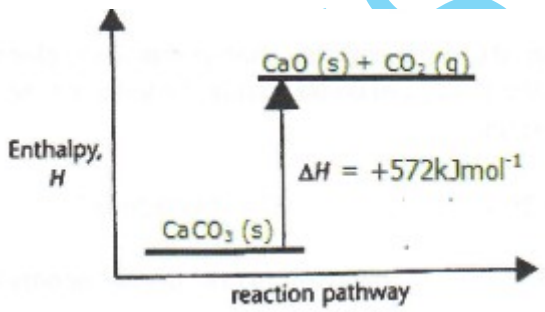
endothermic reaction the enthalpy of the reactants is less than the enthalpy of the products.



In an endothermic reaction, ΔH is positive.
- Heat is taken in (from the surrounding)
- Chemicals gain energy

Example:
Draw an enthalpy level diagram for thermal decomposition of limestone (calcium carbonate) to give carbon dioxide and calcium oxide. ΔH for the reaction is +572kJmol-1.

$CaCO_3$ (s) ⟶ CaO (s) + CO_2 (g)



Energy is conserved:

It is important to understand that energy is not been created by exothermic chemical reaction and it is not destroyed in endothermic chemical reactions.

- Energy is transferred from reacting chemicals to the surroundings or other way round but the total energy of the reacting chemicals and their surroundings remains constant.

- This is applied to the law conservation of energy which states: energy is neither be created nor destroyed. You may also hear the first law of thermodynamics.

Standard enthalpy changes: standard conditions

When we compare the enthalpy changes for various reactions we must use standard conditions, such as known temperature, pressure, amounts and concentrations of reactants or products. This allows us to compare the standard enthalpy change of reaction.

A standard enthalpy change for reaction takes place under these standard conditions:

- A pressure of 100 kilopascals
- A temperature of 298 k
- The reactants and products must be their physical states (solid, liquid and gas) that are normal for these conditions
- Any solutions have a concentration of 1M

The complete symbol for standard enthalpy change of reaction may be written as: $\Delta H_r^{\theta, 298}$

The meaning of the symbol being:

- Θ means standard and assumes a pressure 100Kpa
- r is the reaction and is changed to f for formation and c for combustion
- 298 means all reactants and products are in their physical state

Note: it common practice to omit 298 from the symbol

Quantitative determination of enthalpy changes:

The amount of heat given out or takes in during chemical reaction depends on the quantity of the reactants. To give the quantities we need to use an equation.

The standard enthalpy changes of reaction: ΔH_r^{θ}

SSS BOYS

The standard enthalpy change of reaction is the enthalpy change when amounts of reactants reacted under standard conditions.
The enthalpy change of reaction ΔH_r^θ depends upon the quantities as shown in chemical equations

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H^\theta_r = -286kJ\ mol^{-1}$
1mol ½ mol 1mol

But with twice the quantities, there is twice the enthalpy change:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad \Delta H^\theta_r = -572kJ\ mol^{-1}$
2mol 1mol 2 mol

Standard enthalpy changes of formation: ΔH_f^θ

Standard enthalpy change of formation is the enthalpy change when one mole of compound is formed from its elements

Example:

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H^\theta_r = -286kJ\ mol^{-1}$
1mol ½ mol 1mol

- For an element the standard enthalpy change of formation is zero. Such as H_2, Cl_2, O_2

Standard enthalpy changes of combustion: ΔH_c^θ

Standard enthalpy change of combustion is the enthalpy change when one mole substance is completely burned in oxygen

Example:

$H_2(g) + 1/_2O_2(g) \longrightarrow H_2O(l)$ $\quad \mathbf{\Delta H_c^\theta = -286Kj/mol}$

- In practice it is not possible to measure to achieve complete combustion under standard conditions.

- Measurements are taken under standard conditions. Then value for enthalpy change is determined and this is corrected under standard conditions through calculations.

Measuring enthalpy change of combustion:

We often use simple calorimeter to find the enthalpy change of combustion when fuel burns; the apparatus we used is called calorimeter form the Latin calori meaning heat. This reduced the heat loss
The flame calorimeter is an improved version of the simple calorimeters used for measuring enthalpy change of combustion. It consists of the following features that are designed to reduce heat loss:

- The spiral chimney is made of copper
- The flame is enclosed

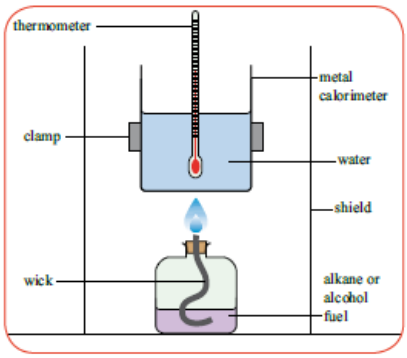
You can calculate the standard enthalpy change of combustion if you know:

- ✓ The mass of the fuel burned
- ✓ The mass of water which is corresponds to the volume of water
- ✓ Initial temperature of water
- ✓ Final temperature of water

Amount of energy lost by the fuel = amount of energy gained by the water

$Q = MC\Delta T$

No of moles of fuel burnt = mass of fuel burnt/molar mass of the fuel



SSS BOYS

Example:

The relative molecular mass of the fuel is 46g, 5g of this fuel was burned to found to raise the temperature of 500g of water from 15C0 to 80Co, calculate the molar heat combustion of the fuel?

Example 2:

0.32g of methanol was burned of 200g of water the temperature in the calorimeter rose by 4K. Calculate the enthalpy change combustion of methanol?

$CH_3OH(l) + 1\frac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Solution

Method 1

$q = mc\Delta T$

$= 200g \times 4.2Jg^{-1}k^{-1} \times 4k$

$= 3360J$ or $3.36kJ$

0.32g of methanol produces 3.36kJ

so, 32g of methanol produce $\frac{3.36kJ \times 32g/mol}{0.32g} = 336kJmol^{-1}$

$\therefore \Delta H_c = -336kJmol^{-1}$ (negative because heat is given out)

Method 2:

a) Calculate the no of moles of methanol burnt
b) Calculate the total heat for the reaction
c) Calculate the molar enthalpy change of combustion
d) Calculate the combustion equation of methanol

SALAAMA SECONDARY SCHOOLS

The standard enthalpy change of neutralization ΔH^{θ}_{neut} :

- Is the enthalpy change when one mole of acid is neutralized or vice versa under standard condition?
- The Neutralization is exothermic

$$\underset{\text{Acid}}{HCl\,(aq)} + \underset{\text{base}}{NaOH\,(aq)} \rightarrow NaCl\,(aq) + \underset{1mol}{H_2O\,(l)} \qquad \Delta H^{\theta}_{neut} = -57.9kJ\ mol^{-1}$$

- Strong acids and bases are completely dissociated in water and their enthalpy change of neutralization are high
- For weak acids, this enthalpy change of neutralization is less because some input of energy is required to dissociate the acid.
- Polystyrene cup is used for the reaction to reduce heat loss

Example

$50cm^3$ of 1 mol/dm^{-3} hydrochloric acid and $50cm^3$ of 1 mol/dm^{-3} sodium hydroxide solution was mixed in an expanded polystyrene beaker. The temperature rose by 6.6K. Calculate the enthalpy change of neutralization for the reaction?

Solutions:

- The solution is not pure water but we assume it
- Total volume of the solution is $100cm^3$ =100g ($50cm^3$ of acid + $50cm^3$ of alkali)
- because the density of water is approximately 1 g/cm^3

Q = mass of × specific heat capacity × temperature change = MCΔT

q = m × c × ΔT

SSS BOYS

$= 100g \times 4.2Jg^{-1}K^{-1} \times 6.6K$

$= 2772J$ or $2.772kJ$

Number of moles of acid = concentration × volume

(and also of alkali) (in $moldm^{-3}$) (in dm^3)

$= 1\ moldm^{-3} \times 0.05dm^3$

$= 0.05$ mol

The neutralization of 0.05 mol of acid gives 2.772kJ.

so 1 mol would give $\frac{2.772kJ}{0.05} = 55.44kJ$

$\therefore \Delta H_{neutralisation} = -55.44kJ\,mol^{-1}$ (negative because it is exothermic)

SSS BOYS

Enthalpy change of displacement:

- A metal that is more reactive than another will displace the less reactive one from a solution of its compound. The reaction can be investigated using a polystyrene beaker as before.

- Enthalpy change of displacement is the enthalpy change that takes place when 1 mole of aqueous ions is displaced from its solution.

- If the reaction takes place under standard conditions, it is known as the standard enthalpy change of displacement (ΔH^{θ}_{dis})

Example

An excess of zinc was added to 25 cm^3 of 0.2 mol/dm^3 copper sulphate solution and the temperature rose by 10 K. calculate the enthalpy change of displacement for the reaction.

Solution

We assume the density of the solution as 1 g/cm^3 and it's specific heat capacity as 4.2 $jg^{-1}k^{-1}$

Enthalpy change = mass of solution × specific heat capacity of solution ×temperature rise

$q = m \times c \times \Delta T$
$= 25\ g \times 4.2\ jg^{-1}k^{-1} \times 10\ K$
$= 1050\ j$ or $1.05\ kj$

Number of moles of copper sulphate in = Concentration × Volume (dm^3)
$= 0.2\ mol/dm^3 \times 0.025\ dm^3$
$= 0.005\ mol$

The displacement of 0.005 moles of copper produces 1.05 kj of energy.

Therefore 1 mol of copper would produce:

$$\frac{1.05\ \text{kj}}{0.005\ \text{mol}} = 210\ \text{kJmol}^{-1}$$

So, ΔH for the reaction is – 210 $kJmol^{-1}$

Bond enthalpy:

SS-BOYS

- For reaction to take place bonds must be broken and others must be formed
- Bond breaking requires input of energy while bond formation gives out heat energy
- Bond breaking is endothermic
- Bond formation is exothermic
- Bond enthalpy is the energy required to break one mole of bond
- However, the same bond, for example C – H, may have slightly different bond enthalpies in different molecules, but we usually use the average value. This value is called the **mean bond enthalpy** (often called the bond energy). calculations using them for specific compounds will only give approximate answers. However, they are useful, and quick and easy to use. Mean bond enthalpy

Example

Calculate the enthalpy change for the following reaction using the bond enthalpies given in the table.

C_2H_6 (g) + Cl_2 (g) → C_2H_5Cl (g) + HCl (g)

Bond	**C – H**	**C – C**	**Cl – Cl**	**C – Cl**	**H – Cl**
Bond enthalpy/ kJmol^{-1}	413	347	243	346	432

Solution

1. First draw out the molecules and show all the bonds. (Formulae drawn showing all the bonds are called displayed formulae.)
2. Now imagine that all the bonds in the reactants break leaving separate atoms. Look up the bond enthalpy for each bond and add them all up. This will give you the total energy that must be put in to break the bonds and form separate atoms.

We need to break these bonds:

6 × C – H	6 × 413 kJmol^{-1}	= 2478 kJmol^{-1}
1 × C – C	1 × 347 kJmol^{-1}	= 347 kJmol^{-1}
1 × Cl – Cl	1 × 243 kJmol^{-1}	= 243 kJmol^{-1}
	Total	= 3068 kJmol^{-1}

SSS BOYS

So 3068 $kJmol^{-1}$ must be put in to convert ethane and chlorine to separate hydrogen, chlorine and carbon atoms.

3. Next imagine the separate atoms join together to give the products. Add up all the bond enthalpies of the bonds that must form. This will give you the total energy given given out by the bonds forming.

We need to make these bonds:

5 × C – H	5 × 413 $kJmol^{-1}$	= 2065 $kJmol^{-1}$
1 × C – C	1 × 347 $kJmol^{-1}$	= 347 $kJmol^{-1}$
1 × C – Cl	1 × 346 $kJmol^{-1}$	= 346 $kJmol^{-1}$
1 × H – Cl	1 × 432 $kJmol^{-1}$	= 432 $kJmol^{-1}$
	Total	= 3190 $kJmol^{-1}$

So 3190 $kJmol^{-1}$ is given out when we convert the separate hydrogen, chlorine and carbon atoms to chloroethane and hydrogen chloride.

4. Finally work out the difference between the energy put in to break the bonds and the energy given out to form bonds. This is the approximate enthalpy change of the reaction.

Enthalpy change = total energy for bond breaking – total energy for bond making

= 3068 $kJmol^{-1}$ – 3190 $kJmol^{-1}$

= – 122 $kJmol^{-1}$

More energy is given out than taken in so the reaction is exothermic.

SSS BOYS