Higher

Chemistry

HSN11200
Unit 1 Topic 2

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Topic 2 – Enthalpy Changes/The Mole

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Enthalpy Changes

This part of the unit studies the energy changes which happen in chemical reactions. We have seen that energy changes are nearly always evident when a reaction happens we will only study the heat energy changes in chemical reactions. All substances contain energy which in previous years we have called 'chemical energy'. This energy can be equated to a 'heat content' or enthalpy (symbol H). During all chemical reactions the enthalpy of the substances changes from that of the reactants to that of the products. ie H_r becomes H_p.

It is agreed by convention that the Enthalpy Change ΔH must be equal to the enthalpy of the reactants subtracted from that of the products.

ie $$\Delta H = H_p - H_r$$

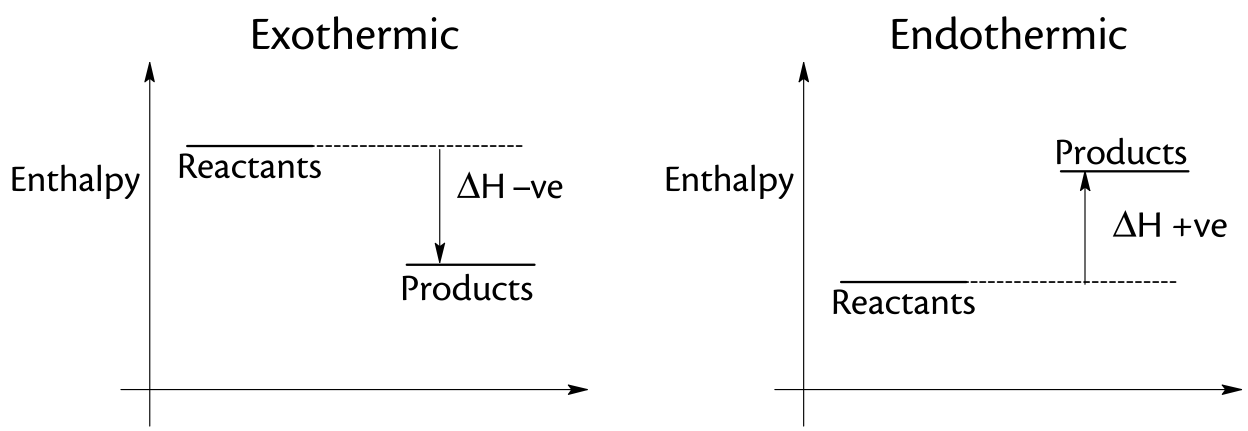
There is no way of measuring the enthalpy of any single substance directly. For this reason we can only discuss enthalpy changes in reaction and this can be measured as an amount of heat given out (exothermic reaction) or taken in (endothermic reaction). Obviously, these amounts of heat energy released or absorbed must be dependent on the quantity of substances reacting so we must define the enthalpy changes in terms of energy changes (kilojoules give convenient numbers) per amount of substance (ie the mole).

Units of enthalpy and enthalpy change are kJ mol^{-1}.

Potential Energy Diagrams

We can represent the level of enthalpy held by reactants and products on a 'Potential Energy Diagram'. We have seen these earlier.

Using these it is easier to help define the direction (sign) of ΔH



Exothermic Reactions: If, in the process reactants to products, the chemicals release some of their enthalpy in the form of heat then the products must have lower enthalpy. It stands to reason that $H_p - H_r$ must be negative, (ie ΔH is –ve).

Endothermic reactions: The converse is true and ΔH must be +ve. Endothermic reactions must proceed with an absorption of heat energy from the surroundings, which must therefore cool down.

Some ΔH Definitions

These are very important and must be learned and understood. Note that ΔH values are quoted as energy changes per mole of substance and it must be understood in each individual case what substance is involved (it is not always a reactant, or a product – it can be either!)

Heat of Combustion (Enthalpy of combustion) is the heat energy given out when one mole of a substance burns completely in oxygen. Here, all equations must be written and balanced with the balancing number of the substance burned being 1.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -892\ kJ\ mol^{-1}$$

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H = -1560\ kJ\ mol^{-1}$$

N.B. In tables of values of heats of combustion the negative sign is often missed out. They are always exothermic!

Enthalpy of solution is the enthalpy change when 1 mole of solute is completely dissolved.

$$NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} \qquad \Delta H = +5\ kJ\ mol^{-1}$$

Enthalpy of neutralisation is the heat energy released when 1 mole of water is formed by neutralisation of an acid with a base.

This always involves the reaction of a mole of $H^+_{(aq)}$ with one mole of $OH^-_{(aq)}$.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -57.3\ kJ\ mol^{-1}$$

Ionisation Energy

We will be referring to this later in the unit so it is defined here. It is the energy required to remove one mole of electrons from one mole of particles (atoms or ions) in the gas state.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + e^- \qquad \Delta H = +494\ kJ\ mol^{-1}$$

It is very important that all of these definitions be learned and fully understood! Note that the state of the particles involved is very important – the ionisation energy is the energy involved in removing the electrons from the atoms only in the gas state and the equation must show this!

Experimental Determination of Enthalpy Changes

Many chemical reactions require complicated methods for calculating the enthalpy changes but a simple determination can be done in the laboratory – the enthalpy of combustion of alkanols can be determined by heating water with burning alcohol and measuring the temperature rise. The energy from the flame is that which is absorbed (ignoring heat losses for the purpose of simplifying the calculations!) and this can be calculated from a formula:

$$\text{Energy absorbed (kJ)} = C \times m \times \Delta T$$

where: C = Specific heat of water, 4.18 kJ kg^{-1} °C^{-1}
m = Mass of water in kg
ΔT = Temperature rise of water in °C

If this is the heat energy absorbed by the water from a known mass of alcohol we can work out the heat energy from 1 mole.

The Mole – The Avogadro Constant

We are used to thinking of the mole as the relative atomic mass of an element or the formula mass of a compound in grams, for example:

1 mole of	Weighs
aluminium (Al)	27g
sulphur (S)	32g
oxygen atoms (O)	16g*
oxygen molecules (O_2)	32g*
water (H_2O)	18g
sodium chloride (NaCl)	58.5g
sodium sulphate (Na_2SO_4)	142g

*Note: It is important to know precisely what type of particle is being considered.

The definition of a mole is that amount of substance that contains the same number of elementary particles as 12g of carbon-12.

The usefulness of the mole in chemistry is that all the above contain the same number of elementary particles (atoms, molecules or 'ionic units' depending on the substance being considered). This number has been calculated from the results of many different experiments and has been shown to be 6.02 x 10^{23}. It is known as the Avogadro constant, L. You should be able to do the following types of question based on this.

Example 1

What is the mass of 0.25 moles of nitrogen gas?

The formula of nitrogen gas is N_2 so the formula mass is 28 amu.

1 mole of nitrogen weighs 28g

so 0.25 moles of nitrogen weighs $28 \times \frac{0.25}{1} = 7\text{g}$

Example 2

How many moles of carbon dioxide are in 4.4g of the gas?

The formula of carbon dioxide is CO_2 so the formula mass is 44 amu.

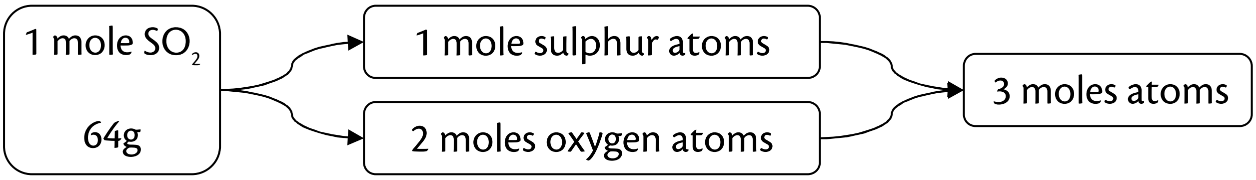
	44g is the mass of	1 mole of CO_2
so	4.4g is the mass of	$1 \times \frac{4.4}{44} = 0.1$ moles of CO_2

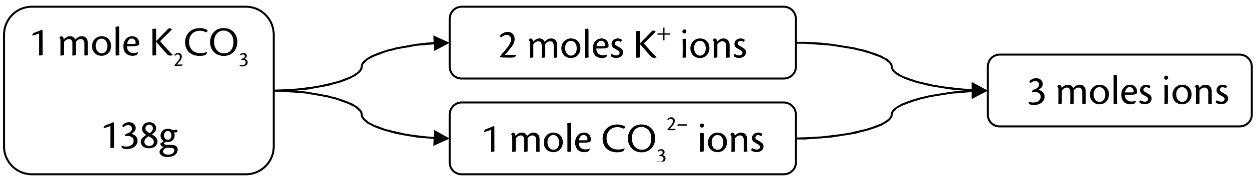
We must always be very careful about the particles we are dealing with.

Consider:

	1 SO_2 molecule contains	3 atoms
so	1 mole of SO_2 molecules contains	3 moles of atoms
	1 $(K^+)_2CO_3^{2-}$ 'formula unit' contains	3 ions
so	1 mole of $(K^+)_2CO_3^{2-}$ 'formula units' contains	3 moles of ions

This is illustrated below:





Using the Avogadro's Constant

We now know that a mole contains 6.02×10^{23} elementary particles. This figure is called the Avogadro Constant. We must be able to do problems involving this number and some examples are given:

Example 3

How many atoms are in 0.69 g of lithium?

The relative atomic mass of Li is 6.9 amu so 1 mole of Li has mass 6.9g.

	6.9g (1 mole) of lithium contains	6.02×10^{23} atoms
So	0.69g of lithium contains	6.02×10^{22} atoms

Example 4

How many molecules are in 3g of water?

Water, H_20, has formula mass 18 amu, so 1 mole of water weighs 18g.

	18g of water (1 mole) contains	6.02×10^{23} molecules
So	3g water contains	$6.02 \times 10^{23} \times \frac{3}{18}$ molecules
		$= 1.003 \times 10^{23}$ molecules

Example 5

How many atoms are in 2.2g of carbon dioxide gas?

Carbon dioxide (CO_2) has formula mass 44 amu, so 1 mole has mass 44g.

Now	1 CO_2 molecule contains	3 atoms
So	1 mole of CO_2 molecules contains	3 moles of atoms
ie.	44g of CO_2 molecules contains	$3 \times 6.02 \times 10^{23}$ atoms
So	2.2g of CO_2 molecules contains	$3 \times 6.02 \times 10^{23} \times \frac{2.2}{44}$ atoms
		$= 9.03 \times 10^{22}$ atoms

We now revise calculations from equations that we did in Standard Grade.

As well as problems of the sort just done, you need to be able to tackle questions in which one of the reactants is in excess.

Example 6

What mass of sodium chloride is formed when 4.6g of sodium burns in 5g of chlorine?

2Na	+	Cl_2	$\longrightarrow$	2NaCl
2 moles		1 mole		2 moles
46g		71g		117g

From the equation:

	46g of sodium reacts with	71 g of chlorine
So	4.6g reacts with	7.1 g of chlorine

So, if all the 4.6g of sodium were to react we would need 7.1 g of chlorine. However we have only 5g of chlorine, so all the sodium cannot react. The sodium is in excess. The mass of sodium chloride formed is calculated using the chlorine, the reactant not in excess.

<u>Chlorine</u>	<u>Sodium chloride</u>
71g	117g
5g	$117 \times \frac{5}{71} = 8.24$g

So 8.24g of sodium chloride are formed

Example 7

What mass of carbon dioxide is formed when 20g of calcium carbonate reacts with 500ml of 1 mol l^{-1} hydrochloric acid?

$CaCO_3$	+	2HCl	$\longrightarrow$	CO_2	+	$CaCl_2$	+	H_2O
1 mole		2 moles		1 mole				
100g		2 moles		44g				

Moles of HCl:

1 mol l^{-1} means: 1000ml contains 1 mole of HCl

so 500ml contains 0.5 moles of HCl

From the equation:

100g of calcium carbonate reacts with 2 moles of HCl so

20g of calcium carbonate reacts with $2 \times \frac{20}{100}$

$= 0.4$ moles HCl

So we have worked out that 20g calcium carbonate reacts with 0.4 moles HCl, but we have been given 0.5 moles of HCl, so the acid is in excess. This means we must calculate the mass of carbon dioxide from the reactant not in excess, ie the calcium carbonate.

Calcium Carbonate	Carbon Dioxide
100g	44g
20g	$44 \times \frac{20}{100} = 8.8g$

So the mass of carbon dioxide formed is 8.8g

Gas Molar Volume

This simply means the volume of a mole of a gas. The volume of a gas is very dependent on temperature and pressure. So when gas molar volumes are stated, the conditions of temperature and pressure are often quoted. However, we will ignore these at this level. Molar volumes can be calculated from density measurements (See 'New Higher Chemistry', page 50). We found, by experiment, the volume of 1 mole carbon dioxide gas. A flask was weighed empty (ie. with the air evacuated) and weighed again when filled with carbon dioxide gas. The exact volume of the flask was found by measuring how much water it could hold.

Results

Mass of empty flask	=	107.38	g
Mass of flask + carbon dioxide	=	108.37	g
So mass of carbon dioxide	=	0.99	g
Volume of flask (ie volume of gas)	=	570	ml

Calculation of Molar Volume

	0.99g of carbon dioxide occupy	570	ml
So	44g (1 mole) of carbon dioxide occupy	25333	ml

So we have found that the molar volume of carbon dioxide is 25.3 litres per mole ($l\ mol^{-1}$)

The experiment was repeated with other gases and their molar volumes were:

Nitrogen = 25333 ml mol^{-1}
Oxygen = 25333 ml mol^{-1}

Experiments of this sort with other gases have shown that the molar volume of all gases is the same as long as the temperature and pressure are the same for each. At 20°C and 1 atmosphere pressure the molar volume of any gas is just over 24 litres per mole ($l\ mol^{-1}$) It seems surprising that 1 mole of any gas occupies the same volume – it certainly is not true for liquids and solids. In a gas, however, the molecules are far apart so the volume of the gas is not dependent on the size of the molecules. In a gas the molecules occupy only about 0.1 % of the total volume – the rest is empty space!

So the molar volume of all gases is the same and it contains 6.02×10^{23} molecules.

Avogadro deduced from this that:

"Equal volumes of all gases, under the same conditions of temperature and pressure, will contain the same number of molecules."

This is known as Avogadro's Hypothesis. The following examples illustrate the use of Molar Volume and Avogadro's Hypothesis.

Volumes of Gases in Reactions

Example 8
What volume of oxygen is required for the complete combustion of 4 litres of methane?

CH_4	+	$2O_2$	$\longrightarrow$	CO_2	+	$2H_2O$
1 mole		2 moles				
1 litre		2 litres				
4 litres		8 litres				

8 litres of oxygen are required

Example 9
What volume of carbon dioxide is produced by roasting 25g of chalk (calcium carbonate)? The molar volume is 24 $l\ mol^{-1}$

$CaCO_3$	$\longrightarrow$	CaO	+	CO_2
1 mole				1 mole
100g				24000 ml
25g				$\frac{25}{100} \times 24000$
				= 6000ml

Example 10

a. How many moles of copper (II) chloride are present in a solution that contains 13.45g of the salt?
b. What is the maximum volume of chlorine which could be obtained by electrolysis of this solution? Take the molar volume as 24 l mol^{-1}.

(a) Formula mass of $CuCl_2$:

$$1 \times Cu = 63.5$$
$$2 \times Cl = 71$$
$$\text{total} = 134.5 \text{ amu}$$

134.5g of $CuCl_2$ is 1 mole so 13.45g of $CuCl_2$ is 0.1 mole

(b) Although we have just calculated that we have 0.1 moles of $CuCl_2$ we have 0.2 moles of chloride ions. This is because each 'formula unit' of $CuCl_2$ contains 2 chloride ions.

	1 mole of $CuCl_2$ contains	2 moles of chloride ions
So	0.1 mole of $CuCl_2$ contains	0.2 moles of chloride ions.

The equation for the formation of chlorine during electrolysis is:

$2Cl^-$	$\longrightarrow$	Cl_2	$+ \; 2e^-$
2 moles		1 mole	
2 moles		24 litres	
0.2 moles		2.4 litres	

So the maximum volume of chlorine is 2.4 litres

Example 11

If 300 cm^3 of a gas weigh 0.55g, what is the formula mass of the gas? The molar volume is 24 l mol^{-1}.

	300 cm^3 of the gas weighs	0.55g
So	24000 cm^3 (1 mole) of the gas weighs	$0.55 \times \frac{24000}{300}$
		= 44g

1 mole of the gas weighs 44g so the formula mass is 44 amu.

Example 12

What is the density of butane in g l^{-1} if its molar volume is 22 l mol^{-1}?

Butane has formula mass 58 amu, so 58g butane occupies 22 litres.

	22 litres weighs	58g
So	1 litre will weigh	$58 \times \frac{1}{22} = 2.64\text{g}$

The density of butane is 2.64 g l^{-1}.

Composition of Gas Mixtures

Example 13

If 25ml of ethene are burned in 100ml of oxygen, what would be the composition of the resulting gas mixture?

$C_2H_{4\,(g)}$	+	$3O_{2\,(g)}$	$\longrightarrow$	$2CO_{2\,(g)}$	+	$2H_2O_{(l)}$
1 mole		3 moles		2 moles		volume ignored
1 vol		3 vol		2 vol		because a liquid
25 ml		75 ml		50 ml		

Volume of CO_2 produced = 50ml
Volume of oxygen used = 75ml
Volume of oxygen left = 100 – 75 = 25ml

The composition of the final gas mixture is 50ml carbon dioxide and 25ml of oxygen.

Summary of Mole Relationships

The following diagram summarises the relationships any question about moles will rely on. Note that this diagram is not yet complete, since there are new facts about the mole to be covered further on.