Equilibrium and Yield

Deciding on the **Best Conditions** to Use

Thanks to Le Chatelier's principle (see page 35) you might think it would be **easy** to work out the **optimum conditions** for a reversible reaction. But in real life it's not quite that simple.

For most reversible reactions that are used on an industrial scale there are other factors, such as **cost** and **time**, that need to be taken into account.

Have a look at the conditions used for the production of ethanol from ethene again:

$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} CH_3CH_2OH_{(g)}$$

Catalyst: H_3PO_4
Temperature: 300 °C
Pressure: 60 atm

Temperature:

1) **Lowering the temperature** would favour the forward reaction and so it should increase the **yield** of ethanol.
2) But lowering the temperature also means that fewer of the particles in the reaction mixture will have **enough energy** to react (see page 32). The particles will also be moving **more slowly**, so there will be **fewer collisions**. So lowering the temperature will **slow down** the **rate** of both the forward and reverse reactions.
3) A low temperature would make the forward reaction **too slow** to be useful. So a compromise temperature of **300 °C** is used.

Pressure:

1) **Increasing the pressure** would favour the forward reaction and increase the **rate** of reaction (as the particles will be **closer together** so will collide **more frequently**). This would increase the **yield** of ethanol.
2) But producing high pressures uses a lot of **energy** and **costs** a lot of money. You'd need some pretty strong equipment to stand up to the high pressures too — and that would be expensive to buy and maintain.
3) To make the reaction economic, a moderately high pressure of **60 atm** is used.

Concentration:

1) Ethanol is **removed** from the reaction vessel as it is produced.
2) This reduces the concentration of products so the equilibrium shifts to favour the **forwards reaction**. This **improves** the **yield** of ethanol.

Catalyst:

1) Using a solid **phosphoric acid(V)** catalyst **increases** the rate of **both** the forward and the backward reactions.
2) The catalyst has **no effect** on the **position** of the equilibrium — it just means the equilibrium is reached **faster** and the **temperature** and **pressure** at which the reaction can happen, at a reasonable rate, are **reduced**.

I should put a dodgy pun here, but I won't yield to the pressure...

1) Explain why the reaction above is not run industrially at a temperature of 40 °C.
2) Explain why the reaction above is not run industrially at a pressure of 500 atm.

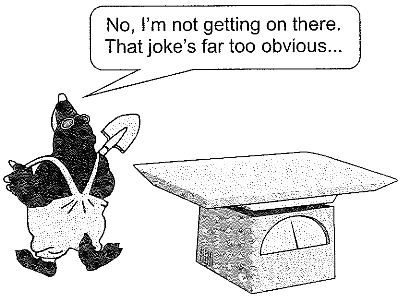
The Mole

A Mole is a Number of Particles

If you had a sample of a substance, and you wanted to **count** the number of atoms that were in it, you'd have to use some very **big numbers**, and spend a very long time counting.
So you need a **unit** to describe the **amount** of a substance that you have — that unit is the **mole**.

One mole of a substance contains **6.02×10^{23}** particles.
6.02×10^{23} mol^{-1} is known as **Avogadro's constant**.

The particles can be **anything** — e.g. atoms or molecules (or even giraffes).
So 6.02×10^{23} atoms of **carbon** is 1 mole of carbon,
and 6.02×10^{23} molecules of CO_2 is 1 mole of CO_2.



Molar Mass is the Mass of One Mole

One mole of atoms or molecules has a **mass in grams** equal to the **relative formula mass** (A_r or M_r) of that substance.

For **carbon**, A_r = **12.0** so 1 mole of carbon weighs **12 g** and the **molar mass** is **12 g mol^{-1}**.
For **CO_2**, M_r = **44.0** so 1 mole of CO_2 weighs **44 g** and the **molar mass** of CO_2 is **44 g mol^{-1}**.
So, **12.0 g** of **carbon** and **44.0 g** of **CO_2** must contain the **same number of particles**.

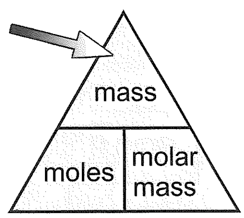
You can use molar mass in calculations to work out how many moles of a substance you have.
Just use this formula:

$$\text{Number of moles} = \frac{\text{Mass of substance (g)}}{\text{Molar mass (g mol}^{-1}\text{)}}$$

g mol^{-1} is the same as g/mol.

> **EXAMPLE:** How many moles of sodium oxide are present in 24.8 g of Na_2O?
>
> Molar mass of Na_2O = $(2 \times 23.0) + (1 \times 16.0) = 62.0$ g mol^{-1}
> Number of moles of Na_2O = 24.8 g ÷ 62.0 g mol^{-1} = **0.400 moles**

You can **rearrange** the formula above and use it to work out the mass of a substance or its relative formula mass (see page 3). It can help to remember this triangle:



> **EXAMPLE:** What is the mass of 1.30 moles of magnesium oxide (MgO)?
>
> Molar mass of MgO = $(1 \times 24.3) + (1 \times 16.0) = 40.3$ g mol^{-1}
> Rearranging the formula, mass = moles × molar mass
> So mass of MgO = 1.30×40.3 = **52.4 g** (3 s.f.)

Avocado's constant: how much I need to satisfy my guacamole craving...

1) Find the molar mass of sulfuric acid, given that 0.700 moles weighs 68.6 g.
2) How many moles of sodium chloride are present in 117 g of NaCl?
3) I have 54.0 g of water (H_2O) and 84.0 g of iron (Fe). Do I have more moles of water or of iron?

Determination of Formulae from Experiments

Empirical and ***Molecular*** *Formulae*

The **empirical formula** of a compound is the **simplest ratio** of the atoms of each element in the compound.

The **molecular formula** of a compound gives the **actual number** of atoms of each element in the compound.

For example, a compound with the molecular formula $\mathbf{C_2H_6}$ has the empirical formula $\mathbf{CH_3}$. The **ratio** of the atoms is one C to every three Hs.

Calculating ***Empirical*** *Formulae*

Often, the only way to find out the formula of a compound is through **experimentation** and **calculation**. You can calculate the formula of a compound from the **masses** of the **reactants**.

Here is a simple set of rules to follow when calculating a formula:

1) Write the **mass** or **percentage mass** of each element.
2) Find the number of **moles** of each substance by dividing by the atomic or molecular mass.
3) Divide all answers by the **smallest** answer.
4) If required: multiply to make up to **whole numbers**.
5) Use the **ratio** of atoms to write the formula (this gives the empirical formula).

EXAMPLE: Find the formula of an oxide of aluminium formed from 9.00 g aluminium and 8.00 g oxygen.

1) First write down the mass of each substance:
   Al: 9.00 g   O: 8.00 g
2) Divide the mass by the atomic masses to find the number of moles of each substance:
   Al: 9.00 ÷ 27.0 = 0.333 moles   O: 8.00 ÷ 16.0 = 0.500 moles
3) Divide by the smallest number, which is 0.333:
   Al: 0.333 ÷ 0.333 = 1.00   O: 0.5 ÷ 0.333 = 1.50
4) Multiply by 2 to give whole numbers:
   Al: 1.00 × 2 = 2   O: 1.50 × 2 = 3
5) The ratio of Al : O is **2 : 3**.
   The empirical formula is $\mathbf{Al_2O_3}$.

Roman empirical formula — 1 Caesar, 3 gladiators & 8 straight roads...

1) Find the empirical formulae of the following oxides:
   a) An oxide containing 12.9 g of lead to every 1.00 g of oxygen.
   b) An oxide containing 2.33 g of iron to every 1.00 g of oxygen.
   (Relative atomic mass values: Pb = 207.2, O = 16.0, Fe = 55.8)
2) Calculate the empirical formula of the carboxylic acid that is comprised of 4.30% hydrogen, 26.1% carbon and 69.6% oxygen.
   (Relative atomic mass values: H = 1.0, C = 12.0, O = 16.0)

Calculation of Molecular Formulae

Use the **Relative Formula Mass** to Work Out the Molecular Formula

To find the **molecular formula** from the **empirical formula**, you need to know the **relative formula mass** (see page 3) of the compound. This will usually be given to you in the question. Read through the example below and then try the questions.

EXAMPLE: Calculate the molecular formula of a hydrocarbon molecule if the compound contains 85.7% carbon and it's relative formula mass is 42.0.

First calculate the empirical formula:

In 100 g of the compound, there will be:

C: 85.7 g H: (100 g – 85.7 g) = 14.3 g

Hydrocarbons only contain carbon and hydrogen, so any mass that isn't carbon will be hydrogen.

Number of moles of each compound:

C: $85.7 \div 12.0 = 7.14$ H: $14.3 \div 1.0 = 14.3$

Divide by the smallest number (7.14):

C: $7.14 \div 7.14 = 1$ H: $14.3 \div 7.13 = 2$

So the ratio of C:H is **1:2**.

The empirical formula is $\mathbf{CH_2}$.

Calculate how many multiples of the empirical formula the molecular formula contains:

The empirical formula (CH_2) has a relative mass of $12.0 + 1.0 + 1.0 = 14.0$.

The molecular formula has a relative mass of 42.0.

$42.0 \div 14.0 = 3$

To find the molecular formula, multiply each of the values in the empirical formula by 3:

C: $1 \times 3 = 3$ H: $2 \times 3 = 6$

The molecular formula is $\mathbf{C_3H_6}$.

The example above uses **percentage compositions** rather than the **mass** of each element in the compound. You can calculate the **percentage composition** yourself using the formula:

$$\text{percentage composition of element X} = \frac{\text{total mass of element X in compound}}{\text{total mass of compound}} \times 100\%$$

The percentage composition of my fridge is 80% cheese & 20% juice...

1) Calculate the molecular formula of a compound containing 52.2% carbon, 13.0% hydrogen and 34.8% oxygen if the relative formula mass of the compound is 46.0.
(Relative atomic mass values: C = 12.0, H = 1.0, O = 16.0)
2) Calculate the molecular formula of a hydrocarbon with a relative formula mass of 78.0 that contains 92.3% carbon.
(Relative atomic mass values: C = 12.0, H = 1.0)
3) Find the percentage composition of oxygen in each of the following compounds:
   a) Ethanol (C_2H_5OH).
   b) Nitric acid (HNO_3).
   c) Propanone (C_3H_6O).

Atom Economy

A Higher **Atom Economy** Means Less **Waste**

1) Lots of reactions make **more than one product**.
   Some of them will be **useful**, but others will just be **waste**.
2) The **atom economy** of a reaction tells you how much of the **mass** of the reactants is converted into **useful products**, and how much is wasted during a reaction.

$$\text{atom economy} = \frac{\text{total } M_r \text{ of desired products}}{\text{total } M_r \text{ of all products}} \times 100$$

3) If a reaction has **100% atom economy** then **all** the atoms in the reactants have been turned into **useful** (desired) **products**. The higher the atom economy, the 'greener' the process.

EXAMPLE: Calculate the atom economy of the reaction to make hydrogen gas from methane and steam: $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$.

First identify the useful product, which in this reaction is hydrogen gas.

$$\text{atom economy} = \frac{\text{total } M_r \text{ of desired products}}{\text{total } M_r \text{ of all products}} \times 100$$

$$= \frac{M_r \text{ of } H_2}{(M_r \text{ of } H_2) + (M_r \text{ of } CO)} \times 100$$

$$= \frac{3 \times (2 \times 1.0)}{3 \times (2 \times 1.0) + 1 \times (12.0 + 16.0)} \times 100 = \frac{6.0}{6.0 + 28.0} \times 100 = \mathbf{17.6\ \%}$$

High Atom Economy is Better in Industry

1) **Industrial reactions** are designed to be as **cheap** and **green** as possible. Generally, reactions with high atom economies are the **most efficient** processes as there is **minimal waste.**
2) The reactions with the **highest** atom economy are the ones that only have **one product**. These reactions have an atom economy of **100%.**
3) Reactions with low atom economies **use up resources** very quickly. They also make lots of **waste** materials that have to be **disposed** of somehow. That tends to make these reactions **unsustainable** — the raw materials run out and the waste has to go somewhere.
4) For the same reasons, low atom economy reactions aren't usually **profitable**. Raw materials are **expensive to buy**, and waste products can be expensive to **dispose of**.
5) The best way around the problem is to find a **use** for the waste products or to find a reaction with a **better** atom economy to make the same product.

Atom (Economy) — upgrade to Superior for only £16.99...

1) a) Ethanol can be made from bromoethane in the following reaction:
   $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$.
   What is the atom economy of this reaction?
   b) In industry, ethanol is made from ethene and steam using the following reaction:
   $CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$.
   Suggest why this reaction is used, rather than the reaction in part a).

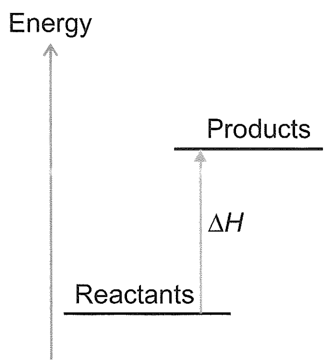
Endothermic and Exothermic Reactions

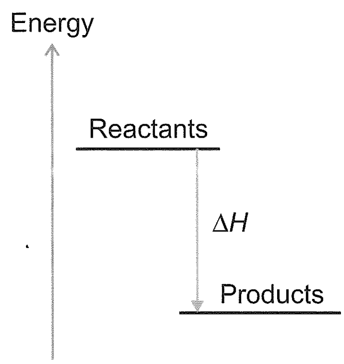
In an **exothermic** reaction, **heat** energy is **given out** (the room temperature rises).
In an **endothermic** reaction, **heat** energy is **taken** from the surroundings (the room temperature drops).

Making *and* ***Breaking*** *Bonds*

1) It takes energy to **break bonds**. When two atoms joined by a bond are **separated**, the energy required to do this must be provided from the surroundings.
2) However, energy is **released** when bonds are made. When two atoms become **joined together** by forming a bond, energy is **released** to the surroundings.
3) In a reaction, if more energy is taken in to break bonds than is given out when bonds are made, the process is **endothermic** — it will take in heat energy. The overall **enthalpy change** of the reaction (ΔH) is **positive**.
4) But, if more energy is given out when bonds are made than is taken in when bonds are broken, the process is **exothermic** — it will give out heat energy. The overall **enthalpy change** of an exothermic reaction (ΔH) is **negative**.

Reactions can be Represented by ***Energy Level Diagrams***





In an **endothermic** reaction, the reactants **take in** energy from the surroundings. The products therefore have **more energy** than the reactants, and ΔH is **positive**.

In an **exothermic** reaction, the reactants **release** energy to the surroundings. The products therefore have **less energy** than the reactants and ΔH is **negative**.

After that I think I need a cup of tea. It'll help improve my energy level...

1) Are the following reactions exothermic or endothermic?
   a) burning coal
   b) sodium hydrogencarbonate + hydrochloric acid (temperature drops)
   c) acid + hydroxide (gets hotter)
   d) methane + steam (cools as they react)
2) a) Draw an energy level diagram for the following reaction:
   $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad \Delta H = -2809 \text{ kJ mol}^{-1}$
   You should label the products, reactants and enthalpy change on your diagram.
   b) Is the reaction in part a) endothermic or exothermic?