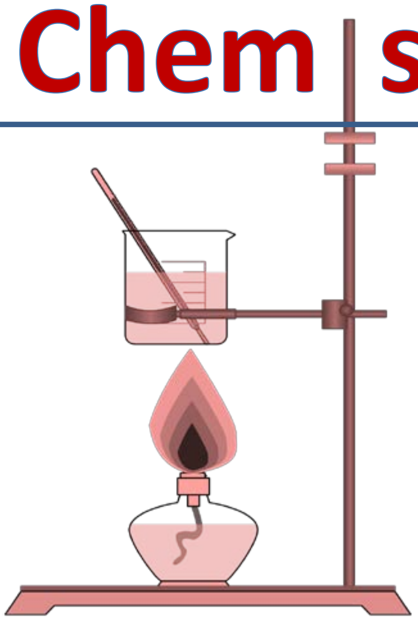
# VCE

# Unit 3

# Chemistry



# TUTOR

3rd Edition

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Chemistry

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# Introduction

Dear friends,

Thank you for choosing this book. I am Mark Molino and I have been teaching VCE chemistry for the past 26 years. During this time I have taught chemistry using many different resources such as text books and study guides. Too often I have been disappointed with the content in these resources. Text books often have pretty glossy pictures but lack thorough explanations of the many difficult concepts encountered in units 3 and 4 chemistry. Quite often these explanations are pitched at a level that is above that of VCE students. Another frustration is that many text books include material that is not relevant to the current study design.

I am confident that in **VCE Unit 3 Chemistry Tutor** you will find a resource that will supplement and possibly replace your text book. No irrelevant material here, just thorough and understandable explanations of the key knowledge required for units 3 chemistry.

An integral part of learning VCE chemistry is the completion of many practice exam questions. At the end of every chapter you will find questions that have been written in a style and to a degree of difficulty that is equivalent to the end of year exam. Most questions are accompanied by thorough solutions and where necessary, emphasis of the traps and difficulties that are typically encountered by students will be made. During this year your chemistry teacher will most likely provide you with practice exam papers that have been prepared by various organisations. In these papers you will occasionally encounter questions that are not relevant to the course. This can cause a lot of confusion and angst amongst both students and teachers. Only questions relevant to the VCE chemistry course are included in this book. *In completing some of these questions you will need to refer to the VCAA examination data book. You can download a copy of this data book at*

*http://www.vcaa.vic.edu.au/Documents/exams/chemistry/chemdata-w.pdf*

Once again thank you for choosing **VCE Unit 3 Chemistry Tutor.** I wish you all the best for the big journey of learning that lies ahead!

If you think this book deserves the thumbs up, like us at

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Mark Molino

# Chapter 1 – The mole, relative atomic mass, relative molecular mass & % composition

*This chapter, along with chapters 2, 4 and 5 cover fundamental material from year 11. You need to have a good grasp of this material in order to be successful in year 12 chemistry.*

## Relative Isotopic Mass

**How much does an atom weigh?**

Chemists need to know the masses of the particles that are present in a substance or that are taking part in a chemical reaction. In chemistry the term **particle** refers to atoms, ions and molecules. Since atoms, ions and molecules are so ridiculously small it is impossible to weigh them individually. Even if it was possible to isolate a single atom it would be impossible to find its mass using a balance. Instead chemists find the mass of these particles indirectly by determining the mass of a known and very large number of particles and from this it is possible to calculate the mass of one atom, ion or molecule. It is however, impractical to know the mass of just one particle as there are usually an enormous number of particles present in substances. Before we can explore how the masses of these tiny particles are determined we need a bit of revision of year 11 chemistry.

The **atomic number** is the number of protons present in the nucleus of an atom. It is unique to the atoms of an element. For example, carbon atoms have 6 protons so the atomic number of carbon is 6. Only carbon atoms have 6 protons so the atomic number of 6 is unique to carbon.

The **mass number** is the number of protons and neutrons in the nucleus of an atom added together. The number of protons in the atoms of an element is always the same but the number of neutrons can vary. For example, all carbon atoms have 6 protons but some carbon atoms have 6 neutrons (mass number of 12), some have 7 neutrons (mass number of 13) and some have 8 neutrons (mass number of 14). These atoms of carbon with the same atomic number of 6 but with different mass numbers are referred to as **isotopes.** Most elements are a mixture of different isotopes.

**Isotopes** are atoms of the same element with the same atomic number but different mass number. Another way of stating this is that isotopes are atoms with the same number of protons but different number of neutrons. The 3 isotopes of carbon can be written as

$^{12}_{6}\mathrm{C}$, $^{13}_{6}\mathrm{C}$, $^{14}_{6}\mathrm{C}$

When atoms are expressed using this notation the number at the bottom left of the element's symbol is the atomic number and the number at the top left is the mass number.

$$\begin{array}{r} \text{Mass number} \rightarrow \\ \text{Atomic number} \rightarrow \end{array} {}^{14}_{6}\mathrm{C} \leftarrow \text{Symbol}$$

The mass number is a convenient way of comparing the masses of different isotopes because the mass of an atom is mainly due to the protons and neutrons in the nucleus. The mass of an electron is so small that it is not considered when comparing the masses of isotopes.
There is a bit of a problem when using mass number to compare the masses of different isotopes. Using mass number would only be accurate if the masses of protons and neutrons were the same in all atoms. There is however, a very slight variation in the masses of protons and neutrons in the nuclei of atoms of different elements. This is due to the strong nuclear binding energy that holds protons and neutrons together in the nucleus of an atom. An understanding of this is not relevant to units 3 and 4 chemistry.

A more accurate way of comparing the masses of different atoms is to determine their **relative isotopic mass.** This is how it works.

The carbon-12 (${}^{12}_{6}\mathrm{C}$ ) isotope of carbon is assigned an isotopic mass value of **exactly 12 units**. It is referred to as an arbitrary number because it wasn't measured using an instrument so it doesn't have any units such as grams, kilograms etc. It is just a number that was chosen to represent the mass of a carbon-12 atom. The number 12 was chosen because the mass number of this isotope is 12. The significance of this will be discussed later.

Now the masses of all of the other isotopes can be compared to the mass of the carbon-12 isotope using an instrument known as a **mass spectrometer.**

The table below shows the masses of some isotopes when compared to the mass of the carbon-12 isotope.

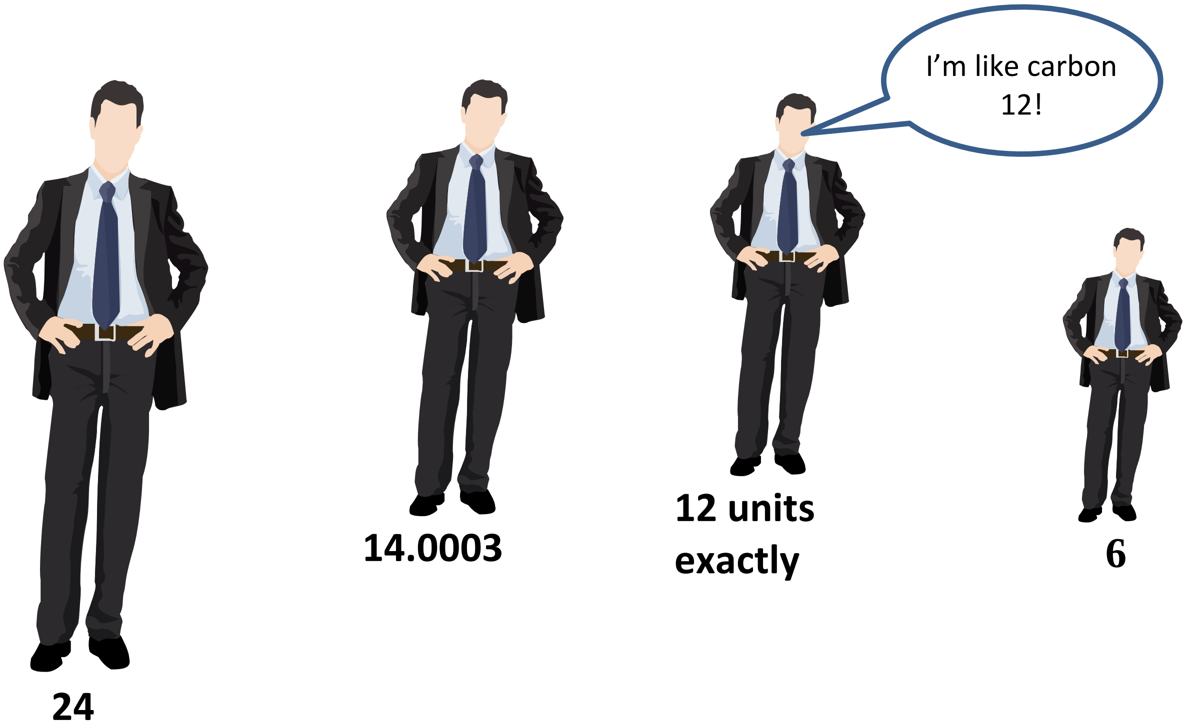
| Isotope | Mass number | Relative isotopic mass |
|---|---|---|
| ${}^{12}_{6}\mathrm{C}$ | 12 | 12 |
| ${}^{13}_{6}\mathrm{C}$ | 13 | 13.003 |
| ${}^{15}_{7}\mathrm{N}$ | 15 | 15.000109 |
| ${}^{16}_{8}\mathrm{O}$ | 16 | 15.9949 |

Notice how these relative isotopic mass values vary slightly from the mass number values. Unlike the mass number the relative isotopic mass takes into account the differences in the masses of protons and neutrons in different elements so the relative isotopic mass is a more accurate way of comparing the masses of isotopes than the mass number.

The relative isotopic mass values have no units because their masses were not directly measured using an instrument such as a balance. They are just relative or compared to the mass of the carbon-12 isotope which is given a mass of 12 units exactly.

Here is a simple analogy which might make this a bit easier to grasp.

A person is given a mass value of **exactly 12 units.** This is not 12 g or 12 Kg because their mass was not measured directly on a balance or scales. The masses of other people can be determined by comparing their mass to this "standard" person who has been assigned a mass of 12 units. Someone who weighs twice as much would have a relative mass of 24. Someone who weighs only half as much would be given a relative mass of 6. Someone who weighs just a little bit more could have a mass of 14.003. In all cases the masses have no units because they were not measured directly using scales. They are just relative values to the standard person who was given a mass of 12 units.



So **relative isotopic mass** can be defined as the mass of an isotope relative to the mass of the carbon-12 isotope which is given a mass of 12 units exactly.

<u>Page 3 of the end of year exam data book has a periodic table with the relative atomic mass values of all the elements.</u>

### Worked Example 1

Calculate the relative atomic mass of the element nitrogen using the isotopic information presented in the table below.

| Isotope | Relative isotopic mass | % abundance |
|---|---|---|
| $^{14}N$ | 14.003074 | 99.63 |
| $^{15}N$ | 15.000109 | 0.37 |

### Worked Example 1 Solutions

$$\text{Ar (N)} = \frac{14.003074 \times 99.63 + 15.000109 \times 0.37}{100} = 14$$

## Relative Molecular Mass (Mr)

Now that we know the average mass of an atom of an element (relative atomic mass), we can use this to calculate the average mass of a molecule of a substance.

**Relative molecular mass –** Is the average mass of a molecule relative to the mass of the carbon-12 isotope which is given an isotopic mass of 12 units exactly.

The Mr of a compound is simply calculated by adding together the Ar values of the elements that make up the compound. For example, the relative molecular mass of $H_2O$ is calculated by

Mr ($H_2O$) = Ar (H) x 2 + Ar (O)
= 1.0 x 2 + 16.0
= 18.0

**Relative formula mass (Mr) –** Is the average mass of the ions that make up the most basic part (the formula) of an ionic compound relative to the mass of the carbon-12 isotope which is given an isotopic mass of 12 units exactly. It is calculated in exactly the same way as the relative molecular mass. For example, the relative formula mass of sodium chloride (NaCl) is calculated by

Mr (NaCl) = Ar (Na) + Ar (Cl) = 23.0 + 35.5 = 58.5

# The Mole

Chemists need to know the number of particles that are present in a substance or that are taking part in a chemical reaction. Atoms, ions and molecules are ridiculously small so even a substance with a small mass will contain an enormous number of particles.

For example, just 1 g of pure water contains 33 400 000 000 000 000 000 000 $H_2O$ molecules. It is inconvenient and impractical to refer to such a large number, especially in written form. This problem is partially solved by expressing the number in scientific form, $3.34 \times 10^{22}$. An even better solution to this problem is to express the number using a unit of measurement known as the **mole.** This unit is similar to “dozen”.

**1 dozen** = 12 particles of anything.

For example,

12 bananas = 1 dozen bananas
12 apples = 1 dozen apples
12 Na atoms = 1 dozen Na atoms
12 $H_2O$ molecules = 1 dozen $H_2O$ molecules

*Outside of the chemistry context, bananas and apples can be considered to be particles.*

In a similar way,

**1 mole** = 602 000 000 000 000 000 000 000 ($6.02 \times 10^{23}$) particles of anything.

For example,

$6.02 \times 10^{23}$ bananas = 1 mole of bananas
$6.02 \times 10^{23}$ apples = 1 mole of apples
$6.02 \times 10^{23}$ Na atoms = 1 mole of Na atoms
$6.02 \times 10^{23}$ $H_2O$ molecules = 1 mole of $H_2O$ molecules

The number of particles present in 1 mole ($6.02 \times 10^{23}$) is known as **Avogadro’s constant ($N_A$ or L )**.

**$N_A$ or L = $6.02 \times 10^{23}$** Avogadro’s constant is included on page 5 of the end of year exam data book.

When converting a number of particles into dozen, the number of particles is divided by 12

For example,

36 bananas: $\frac{36}{12}$ = 3 dozen

48 apples: $\frac{48}{12}$ = 4 dozen

54 $H_2O$ molecules: $\frac{54}{12}$ = 4.5 dozen

When converting a number of particles into moles, the number of particles is divided by $6.02 \times 10^{23}$

For example,

$3.01 \times 10^{24}$ Na atoms: $\frac{3.01 \times 10^{24}}{6.02 \times 10^{23}}$ = 5.00 mol

$3.34 \times 10^{22}$ $H_2O$ molecules: $\frac{3.34 \times 10^{22}}{6.02 \times 10^{23}}$

= 0.0550 mol

When giving the unit for moles we take out the "e" and write **mol.**

When converting a number of dozen particles into the actual number of particles, the number of dozen is multiplied by 12

For example,

5 dozen bananas:

5 x 12 = 60 bananas

When converting a number of moles of particles into the actual number of of particles, the number of moles is multiplied by $6.02 \times 10^{23}$

For example,

5 moles of $H_2O$:

$5 \times 6.02 \times 10^{23} = 3.01 \times 10^{24}$ $H_2O$ molecules.

These simple calculations show that the concept of the mole is exactly the same as the concept of dozen. So if 5 dozen bananas means that the bananas are in 5 groups of 12, then 5 moles of bananas means that the bananas are in 5 groups of $6.02 \times 10^{23}$. One mole just represents a much larger number than one dozen.

The relationship between the number of moles of a substance and the actual number of particles can be shown by the following equation:

**Number of particles (N) = number of moles (n) x $6.02 \times 10^{23}$ ($N_A$)**

**Or**

**$N = n \times N_A$ Or $N = n \times 6.02 \times 10^{23}$**

$n = \frac{N}{N_A}$ **Or** $n = \frac{N}{6.02 \times 10^{23}}$

**1 millimole = $10^{-3}$ mole**
**OR**
**1 mmole = $10^{-3}$ mole**

Remember that the mole is a unit of convenience. It is better to say or write down that there are 5 moles of $H_2O$ rather than $3.01 \times 10^{24}$ molecules of $H_2O$.

## Worked Example 2

Find the number of moles present in the following

**a.** $5.0 \times 10^{23}$ Ca atoms.

**b.** $7.2 \times 10^{25}$ $H_2O$ molecules.

**c.** 1 H atom.

- Refer to appendix 1 which explains how to round off the answers to calculations to the correct number of significant figures.

## Worked Example 2 Solutions

**a.** $N = n \times 6.02 \times 10^{23}$

therefore $n = \dfrac{N}{6.02 \times 10^{23}}$

$= \dfrac{5.0 \times 10^{23}}{6.02 \times 10^{23}}$

$= 0.83$ mol

**b.** $n = \dfrac{7.2 \times 10^{25}}{6.02 \times 10^{23}} = 119.6 = 1.2 \times 10^{2}$ mol

**c.** $n = \dfrac{1}{6.02 \times 10^{23}} = 1.661 \times 10^{-24} = 2 \times 10^{-24}$ mol (only 1 significant figure)

## Worked Example 3

Find the number of particles present in the following.

**a.** 2.0 moles of Helium atoms

**b.** 1.20 moles of $H_2SO_4$ molecules

**c.** 0.500 mol of $CO_2$ molecules

## Worked Example 3 Solutions

**a.** $N = n \times 6.02 \times 10^{23}$

$N = 2.0 \times 6.02 \times 10^{23}$
$= 1.204 \times 10^{24} = 1.2 \times 10^{24}$

**b.** $N = 1.20 \times 6.02 \times 10^{23}$
$= 7.224 \times 10^{23} = 7.22 \times 10^{23}$

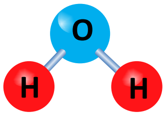
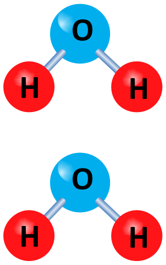
**c.** $N = 0.500 \times 6.02 \times 10^{23}$
$= 3.01 \times 10^{23}$ mol

## Worked Example 4

How many moles of atoms are present in 2.5 moles of $H_2O$?

## Worked Example 4 Solutions

1 molecule of $H_2O$ contains 2 hydrogen atoms and 1 oxygen atom. This is a total of 3 atoms. Therefore any number of $H_2O$ molecules will contain 3 times that number of atoms as can be seen in the table below:

| **Number of $H_2O$ molecules** | | **Number of atoms** |
|---|---|---|
| 1 |  | 2 H + 1 O = 3 atoms<br>or<br>3 x 1 = **3 atoms** |
| 2 |  | 4 H + 2 O = 6 atoms<br>or<br>3 x 2 = **6 atoms** |

The above table shows that 1 $H_2O$ molecule has 3 atoms and 2 $H_2O$ molecules has 6 atoms etc. The clear pattern here is that the number of atoms is always 3 times the number of $H_2O$ molecules.
n (atoms) = 3 x n ($H_2O$)
= 3 x 2.5 = 7.5 mol (the number “3” was not considered when rounding the final answer

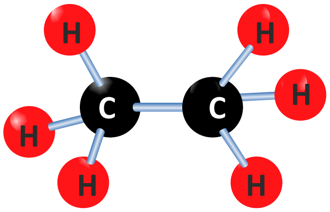
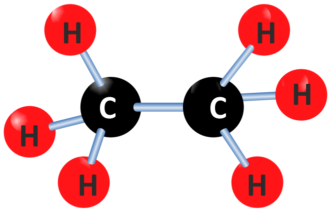
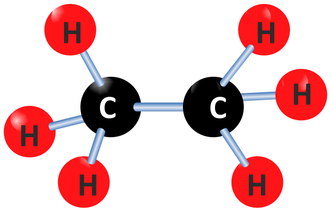
off to the correct number of significant figures. This is because the “3” was not a measured piece of data like the 2.5 mol of $H_2O$.

## Worked Example 5

How many hydrogen atoms are present in 5.0 moles of ethane ($C_2H_6$)?

## Worked Example 5 Solutions

One molecule of $C_2H_6$ contains 2 C atom and 6 H atoms. Therefore any number of $C_2H_6$ molecules will contain 6 times that number of H atoms as can be seen in the table below.

| **Number of $C_2H_6$ molecules** | | **Number of H atoms** |
|---|---|---|
| 1 |  | 6 x 1 = **6 H atoms** |
| 2 |  <br> | 6 x 2 = **12 H atoms** |

$n(H) = 6 \times n(C_2H_6)$
$= 6 \times 5.0 = 30$ mol

Since the question asked for the number of H atoms, the moles of H atoms must be multiplied by Avogadro’s constant to convert the moles of H atoms into the actual number of H atoms.

$N(H) = 30 \times 6.02 \times 10^{23} = 1.8 \times 10^{25}$

# Why 6.02 x $10^{23}$ ?

A question asked by many students is **why was the number 6.02 x $10^{23}$ chosen for the number of particles equal to one mole?** It seems to be such a random and specific number. Why not make one mole equal to exactly 6 x$10^{23}$ or 7.2 x $10^{21}$ or maybe 1.0 x $10^{20}$ etc.

**To answer this question we need to go back to the carbon-12 isotope.**

Many years ago scientists isolated the carbon -12 isotope from the other 2 carbon isotopes and performed experiments on 12 grams of the isotope. These experiments showed that 12 grams of the carbon -12 isotope contained exactly 6.02 x $0^{23}$ carbon atoms. The instrument used, the mass spectrometer, was actually able to count the number of atoms present in 12 g of carbon-12. This became the standard unit of measurement for counting the number of particles in all substances – the mole. So if any other substance contains 6.02 x $10^{23}$ particles it also contains 1 mole. So in summary:

$^{12}_{6}\mathrm{C}$ $^{13}_{6}\mathrm{C}$ $^{14}_{6}\mathrm{C}$

$\downarrow$

12 grams

$\downarrow$

6.02 x $10^{23}$ carbon-12 atoms

$\downarrow$

1 mole

# Molar Mass

**Molar mass –** Is the mass of one mole (6.02 x $10^{23}$) of anything. It has the units **g $mol^{-1}$ or g/mol.**

**How much does one mole weigh?**

This is like asking "how long is a piece of string"? Since one mole is equal to 6.02 x $10^{23}$ particles of anything, we need to know what type of particles we are weighing. For example, 1 mole of bowling balls will weigh much more than 1 mole of marshmallows for the simple reason that a bowling ball has a much greater mass than a marshmallow.

**If one bowling ball has a mass of 7,000 g how much would 1.0 mole of bowling balls weigh?**

1.0 mole of bowling balls is equal to exactly 6.02 x $10^{23}$ bowling balls.

$6.02 \times 10^{23} \times 7{,}000 = 4.2 \times 10^{27}$ g

So the molar mass of bowling balls can be expressed as $4.2 \times 10^{27}$ g mol$^{-1}$

In chemistry we are interested in the molar mass of elements and compounds.

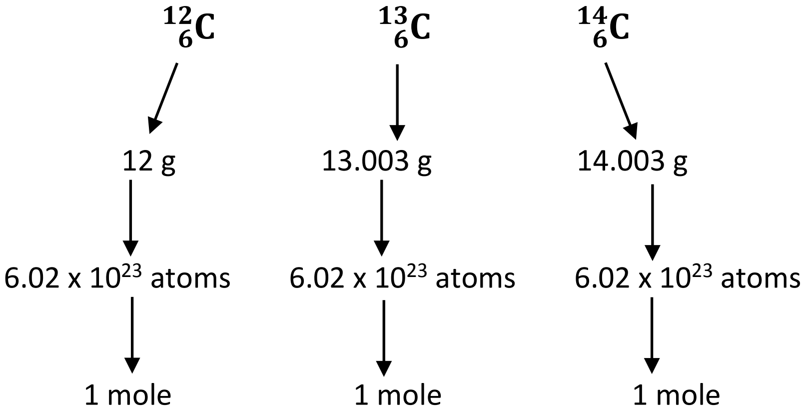
Calculating the molar mass of large things like bowling balls and marshmallows is very easy because all you have to do is weigh one and then multiply its mass by $6.02 \times 10^{23}$. The molar mass of an element or compound cannot be calculated this way because atoms, ions and molecules are too tiny to be weighed on a balance. So how can the molar masses of such substances be calculated? The answer to this question lies in the answer to another question that is often asked by students:

**Why was 12 grams of carbon-12 analysed for the number of particles present in one mole?**

Why not some other mass like 15 g or 10 g etc. It is no coincidence that the mass of the isotope analysed, 12 g , was the same as its mass number and isotopic mass which are both equal to 12.

If 12 g of the carbon-12 isotope contains $6.02 \times 10^{23}$ carbon atoms, then it would follow that a mass in grams of any isotope that was equivalent to its relative isotopic mass would also contain $6.02 \times 10^{23}$ atoms of that isotope.

Using the isotopes of carbon as an example:



<ins>Analysing 12 g of the carbon-12 isotope has helped chemists to know the mass of one mole of any isotope without having to weigh it out on a balance.</ins> The mass of one mole of any isotope is very conveniently equivalent to its mass number or more specifically its relative isotopic mass in grams. By extension , the relative atomic mass expressed in grams gives the **molar mass** of an element, relative molecular mass expressed in grams gives the **molar mass** of a molecular compound and relative formula mass gives the **molar mass** of an ionic compound.

## Worked Example 6

Calculate the molar mass of the following

**a.** $H_2$
**b.** C
**c.** $H_2O$
**d.** $MgCl_2$

## Worked Example 6 Solutions

Calculating the molar mass of a substance is the same as calculating the relative atomic mass, relative molecular mass and relative formula mass of a substance. The only difference is that the molar mass has the **units $gmol^{-1}$.**

**a.** $M(H_2) = 1.0 \times 2 = 2.0\ gmol^{-1}$

**b.** $M(C) = 12.0\ gmol^{-1}$

**c.** $M(H_2O) = 1.0 \times 2 + 16.0 = 18.0\ gmol^{-1}$

**d.** $M(MgCl_2) = 24.3 + 2 \times 35.5 = 95.3\ gmol^{-1}$

## Finding the mass of a substance from its molar mass

Once you know the molar mass of a substance, you can use it to find the mass of any number of moles of that substance.

For example, if the mass of 1 mole of bananas is $7.224 \times 10^{24}$ g (molar mass), then the mass of 5.0 moles of bananas would be calculated by multiplying the number of moles of bananas by the mass of 1 mole bananas.

Mass of bananas (m) = moles (n) of bananas x molar mass (M):

$$\begin{aligned} m &= n \times M \\ &= 5.0 \times 7.224 \times 10^{24} \\ &= 3.6 \times 10^{25}\ g \end{aligned}$$

So

**Mass = Moles x Molar Mass or $m = n \times M$**

Now we can answer the question proposed at the start of the chapter, **how much does an atom weigh?** Using a carbon atom as an example:

Convert one carbon atom into moles:

$$n\,(C) = \frac{1}{6.02 \times 10^{23}} = 1.661 \times 10^{-24} \text{ mol}$$

$m\,(C) = n \times M$

$= 1.661 \times 10^{-24} \times 12.0$

$= 2 \times 10^{-23}$ g

A given mass of any particles can be converted into the number of moles by dividing the mass by its molar mass.

So a mass of $7.224 \times 10^{25}$ g of bananas can be converted into the equivalent number of moles by dividing this mass by the mass of one mole of bananas ($7.224 \times 10^{24}$).

$$n = \frac{7.224 \times 10^{25}}{7.224 \times 10^{24}} = 10 \text{ mol of bananas}$$

So

Moles = mass divided by molar mass

or

$$\mathbf{n = \frac{m}{M}}$$

## Worked Example 7

Find the number of moles of the following.

**a.** 5.85 g of NaCl
**b.** 2.0 g of $H_2O$
**c.** 1.0 Kg of $CuSO_4$

## Worked Example 7 Solutions

Use

n = $\frac{m}{M}$

**a.** n (NaCl) = $\frac{5.85}{58.5}$ = 0.100 mol

**b.** n ($H_2O$) = $\frac{2.0}{18.0}$ = 0.11 mol

**c.** 1.0 Kg x 1,000 = 1,000 g

n ($CuSO_4$) = $\frac{1,000}{159.6}$ = 6.3 mol

## Worked Example 8

Find the mass in grams of the following.

**a.** 2.50 moles of $LiNO_3$
**b.** 0.15 mole of $H_2SO_4$
**c.** 1.5 moles of nitrogen ($N_2$)

## Worked Example 8 Solutions

Use

m = n x M

**a.** m ($LiNO_3$) = 2.50 x 68.9
= 172 g

**b.** m ($H_2SO_4$) = 0.15 x 98.1
= 15 g

**c.** m ($N_2$) = 1.5 x 28 = 42 g

## Percentage composition

The **percentage composition** of a compound gives the % by mass of the elements present in any sample of a compound.

### Worked Example 9

Find the % composition of the elements in $CuSO_4$?

### Worked Example 9 Solutions

First of all find the molar mass of $CuSO_4$ .

M ($CuSO_4$) = 63.5 + 32.1 + 16.0 x 4 = 159.6 g $mol^{-1}$

Now the fraction of the mass of each element in 1.0 mole of the compound can be found by dividing the molar mass of each element by the molar mass of the $CuSO_4$. The fraction is converted into a % by multiplying by 100.

$$\% \text{ Cu} = \frac{\text{M (Cu)}}{\text{M}(\text{CuSO}_4)} \text{ x } 100$$

$$= \frac{63.5}{159.6} \text{ x } 100 = 39.8 \%$$

$$\% \text{ S} = \frac{\text{M (S)}}{\text{M}(\text{CuSO}_4)} \text{ x } 100$$

$$= \frac{32.1}{159.6} \text{ x } 100 = 20.1 \%$$

$$\% \text{ O} = \frac{\text{M (O) x 4}}{\text{M}(\text{CuSO}_4)} \text{ x } 100$$

$$= \frac{16.0 \text{ x } 4}{159.6} \text{ x } 100 = 40.1 \%$$

As there are 3 elements in the compound, the % of the last element O, can be calculated by subtracting the sum of the % of Cu and S from 100.

% O = 100 – (39.8 + 20.1) = 40.1 %

## Worked Example 10

What mass of iron in grams can be extracted from 5.0 tonnes of $Fe_2O_3$?  1.0 tonne = $1.0 \times 10^6$ g

## Worked Example 10 Solutions

First of all calculate the % of Fe in $Fe_2O_3$.

$$\% \text{ Fe} = \frac{\text{M (Fe) x 2}}{\text{M (Fe}_2\text{O}_3\text{)}} \text{ x } 100$$

$$= \frac{55.8 \text{ x } 2}{159.6} \text{ x } 100 = 69.92 \ \%$$

- *The final answer needs to be rounded off to 2 significant figures.  However, calculated values that will be used to derive the final answer SHOULD NOT be rounded according to the least precise piece of data.  So the calculated % of Fe to be used in the next part of the calculation is 69.92 % not 70%.*

So 69.92 % of the mass of any sample of $Fe_2O_3$ is due to Fe.

$$\text{m (Fe)} = \frac{69.92}{100} \text{ x } 5.0 = 3{,}496 \text{ tonnes} = 3.496 \text{ x } 10^6 \text{ g}$$

$3.3496 \times 10^6 = 3.3 \times 10^6$ g

- *If 70% was used to calculate the mass of Fe, the final answer may be slightly off when it is rounded off to 2 significant figures.*

## SUMMARY

- **Relative isotopic mass –** The mass of an isotope relative to the mass of the $^{12}C$ isotope which is given an isotopic mass of 12 units exactly.  It has no units.

- **Relative atomic mass –** The average mass of an atom of an element relative to the mass of the $^{12}C$ isotope which is given an isotopic mass of 12 units exactly.  It has no units.

- **Relative molecular mass –** The average mass of a molecule relative to the mass of the $^{12}C$ isotope which is given an isotopic mass of 12 units exactly.  It has no units.

- **Relative formula mass –** The average mass of the ions that make up the formula of an ionic compound relative to the mass of the $^{12}C$ isotope which is given an isotopic mass of 12 units exactly.  It has no units.

- **Mole (n) –** One mole is equivalent to $6.02 \times 10^{23}$ particles of anything.

  $\mathbf{n = \dfrac{N}{6.02 \times 10^{23}}}$ $\qquad$ $\mathbf{N = n \times 6.02 \times 10^{23}}$

- **Molar Mass (M) –** The mass of one mole of anything.  It has the units g $mol^{-1}$.

  $\mathbf{m = n \times M}$

  $\mathbf{n = \dfrac{m}{M}}$ $\qquad$ *This formula is included in the end of year exam data book.*

- The **percentage composition** of a compound gives the % by mass of the elements present in any sample of a compound.

# CHAPTER 1 REVIEW QUESTIONS

## Multiple Choice

### Question 1

Which of the following describes relative isotopic mass?

**A.** The mass of the carbon-12 isotope.
**B.** The mass of one mole of any substance.
**C.** The average mass of the isotopes that make up an element.
**D.** None of the above.

### Question 2

The mass in gram of one molecule of $C_5H_{12}$ is

**A.** 72

**B.** $\frac{72}{6.02 \text{ x } 10^{23}}$

**C.** $6.02 \text{ x } 10^{23} \text{ x } 72$

**D.** $\frac{6.02 \text{ x } 10^{23}}{72}$

### Question 3

The greatest number of particles is found in

**A.** $7.5 \text{ x } 10^{23}$ $H_2O$ molecules
**B.** $1.5 \text{ x } 10^{23}$ Na atoms
**C.** 100 g of $C_6H_{12}O_6$
**D.** 1.5 moles of $H_2$

### Question 4

The greatest number of atoms are found in

**A.** $7.5 \text{ x } 10^{23}$ $H_2O$ molecules
**B.** $1.5 \text{ x } 10^{23}$ Na atoms
**C.** 100 g of $C_6H_{12}O_6$
**D.** 1.5 moles of $H_2$

### Question 5

The value of Avogadro's constant is equivalent to

**A.** the number of atoms present in 18 g of $H_2O$.
**B.** the number of atoms present in 1.0 g of $H_2$ gas.
**C.** the number of atoms in 2.0 g of $H_2$ gas.
**D.** the number of atoms of Na in 1.0 mole of $Na_2CO_3$.

### Question 6

The mass of sodium atoms in $\frac{1}{3}$ of a mole of $Na_3PO_4$ is the same as

**A.** the molar mass of sodium.
**B.** the mass of $\frac{1}{3}$ of a mole of sodium.
**C.** the mass of 3 moles of sodium.
**D.** 41 % of the molar mass of $Na_3PO_4$.

### Question 7

The number of atoms in 1.5 moles of $(NH_2)_2CO$ is equivalent to

**A.** the number of atoms in 6.0 moles of $CO_2$.
**B.** the number of chlorine atoms in 6.0 moles of $Cl_2$.
**C.** the number of molecules in 3.0 moles of $Cl_2$.
**D.** the number of ions in 3.0 moles of $Na_2O$.

**Question 8**

The percentage by mass of nitrogen in $(NH_4)_2SO_4$ is

**A.** 21.2 %
**B.** 10.6 %
**C.** 13.3 %
**D.** 25%

**Question 9**

A rock contains 30 % $CaCO_3$ and 70% $SiO_2$ by mass. What is the percentage of carbon in the rock?

**A.** 30 %
**B.** 3.6 %
**C.** 12 %
**D.** 36 %

**Question 10**

Analysis of a sample of fertilizer shows that it contains 58.8 % potassium nitrate. The remaining mass of the fertilizer is due to potassium chloride. What mass of nitrogen is present in 0.500 Kg of fertilizer?

**A.** 0.294 Kg
**B.** 0.06925 Kg
**C.** 0.041 Kg
**D.** 0.206 Kg

## Short Answers

**Question 1**

What is the mass of 5.50 x $10^{25}$ molecules of glucose ($C_6H_{12}O_6$)?

**Question 2**

What is the mass of 10.0 moles of $KNO_3$?

**Question 3**

How many molecules are present in 42 g of $SO_2$?

**Question 4**

How many moles of $O^{2-}$ ions are present in 2.65 g of MgO?

**Question 5**

What is the mass of oxygen in 5.0 moles of $H_2SO_4$?

**Question 6**

What is the amount of carbon in **mmole,** present in 2.5 mg of $C_8H_{10}N_4O_2$?

**Question 7**

What is the total number of atoms present in 1.0 Kg of $Fe(NO_3)_2$?

**Question 8**

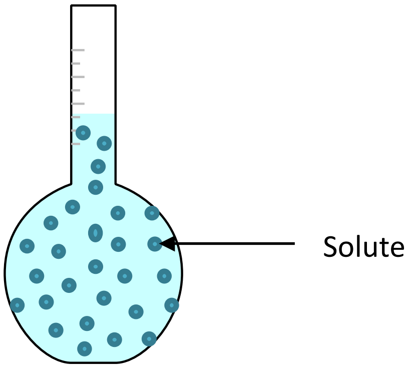
How much does one atom of oxygen weigh?

**Question 9**

How much does one atom of oxygen weigh in a molecule of $CO_2$?

# Chapter 2 – Concentration of solutions

A solution is a mixture consisting of a **solute** and **solvent.** A **solute** is either a solid, liquid or gas that can dissolve into a solvent. A **solvent** is the liquid that the solute dissolves into. The solvent that we will mainly be dealing with is water. When a solute dissolves into a solvent the solute particles are uniformly spread throughout the solution. That is, the solute particles are evenly spread through the solution where the distance between any 2 adjacent particles is the same. The arrangement of the solute particles in a solution is similar to the arrangement of gas particles in a container. The particles of solute in a solution however, do not exert pressure on the walls of their holding container as is the case with gas particles.



## Solution Concentration

The **concentration** of a solution gives an indication of the ratio of the solute to solvent in a solution. It shows how much solute is present in a given amount of solvent or solution.

**Molarity or Molar concentration –** Is the number of moles of solute present in 1.0 L of solvent or solution. It has the units **M, mol/L** or **mol $L^{-1}$.**

For example a **0.10 M HCl solution contains 0.10 mole of HCl per 1 litre of the solution.**

0.10 M is read as 0.10 molar. The concentration of this solution in molarity can also be written as 0.10 mol/L or 0.10 mol $L^{-1}$

Just because the HCl solution has a concentration of 0.10 mol/L doesn't mean that the volume of the solution is 1 litre and that there is 0.10 mole of HCl present. Remember that concentration shows the ratio of solute to solvent. There could be 0.20 mole in 2 L, 0.005 mole in 50 mL, 0.0005 mole in 5 mL etc. In each case the ratio of the solute to solvent is 0.10 mole of HCl for every 1 litre of the solution. Molarity is the main way that the concentration of a solution is measured in units 3 and 4 chemistry. The molarity of a solution is calculated by applying the following formula:

$$\textbf{Concentration (M)} = \frac{\text{moles (n)}}{\text{Volume (L)}} \qquad C = \frac{n}{V} \qquad n = C \times V \text{ or } n = CV$$

$$\uparrow$$

*This formula is provided on page 5 of the end of year exam data book.*

## Worked Example 1

Find the molarity of a solution that was produced by dissolving 5.0 moles of $CuSO_4$ in 2.5 L of water.

## Worked Example 1 solutions

$$C = \frac{n}{V}$$

$$= \frac{5.0}{2.5} = 2.0\ M$$

> When a solute dissolves into a solvent, the volume of the solvent is unaffected. So when the 5.0 moles of $CuSO_4$ dissolves into the 2.5 L of water, the resultant solution still has a volume of 2.5 L. The $CuSO_4$ has a negligible (insignificant) effect on the volume of the solution.

Another way to calculate the molarity of the $CuSO_4$ solution is to use a process known **as CROSS MULTIPLYING.** Cross multiplication can be used in calculations where 2 variables are *directly proportional* to each other. That is, when one variable increases the other one increases by a proportionate amount. It also applies to when one variable decreases and the other one decreases by a proportionate amount.

A simple application of cross multiplication is the calculation of **the cost of 2 meat pies if 1 meat pie cost $2.** The variables which are the number of meat pies and the cost of meat pies are directly proportional to each other. So as the number of meat pies increases so does the cost by a proportionate amount. If 1 meat pie costs $2 then 2 meat pies will have twice the cost - $4. If using the cross multiplication method:

1 meat pie and its cost of $2 are connected by an arrow. The unknown cost of 2 meat pies is shown with an ***X.*** 2 meat pies and its unknown cost of ***X*** are also connected with an arrow.

1 meat pie → $2
2 meat pies → ***X***

Now we literally cross multiply and make the multiplication statements equal each other to form an equation. Finally we solve the equation for the value of ***X.***

$$X \times 1 = 2 \times 2$$

$$X = \frac{2 \times 2}{1} = \$4$$

Many of the calculations that we do in units 3 and 4 chemistry involve 2 variables that are directly proportional to each other so cross multiplying is a very useful tool. Solutions are an example of this because as the volume of a solution increases so does the quantity of the dissolved solute.

Now we can do worked example 3 using cross multiplying:

2.5 L water → 5.0 moles $CuSO_4$
1.0 L water → ***X*** moles

$X \times 2.5 = 1.0 \times 5.0$

$$X = \frac{1.0 \times 5.0}{2.5} = 2.0 \text{ M}$$

**Percentage weight to volume (% w/v) –** Also known as percentage mass to volume (% m/v). This measure of concentration shows the mass of solute in gram per 100 mL of solvent or solution. It has the units **% w/v** or **% m/v.**

For example, a **0.90 % w/v NaCl solution contains 0.90 g of NaCl in every 100 mL of solution or solvent.**

## Worked Example 2

Express the concentration of a solution containing 35 g of $Na_2CO_3$ in 3.0 L of water as % m/v.

## Worked Example 2 Solutions

35 g → 3,000 mL

$X$ g → 100 mL

$$X = \frac{35 \times 100}{3{,}000} = 1.66667 = 1.2 \text{ % w/v}$$

$X \times 3{,}000 = 35 \times 100$

- *"100 mL" is not considered in the rounding off with regards to significant figures because it was not a measurement that was recorded. We know that % m/v means that there is a mass in grams of solute in 100 mL but no measurement of 100 mL was actually made.*

- *"3,000 mL" is not considered in the rounding off with regards to significant figures because it was derived from 3.0 L which was the original data.*

**Percentage weight to weight (% w/w)** – Also known as % m/m. This shows the mass of solute in gram, in 100 g of solution. It has the units **% w/w** or **% m/m.** As was mentioned earlier, a dissolved solute will not affect the volume of a solution. That is, the volume of the solution and volume of the solvent will always be the same. A dissolved solute will however, affect the mass of a solution. As a solution contains solute and solvent, the mass of the solution will always be higher than the mass of the solvent so % w/w can only be defined in terms of the mass of the solution.

For example, **a 10 % w/w $CuSO_4$ solution contains 10 g of $CuSO_4$ dissolved in 100 g of solution.**

**Percentage volume to volume (% v/v) –** This is relevant to solutions where the solute is in liquid form. It shows the volume of solute, in mL, for every 100 mL of solution. It has the units **%v/v.**

For example, **a 20 % v/v $C_2H_5OH$ bottle of wine contains 20 mL of $C_2H_5OH$ for every 100 mL of solution.** *The volume of the solution is due to the volume of the solvent and solute.*

**Mass of solute per unit volume of solution** – There are many examples of this such as:

**Grams per litre (g/L or g $L^{-1}$) –** This shows the grams of solute per 1.0 L of solvent or solution.

For example, a **5.0 g/L solution of NaOH contains 5.0 g of NaOH for every 1.0 L of solution.**

**Milligrams per litre (mg/L) –** This shows the mg of solute per 1.0 L of solution.

For example, a **2.0 mg/L solution of $KNO_3$ contains 2.0 mg of $KNO_3$ for every 1.0 L of solution.**

**Mass of solute per unit mass of solution** – There are many examples of this such as

**Milligrams per gram (mg $g^{-1}$ or mg/g) –** This shows the mg of solute per 1.0 g of solution.

For example a **1.5 mg $g^{-1}$ solution of glucose contains 1.5 mg of glucose in every 1.0 g of solution.**

The mass of a chemical that is spread throughout the tissue of a living thing is often expressed as a concentration using mass of solute per unit mass of tissue (not solution).

For example, a fish contaminated with mercury can have the concentration of mercury expressed as mg $g^{-1}$. **A fish with a mercury concentration of 0.00050 mg/g has 0.00050 mg of mercury in every 1.0 g of its tissue.**

**Parts per million (ppm)** – If it's a solution, it is the mass of solute in grams, dissolved in $10^6$ mL of solution. The same ratio is shown by mg/L. In reference to a living organism, ppm shows the number of grams of a chemical per $10^6$ g of its tissue. Some examples of ppm are:

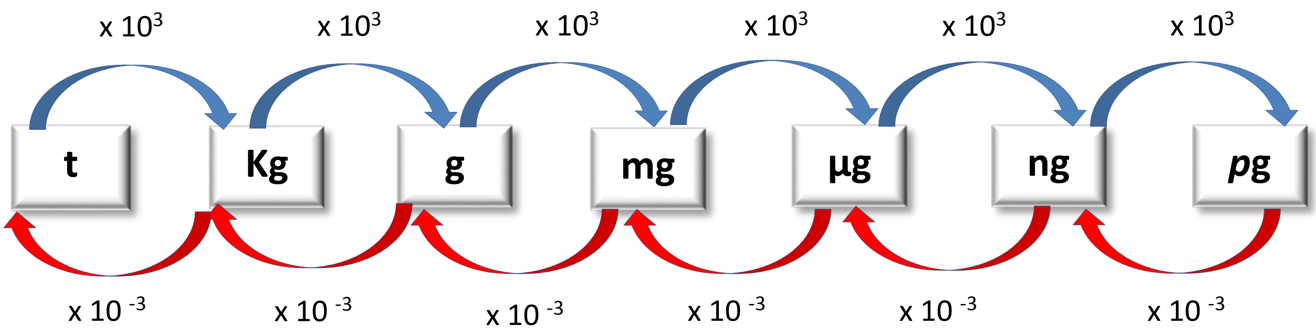
**A 10 ppm $Fe^{2+}$ solution contains 10 g of $Fe^{2+}$ dissolved in every $10^6$ mL of solution or 10 mg of $Fe^{2+}$ dissolved in 1.0 L of solution.**

**An oyster with a 9 ppm concentration of Cd has 9 g of Cd per $10^6$ g of its tissue. Remember it is just a ratio. Of course no oyster is big enough to have $10^6$ g (1 tonne) of tissue!**

**Parts per billion (ppb)** – Very similar to ppm. It is the mass of solute per $10^9$ g of solution or the mass of a chemical present in every $10^9$ g of the tissue of a living organism.

- *ppm and ppb are used when the concentration of solute in a solution is extremely low.*

# Converting between different units of mass



**t = tonnes**
**Kg = Kilograms**
**g = grams**
**mg = milligrams**
**µg = micrograms**
**ng = nanograms**
***pg* = picograms**

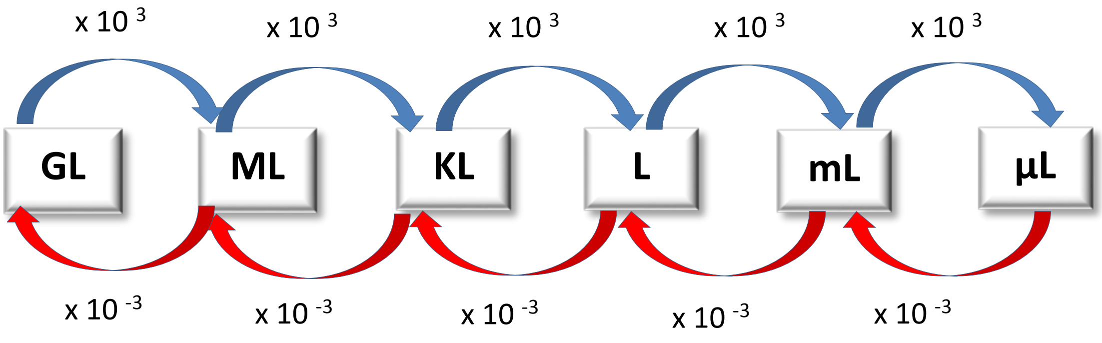
*A table similar to the one below is included on page 6 of the end of year exam data book.*

| **SI prefix** | **Symbol** | **Multiplying factor** |
|---|---|---|
| Giga (used for volume) | G | $10^{9}$ (1,000,000,000) |
| Mega (used for volume) | M | $10^{6}$ (1,000,000) |
| Kilo (used for mass) | K | $10^{3}$ (1,000) |
| Deci (used for volume) | d | $10^{-1}$ (0.1) |
| Centi (used for volume) | c | $10^{-2}$ (0.01) |
| Milli (used for volume) | m | $10^{-3}$ (0.001) |
| Micro (used for mass and volume | µ | $10^{-6}$ (0.000001) |
| Nano (used for mass and volume) | n | $10^{-9}$ (0.000000001) |
| Pico (used for mass and volume) | *p* | $10^{-12}$ (0.000000000001) |

*The table below shows how this table can be used to convert between different units of mass.*

| | | | |
|---|---|---|---|
| **Kilo** | 1 kg | = | $10^{3}$ g or 1,000 g |
| **Milli** | 1 mg | = | $10^{-3}$ g or 0.001 g |
| **Micro** | 1 µg | = | $10^{-6}$ g or 0.000001 g |
| **Nano** | 1 ng | = | $10^{-9}$ g or 0.000000001 g |
| **Pico** | 1 *pg* | = | $10^{-12}$ g or 0.000000000001 g |

## Converting between different units of volume



**GL = Gigalitres**
**ML = Megalitres**
**KL = Kilolitres**

**L = Litres**
**mL = Millilitres**
**µL = microliters**

The table below shows how the table on page 6 on the end of year exam data book can be used to convert between different units of volume.

| | | | |
|---|---|---|---|
| Giga | 1 GL | = | $10^9$ L or 1,000,000,000 L |
| Mega | 1 ML | = | $10^6$ L or 1,000,000 L |
| Kilo | 1 KL | = | $10^3$ L or 1,000 L |
| Milli | 1 mL | = | $10^{-3}$ L or 0.001 L |
| Micro | 1 µL | = | $10^{-6}$ L or 0.000001 L |
| Nano | 1 nL | = | $10^{-9}$ L or 0.000000001 L |
| Pico | 1 *p*L | | $10^{-12}$ or 0.000000000001 L |

## Worked Example 3

The concentration of ethanol in a popular brand of beer is 4.9 % v/v. What volume of ethanol would be present in a 250 mL glass of this beer?

## Worked Example 3 Solutions

100 mL beer → 4.9 mL ethanol
250 mL beer → ***X*** mL of ethanol

$X \text{ x } 100 = 250 \text{ x } 4.9$

$$X = \frac{250 \text{ x } 4.9}{100} = 12.25 = 12 \text{ mL}$$

## Worked Example 4

A can of a cola containing 330.0 mL of drink contains 22.1 g of sugar. What is the concentration of sugar in this can in g $L^{-1}$?

## Worked Example 4 Solutions

330.0 mL cola drink → 22.1 g sugar
1,000 mL cola drink → $X$ g of sugar

$X \times 330.0 = 1{,}000 \times 22.1$

$$X = \frac{1{,}000 \times 22.1}{330.0} = 66.9697 = 67.0 \text{ g L}^{-1}$$

## Worked Example 5

A 250 mL glass of water has a calcium ion concentration of $3.14 \times 10^3$ mg/L. How many micrograms (µg) of calcium will be present in 1.0 mL of this water?

## Worked Example 5 Solutions

1,000 mL water → $3.14 \times 10^3$ mg of Ca
1.0 mL water → $X$ mg

$X \times 1000 = 1.0 \times 3.14 \times 10^3$

$$X = \frac{1.0 \times 3.14 \times 10^3}{1{,}000} = 3.14 \text{ mg}$$

$3.14 \times 10^3 = 3.1 \times 10^3$ µg

The 250 mL of water was not needed for the calculation.

## Worked Example 6

An adult male weighing 80.0 Kg has 1.4 mg of cobalt in their body.

**a.** Express the amount of cobalt in this person in ppm.
**b.** How many mg of cobalt would be present in each kilogram of this adult male?

**a.** Mass of adult male in grams = 80.0 Kg x $10^3$ = $8.00 \times 10^4$ g
Mass of cobalt in grams = $1.4 \times 10^{-3}$ = $1.4 \times 10^{-3}$ g

$8.00 \times 10^4$ g adult male → $1.4 \times 10^{-3}$ g of Co
$10^6$ g adult male → ***X*** g of Co

***X*** x $8.00 \times 10^4 = 10^6 \times 1.4 \times 10^{-3}$

$$X = \frac{10^6 \times 1.4 \times 10^{-3}}{8.00 \times 10^4} = 1.75 \times 10^{-2}\ \text{g} = 1.8 \times 10^{-2}\ \text{ppm}$$

**b.** 80.0 Kg → 1.4 mg
1.0 Kg → ***X*** mg

***X*** x 80.0 = 1.0 x 1.4

$$X = \frac{1.0 \times 1.4}{80.0} = 0.0175 = 0.018\ \text{mg}$$

## Density

Density shows the mass of a unit volume (usually 1 mL) of a substance.

For example liquid ethanol has a density of 0.789 g $\text{mL}^{-1}$. This means that 1 mL of ethanol has a mass of 0.789 g.

Density is not the same as concentration even though the units, g $\text{mL}^{-1}$, can also be used for concentration. If a solution has a concentration of 0.789 g $\text{mL}^{-1}$, this would mean that 1 mL of the solution has 0.789 g of solute dissolved in it.

Density can be calculated by using the following formula:

**Density (d)** $= \dfrac{\textbf{mass (m)}}{\textbf{volume (v)}}$ **d** $= \dfrac{\textbf{m}}{\textbf{v}}$

## Worked Example 7

Calculate the density of octane in g mL$^{-1}$ if a volume of 25.0 mL of octane has a mass of 1.73 x 10$^{7}$µg.

## Worked Example 7 Solutions

Mass of octane in grams = 1.73 x 10$^{7}$ x 10$^{-6}$ = 17.3 g

$$d = \frac{m}{v} = \frac{17.3}{25.0} = 0.692 \text{ g mL}^{-1}$$

## Worked Example 8

A popular liqueur has an ethanol concentration of 17 %v/v. What mass of ethanol would be present in a 700.0 mL bottle of this liqueur? The density of ethanol is 0.789 g/mL.

## Worked Example 8 Solutions

100 mL liqueur → 17 mL ethanol
700.0 mL liqueur → ***X*** mL ethanol

***X*** x 100 = 700 x 17

$$X = \frac{700 \text{ x } 17}{100} = 119 \text{ mL}$$

$$d = \frac{m}{v}$$

m = d x v
= 0.789 x 119 = 93.891 = 94 g

# Converting between different units of concentration

Converting between different units of concentration is challenging for many students. Before we can convert between different units of concentration, we need to be crystal clear as to what the units of concentration are showing. The units of concentration are always in 2 parts. The first part shows the quantity of the solute and the second part shows the quantity of solution that the solute is dissolved in. For example

$$\underbrace{\text{25 g}}_{\text{25 g } CuSO_4 \text{ solute}}\ \underbrace{L^{-1}}_{\text{1.0 Litre of solution}}\ CuSO_4$$

So a 25 g $L^{-1}$ $CuSO_4$ solution has 25 g of $CuSO_4$ solute dissolved in every 1.0 L of solution. Expressing this concentration using different units, for example, **mg $mL^{-1}$**, can be done in 3 steps.

- **The first step is to express the quantity of solute in the required units for the new concentration.**

In this example the 25 g of $CuSO_4$ must be converted into mg: $25 \times 10^3 = 2.5 \times 10^4$ mg.

So 1.0 L of the solution contains $2.5 \times 10^4$ mg of $CuSO_4$.

- **The second step is to express the quantity of solvent or solution in the required units for the new concentration.**

In this case 1.0 Litre of solution is converted into mL.

$1.0\ L \times 10^3 = 1{,}000\ mL$ So 1,000 mL of solution contains $2.5 \times 10^4$ mg of $CuSO_4$.

- **The third and final step is to use cross multiplication to find the quantity of solute in the appropriate quantity of solution for the new concentration.**

In this example it is the mg of $CuSO_4$ in 1.0 mL of solution.

$2.5 \times 10^4$ mg $CuSO_4$ → 1,000 mL
$\boldsymbol{X}$ mg $CuSO_4$ → 1.0 mL

$\boldsymbol{X} \times 1{,}000 = 2.5 \times 10^4 \times 1.0$

$$\boldsymbol{X} = \frac{2.5 \times 10^4 \times 1.0}{1{,}000} = 25\ mg\ mL^{-1}$$

So a 25 g $L^{-1}$ $CuSO_4$ solution can also be expressed as 25 mg $mL^{-1}$.

When converting from one unit of concentration into another one:

- **Express the quantity of solute in the required units for the new concentration.**
- **Express the quantity of solvent or solution in the required unit for the new concentration.**
- **Use cross multiplication to find the quantity of solute in the appropriate quantity of solution for the new concentration.**

## Worked Example 9

Change the following solution concentrations into the units given in brackets.

**a.** 0.10 M HCl (%w/v)
**b.** 0.90 g $L^{-1}$ $K_2Cr_2O_7$ (M)
**c.** 2.5 M $Ba(OH)_2$ (mg/mL)

## Worked Example 9 Solutions

**a.** 0.10 M = 0.10 mol/L

%w/v is the ***grams of solute*** in ***100 mL of solution.***

- **Express the quantity of solute in the required units for the new concentration.**

Change 0.10 mol of HCl solute into a mass in grams:

m (HCl) = n x M
= 0.10 x 36.5 = 3.65 g

- **Express the quantity of solvent or solution in the required units for the new concentration.**

Convert 1 L of solution into mL. 1 x $10^3$ = 1,000 mL

So 1,000 mL of this solution contains 3.65 g HCl.

- **Use cross multiplication to find the quantity of solute in the appropriate quantity of solution for the new concentration.**

Now use cross multiplying to find the equivalent mass of HCl in 100 mL of solution. Remember that %w/v is the mass of solute, in grams, in 100 mL of solution.

1,000 mL → 3.65 g HCl
100 mL → ***X*** g

***X*** x 1,000 = 100 x 3.65

$$\boldsymbol{X} = \frac{100 \text{ x } 3.65}{1{,}000} = 0.365 \text{ g} = 0.37 \text{ \%w/v}$$

**b.**

- **Express the quantity of solute in the required units for the new concentration.**

  Change 0.90 g of $K_2Cr_2O_7$ into moles.

  $$n\ (K_2Cr_2O_7) = \frac{0.90}{294.2} = 0.0030591 \text{ mol in 1 L}$$

- **Express the quantity of solvent or solution in the required units for the new concentration.**

  Don’t need to do anything here as the new concentration has a volume of solution that is also 1 L.

- **Use cross multiplication to find the quantity of solute in the appropriate quantity of solution for the new concentration.**

  Don’t need to do anything here either. The molar concentration (M) is the number of moles of solute in 1 L of solution. As the mass of 0.90 g of $K_2Cr_2O_7$ was already in 1.0 L, converting the 0.90 g into moles means that the solution has 0.0030591 mol of $K_2Cr_2O_7$ in 1 L. So the molar concentration = 0.0031 M

**c.**

- **Express the quantity of solute in the required units for the new concentration.**

  2.5 M $Ba(OH)_2$ = 2.5 moles of $Ba(OH)_2$ in 1 L of solution.

  m ($Ba(OH)_2$) = 2.5 x 171.3 = 428.25 g in 1 L

  428.25 g x 1,000 = $4.28250 \times 10^5$ mg in 1 L

- **Express the quantity of solvent or solution in the required units for the new concentration.**

  Convert 1 L into mL = $1 \times 10^3$ = 1,000 mL

- **Use cross multiplication to find the quantity of solute in the appropriate quantity of solution for the new concentration.**

  1,000 mL → 428,250 mg $Ba(OH)_2$

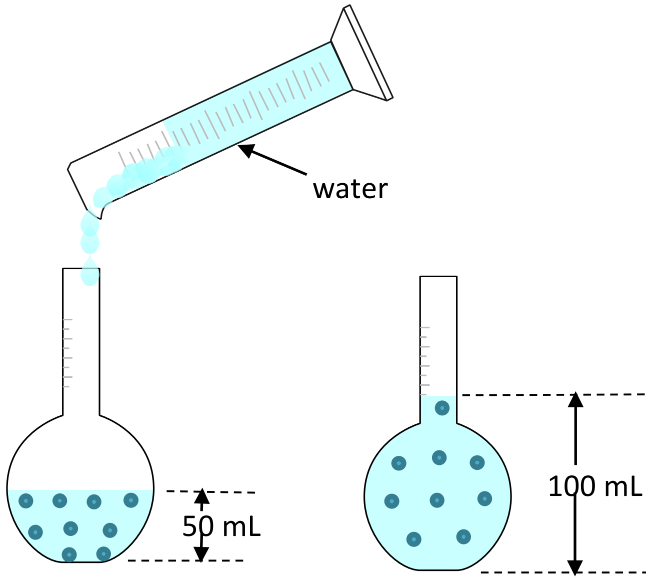
  1.0 mL → ***X*** mg $Ba(OH)_2$

  $$\boldsymbol{X} = \frac{1.0 \times 428{,}250}{1{,}000} = 428.250 \text{ mg}$$

  $$= 4.3 \times 10^2 \text{ mg/mL}$$

# Dilution

A **dilution** is when water is added to a solution resulting in a decrease in concentration. Since water is added, the volume of a solution will always increase after a dilution. The concentration of a solution will always decrease after a dilution because the solute particles will spread out to fill up the extra space created by the addition of the water.



When a solution is diluted, the concentration of the solution will decrease but the **number of moles and mass** of the solute will be UNCHANGED. As can be seen in the diagram, the particles of solute just spread further away from each other after the solution has been diluted. The actual number of solute particles however, is not affected by the addition of water.

**Before dilution**
**(2.0 M)**

**After dilution**
**(1.0 M)**

In the above example of a dilution, the volume of the solution after the dilution is twice the volume of the solution before the dilution. This means that the concentration of the diluted solution is exactly half the concentration of the solution before the water was added. For example, if the concentration of the solution before the dilution was 2.0 M, then after the dilution it will be 1.0 M.

When a solution is diluted it is useful to calculate the **dilution factor.** The dilution factor is calculated by:

$$\text{Dilution factor} = \frac{\text{Volume of solution after dilution}}{\text{Volume of solution before dilution}}$$

The dilution factor for the above example is:

$$\text{Dilution factor} = \frac{100}{50} = 2$$

When a solution is diluted, distilled or deionised water is usually used because it does not contain any dissolved ions and will not contaminate the solution.

This tells us that the volume of the solution after the dilution has increased 2 fold (doubled) and that the concentration of the original solution is 2 times greater than the concentration of the solution after it was diluted.

A dilution factor can be used to calculate the concentration of a solution before a dilution or after a dilution. For example, if a 5.0 g/L solution has been diluted with a dilution factor of 10, then we know that the volume of the solution after the water has been added is 10 times greater than the volume before the dilution. Therefore the concentration of the diluted solution is one tenth or 10 times lower than the undiluted solution.

$5.0 \div 10 = 0.50$ g/L (concentration of diluted solution)

- Never use cross multiplying when doing calculations involving dilutions. When a solution is diluted the volume of the solution and the concentration of the solution do not share a directly proportional relationship. Instead the concentration of a diluted solution is inversely proportional to the volume of the solution after the dilution. That is, as the volume of the solution increases, the concentration of solute decreases.

When doing calculations involving dilutions the following formula should be used:

$$C_1 V_1 = C_2 V_2$$

**$C_1$ = original concentration (undiluted)**
**$V_1$ = volume of undiluted solution**

**$C_2$ = concentration of solution after dilution**
**$V_2$ = Volume of solution after dilution**

So for the example on the previous page,

$C_1 = 2.0$ M
$V_1 = 50$ mL

$C_2 = 1.0$ M
$V_2 = 100$ mL

When using this equation the volume and concentration can be expressed in any units provided they are the same on both sides of the equation. That is, if $C_1$ is in g $L^{-1}$ then $C_2$ must also be in g $L^{-1}$. If $V_1$ is in mL then $V_2$ must also be in mL.

## Worked Example 10

2.0 mL of a 0.50 M $H_2SO_4$ solution is diluted up to 100.0 mL with distilled water. What is the concentration of the diluted solution?

## Worked Example 10 Solutions

$C_1 V_1 = C_2 V_2$

$C_1 = 0.50$ M
$V_1 = 2.0$ mL

$C_2 = ?$
$V_2 = 100.0$ mL

$$C_2 = \frac{C_1 V_1}{V_2} = \frac{0.50 \text{ x } 2.0}{100.0} = 0.010 \text{ M}$$

An alternative way to solve this problem is to divide the concentration of the undiluted solution by the dilution factor:

Dilution factor = $\frac{100.0}{2.0} = 50$

$0.50 \div 50 = 0.010$ M

## Worked Example 11

What is the concentration of the solution formed when 25 mL of a 0.12 M solution is diluted with 100.0 mL of water?

## Worked Example 11 Solutions

$C_1 V_1 = C_2 V_2$

$C_1 = 0.12$ M $\quad\quad$ $C_2 = ?$
$V_1 = 25$ mL $\quad\quad$ $V_2 = 125.0$ mL

$$C_2 = \frac{C_1 V_1}{V_2} = \frac{0.12 \text{ x } 25}{125} = 0.024 \text{ M}$$

"diluted with 100.0 mL of water" means that 100 mL of water was added to the original 25 mL solution so $V_2 = 100 + 25 = 125$ mL. In worked example 10, "diluted up to 100 mL" means enough water (98 mL) was added to the 2.0 mL solution to produce a final volume of 100 mL. $V_2 = 100$ mL

## Worked Example 12

A stock solution of 15 %m/v $CuSO_4$ is diluted to produce 50.0 mL of solution with a concentration of 0.50 %m/v. What volume of stock solution was required for this dilution?

## Worked Example 12 Solutions

$C_1 V_1 = C_2 V_2$

$C_1 = 15$ %m/v $\quad\quad$ $C_2 = 0.50$ %m/v
$V_1 = ?$ $\quad\quad$ $V_2 = 50.0$ mL

$$V_1 = \frac{C_2 V_2}{C_1} = \frac{0.50 \text{ x } 50.0}{15} = 1.6667 = 1.7 \text{ mL}$$

The term stock solution is used to describe a solution that is diluted in order to make other solutions of lower concentration.

## Worked Example 13

What volume of water must be added to 20.0 mL of a 20.0 ppb solution in order to produce a solution with a concentration of 12.5 ppb?

## Worked Example 13 Solutions

$C_1 V_1 = C_2 V_2$

$C_1 = 20.0$ ppb $\quad\quad$ $C_2 = 12.5$ ppb
$V_1 = 20.0$ mL $\quad\quad$ $V_2 = ?$

$$V_2 = \frac{C_1 V_1}{C_2} = \frac{20.0 \text{ x } 20.0}{12.5} = 32.0 \text{ mL}$$

The volume of water added = 32.0 – 20.0
= 12.0 mL

The original volume of the solution was 20 mL so 12 mL of water must be added in order to bring the final volume of the solution ($V_2$) up to 32.0 mL.

# CHAPTER 2 REVIEW QUESTIONS

## Multiple Choice

**Question 1**

A solution containing 0.25 g of NaCl in 50 mL of deionised water will also contain 0.25 mg of NaCl in

**A.** 0.50 mL of deionised water.
**B.** 5.0 mL of deionised water.
**C.** 0.050 mL of deionised water.
**D.** 0.0005 L of deionised water.

**Question 2**

The concentration that is equivalent to 1.0 M $KNO_3$ is

**A.** 1.0 x $10^2$ mg $mL^{-1}$ $KNO_3$
**B.** 1.0 x $10^{-7}$ $\mu g$ $mL^{-1}$ $KNO_3$
**C.** 101.1 % w/v $KNO_3$
**D.** 1.0 x $10^2$ Kg/L

**Question 3**

When 2.5 x $10^{24}$ molecules of $NH_3$ are dissolved in 1.0 L of distilled water, the resultant solution will have a molar concentration of

**A.** 4.2 M
**B.** 2.5 x $10^{24}$ mol $L^{-1}$
**C.** 71 mol/L
**D.** 71 g $L^{-1}$

**Question 4**

When a solution is diluted,

**A.** the moles of solute are unchanged.
**B.** the mass of solute and solution both increase.
**C.** the concentration of the solution will increase but the moles of solute remain unchanged.
**D.** All of the above are correct.

**Question 5**

On average, an adult has a concentration of creatine in their urine that is equal to 0.10 %w/v. Creatine is also found in the blood where its concentration is 100 times less than in the urine. On average, what mass of creatine would be present in 1.0 L of blood from an adult?

**A.** 0.010 g
**B.** 0.00010 g
**C.** 0.10 g
**D.** 1.0 g

**Question 6**

25 mL of a 0.12 M $HNO_3$ solution is poured into 100 mL of distilled water. The concentration of the resultant solution is

**A.** 0.48 M
**B.** 0.030 M
**C.** 0.024 M
**D.** 0.60 M

## Short Answers

**Question 1**
How many carbon atoms are present in 100.0 mL of a 10.0 ppm solution of $C_6H_{12}O_6$?

**Question 2**
How many nanograms of $Fe^{2+}$ ions are contained in 50.0 mL of a 0.026 M $Fe^{2+}$ solution?

**Question 3**
Express 25 mL of 2.0 M $Al(NO_3)_3$ solution as % m/v.

**Question 4**
Convert a solution with a concentration of 23 %w/v into mg $L^{-1}$.

**Question 5**
A batch of oysters is suspected of being contaminated with mercury (Hg). Analysis of one of the oysters reveals a concentration of Hg that is equal to 200.0 ppb. Express the level of Hg in the oyster as mg/Kg.

**Question 6**
2,500 gigalitres of water pass through a dam each day. Discharge from a nearby steel works plant has contaminated the water passing through the dam with highly toxic metals such as lead. The concentration of lead in a sample of water taken near the dam was 2.88 ppm during each day of testing during a 5 day period. How many micrograms of lead passed through the dam during this 5 day testing period?

**Question 7**
What volume of water, in mL, is required to produce a 1.0 L bottle of 3.0 M NaOH solution. The stock solution used for this dilution has a concentration of 10.0 M.

**Question 8**
10.0 g of $Na_2CO_3$ is dissolved in 250 mL of water. A 100.0 mL sample of this $Na_2CO_3$ solution is transferred to an empty beaker.

**a.** What is the number of moles of $Na_2CO_3$ dissolved in the 250 mL of water.

**b.** What is the molarity of the original 250 mL solution of $Na_2CO_3$?

**c.** What is the molarity of the 100.0 mL sample of $Na_2CO_3$ ?

**d.** How many moles of $Na_2CO_3$ are present in the 100.0 mL sample?

**e.** The beaker containing the 100.0 mL solution of $Na_2CO_3$ is diluted with 100.0 mL of water. How many moles of $Na_2CO_3$ are present after the dilution with 100.0 mL of water?

**f.** What is the molarity of the 100 mL $Na_2CO_3$ solution after dilution with 100 mL of water.

**g.** How many $Na^+$ ions are present in 1.0 µL of the diluted $Na_2CO_3$ solution from part f?

# Chapter 3 – Gases

Three important characteristics of gases are:

- Volume
- Temperature
- Pressure

## Volume

Gas molecules are in a state of constant motion which includes vibration and movement through space. Unlike solids and liquids, gas molecules have virtually no attraction for each other so they move around independently of each other. As a result of this continual and random motion gases take up the **total volume** of the container they are placed in. The units used for measuring the volume of gases are the same as those used for measuring the volume of liquids: **litres (L) and millilitres (mL).**

$$\begin{tikzcd} \textbf{mL} \arrow[r, bend left, "\div 10^3"] & \textbf{L} \arrow[l, bend left, "\times 10^3"] \end{tikzcd}$$

**1 L = 1,000 mL**

## Temperature

Temperature is a measure of the kinetic energy (energy of movement) of the particles (atoms, ions or molecules) that make up a substance. The higher the temperature the greater the kinetic energy of the particles. At -273 $^0$C, atoms, ions and molecules have zero kinetic energy. That is, they do not move at all. Since temperature is a measure of the kinetic energy of particles, it makes sense that when particles have zero kinetic energy (not moving) their temperature should also be zero. So in chemistry an alternative scale to degrees Celsius ($^0$C) is used. This scale is known as **the absolute temperature scale** or the **Kelvin scale (K).** At absolute zero or zero degrees Kelvin (0 K), atoms, ions and molecules are believed to have zero kinetic energy. Therefore -273 $^0$C = 0 K.

$$\begin{tikzcd} \text{Celsius } (^0\text{C}) \arrow[r, bend left, "+273"] & \text{Kelvin (K)} \arrow[l, bend left, "-273"] \end{tikzcd}$$

**0 $^0$C = 273 K**

**T (K) = t ($^0$C) + 273**
**t ($^0$C) = T (K) – t273**

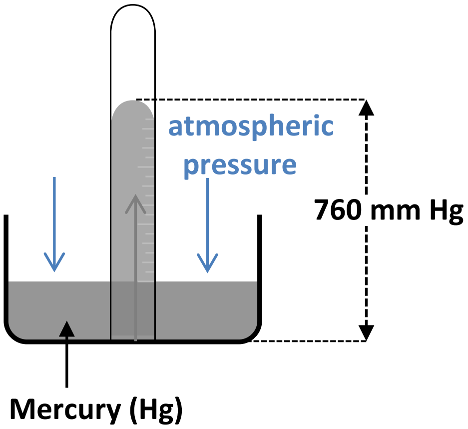
This information is provided on page 6 of the end of year exam data book.

## Pressure

Pressure is a property that is unique to gases. Solids and liquids do not have pressure. Due to their continuous and random movement, gas molecules are constantly colliding with each other and with the walls of the container that is holding them. The **pressure** of a gas is a measure of the force that the gas molecules are exerting on the walls of their container. This force is mainly due to the number of collisions that the gas molecules make with the walls of their container.

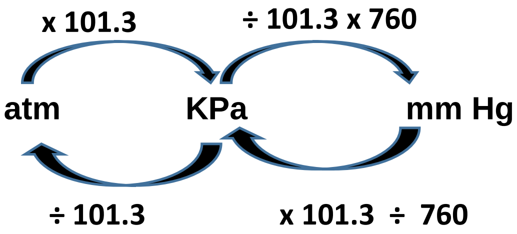
Every object and living organism on Earth is continually colliding with the gas molecules that make up the atmosphere (all the air that surrounds us). The pressure of our atmosphere is referred to as **atmospheric pressure.** Atmospheric pressure is also referred to as **1 atmosphere** or **1 atm.**

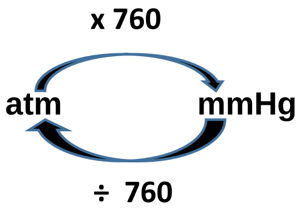
A mercury (Hg) filled barometer is a device that can be used to measure the pressure of the atmosphere. As can be seen in the diagram below, the gas molecules in the atmosphere exert pressure on the mercury which causes it to rise up a glass tube. At sea level the pressure of the atmosphere is such that it causes the mercury to rise up to a height of 760 mm. Therefore atmospheric pressure or 1 atm is equivalent to **760 mm of Hg (mercury).** Atmospheric pressure can also be expressed as **101.3 KPa**. **KPa** stands for **Kilopascals.**



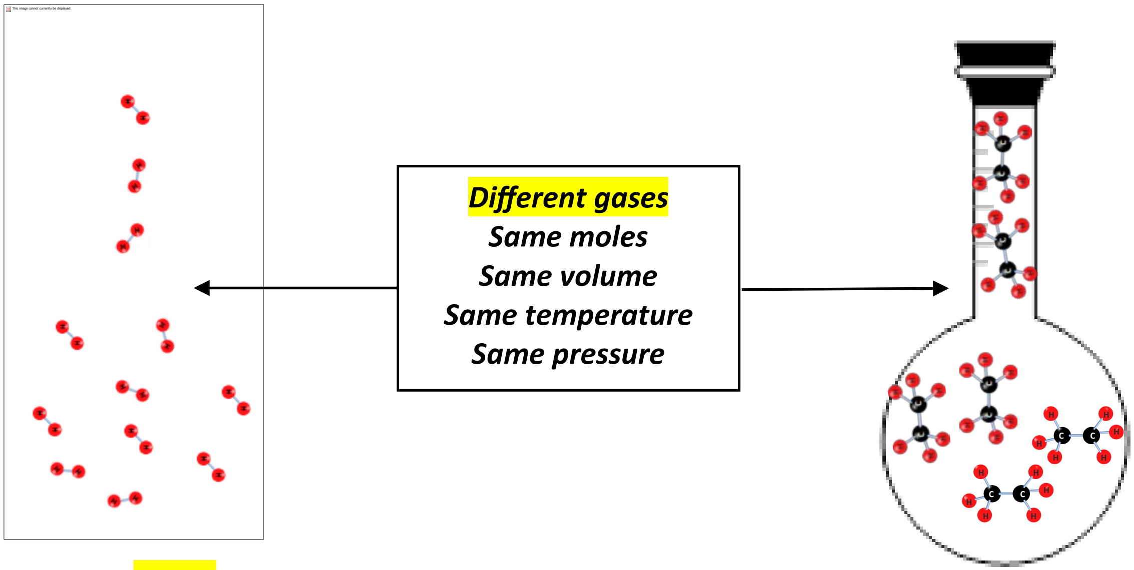
**1 atm = 760 mmHg = 101.3 KPa**

**Pressure Conversions**





The diagram below shows 2 sealed 10 litre bottles of gas. The first bottle contains 1 mole of $H_2$ molecules and the second one 1 mole of $C_2H_6$ molecules. The pressure of the gases is the same in both bottles even though the mass of the molecules is different. **The pressure that a gas exerts in a container is not related to the size or mass of the gas molecules colliding with the walls of the container.** Since both bottles contain the same number of gas molecules the number of collisions between the molecules and walls of the container will be the same for both gases. **A gas containing heavier molecules will not exert a higher pressure than the same number of lighter gas molecules, provided the temperature and volume is the same for both gases (298 K and 10 litres for this example).**



***Different gases***
***Same moles***
***Same volume***
***Same temperature***
***Same pressure***

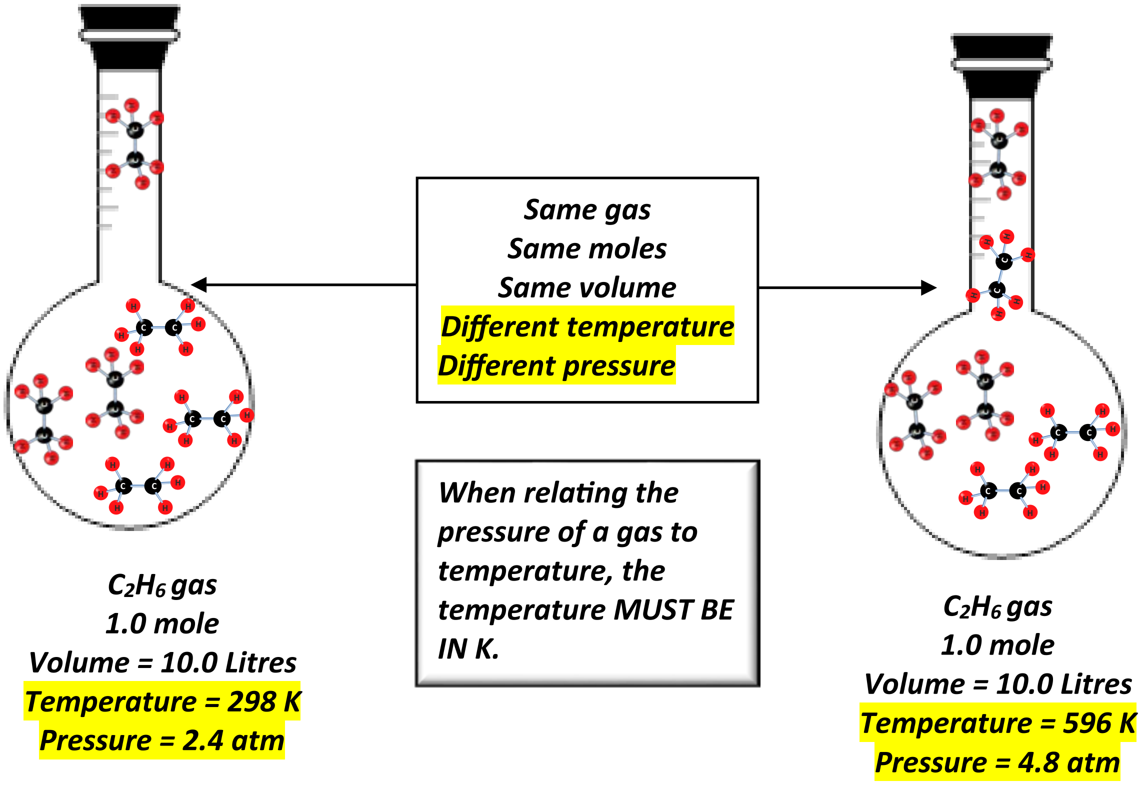
***$H_2$ gas***
***1.0 mole***
***Volume = 10.0 Litres***
***Temperature = 298 K***
***Pressure = 2.4 atm***

***$C_2H_6$***
***1.0 mole***
***Volume = 10.0 Litres***
***Temperature = 298 K***
***Pressure = 2.4 atm***

## Increasing pressure by increasing temperature

**The pressure of a gas will increase if the temperature is increased provided the moles and volume remain constant.**

The diagram below shows 2 bottles containing ethane gas. The bottle on the right is at twice the temperature (596 K) of the other bottle on the left (298 K). The pressure of the gas at the higher temperature will be double (4.8 KPa) that of the gas at the lower temperature. **This is because the molecules of gas at the higher temperature have more kinetic energy (moving faster) and as a result are making more collisions with the walls of the container.** <u>The fact that the molecules are hitting the walls of the container at faster speeds does not cause the increase in pressure.</u>



***Same gas***
***Same moles***
***Same volume***
***Different temperature***
***Different pressure***

***When relating the pressure of a gas to temperature, the temperature MUST BE IN K.***

*$C_2H_6$ gas*
*1.0 mole*
*Volume = 10.0 Litres*
***Temperature = 298 K***
***Pressure = 2.4 atm***

*$C_2H_6$ gas*
*1.0 mole*
*Volume = 10.0 Litres*
***Temperature = 596 K***
***Pressure = 4.8 atm***

# The Universal Gas Equation

The **universal gas equation** provides a mathematical relationship that can be used to calculate the variables of moles, pressure, volume or temperature of a gas when either one or several of these variables are changing. The universal gas equation is

$$\frac{\mathbf{P_1V_1}}{\mathbf{T_1n_1}} = \frac{\mathbf{P_2V_2}}{\mathbf{T_2n_2}}$$

**$P_1$ = initial pressure.**
**$V_1$ = initial volume.**
**$T_1$ = initial temperature.**
**$n_1$ = initial moles.**

**$P_2$ = new pressure.**
**$V_2$ = new volume.**
**$T_2$ = new temperature.**
**$n_2$ = new moles.**

- *Any units can be used for pressure and volume provided they are the same on both sides of the equation.* ***The temperature MUST be in K.***

This equation can be used to prove the situation described on the previous page where *the pressure of a gas will increase when the temperature increases provided the moles and volume remain constant.*

Bottle on the left

$P_1$ = 2.4 atm
$V_1$ = 10.0 L
$T_1$ = 298
$n_1$ = 1.0

Bottle on the right

$P_2$ = ?
$V_2$ = 10.0
$T_2$ = 596
$n_2$ = 1.0

Transpose the equation to make $P_2$ (the new pressure is the unknown) the subject.

$$P_2 = \frac{P_1V_1T_2n_2}{T_1n_1V_2}$$

$$= \frac{2.4 \text{ x } 10.0 \text{ x } 596 \text{ x } 1.0}{298 \text{ x } 1.0 \text{ x } 10.0} = 4.8 \text{ atm}$$

This calculation can be simplified by removing from the equation the variables that remain constant (do not change). In this case it is the moles and volume.

$$\frac{P_1\cancel{V_1}}{T_1\cancel{n_1}} = \frac{P_2\cancel{V_2}}{T_2\cancel{n_2}}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

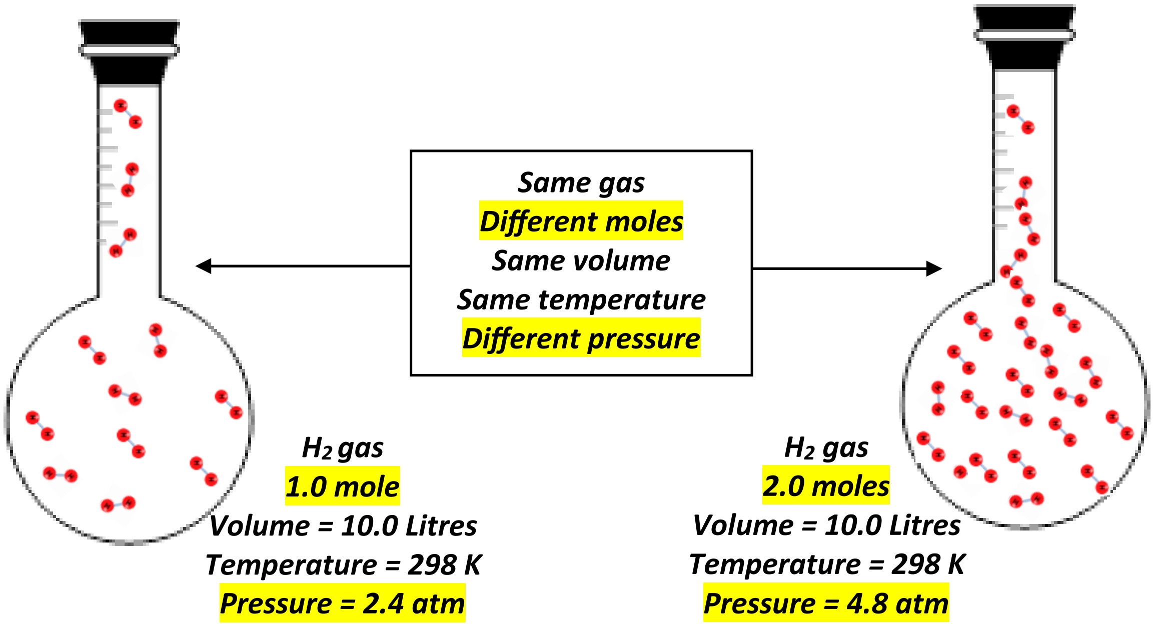
$$P_2 = \frac{P_1 T_2}{T_1}$$

$$P_2 = \frac{2.4 \times 596}{298} = 4.8 \text{ atm}$$

## Increasing pressure by increasing the number of gas particles.

- **The pressure of a gas will increase if more gas particles are added at constant volume and temperature.**

If the volume and temperature of a gas remain constant, the pressure of a gas can be increased by simply adding more gas particles / increasing the moles of gas. If there are more particles of gas in a container the number of collisions between the gas particles and the walls of the container will increase. The diagram below shows how the pressure of a container holding $H_2$ molecules will increase when there are more $H_2$ molecules present. The container on the right has twice the number of moles of gas molecules so its pressure is twice as high.



Using universal gas equation:

Remove the constant variables of volume and temperature.

$$\frac{P_1\cancel{V_1}}{\cancel{T_1}n_1} = \frac{P_2\cancel{V_2}}{\cancel{T_2}n_2}$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

$$P_2 = \frac{P_1 n_2}{n_1}$$

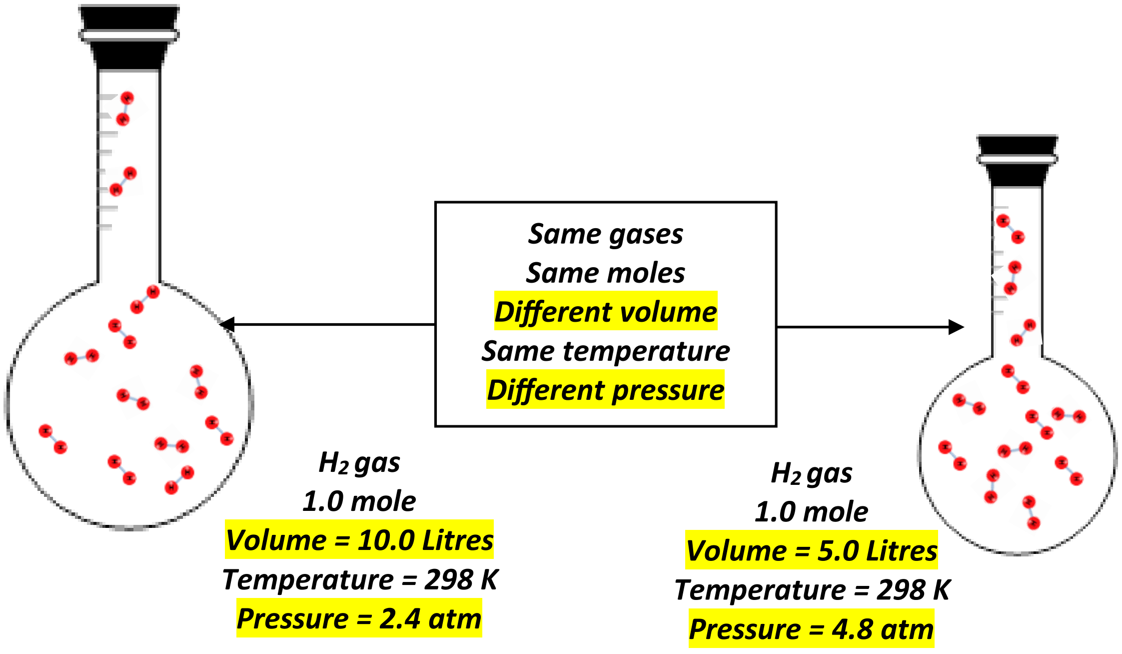
$P_1$ = 2.4 atm　　　$P_2$ = ?
$n_1$ = 1.0 mol　　　$n_2$ = 2.0

$$P_2 = \frac{2.4 \text{ x } 2.0}{1.0} = 4.8 \text{ atm}$$

## Increasing the pressure of a gas by reducing the volume of the container

- **The pressure of a gas will increase if the volume of its container is reduced provided the temperature and moles of gas remain the constant.**

The diagram below shows 2 bottles containing 1.0 mole of $H_2$ gas at the same temperature. The volume of the bottle on the right is only half the volume of the bottle on the left. Therefore the 1.0 mole of $H_2$ molecules in the smaller container will be more tightly packed together (more concentrated) and will make more collisions (twice as many collisions) with the walls of the container when compared with the $H_2$ gas in the larger bottle. The pressure of the gas in the 5.0 L bottle will be double that in the 10 L bottle.



Using universal gas equation:

Remove the constant variables of temperature and moles.

$$\frac{P_1V_1}{\cancel{T_1}\cancel{n_1}} = \frac{P_2V_2}{\cancel{T_2}\cancel{n_2}}$$

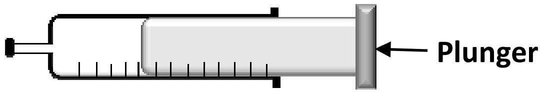
$P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2}$$

$P_1$ = 2.4 atm　　　$P_2$ = ?
$V_1$ = 10.0 L　　　$V_2$ = 5.0 L

$$P_2 = \frac{2.4 \text{ x } 10.0}{5.0} = 4.8 \text{ atm}$$

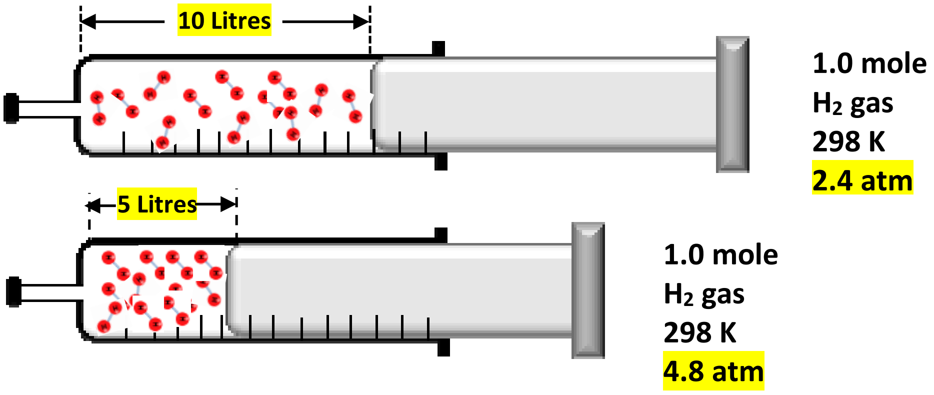
The volume of a gas can also be altered by using a device known as a gas syringe which is shown below.



**Gas syringe**

The volume of a gas can be reduced when the plunger is pushed in or increased when the plunger is pulled out.

So the effect of volume on the pressure of a gas can also be illustrated using a gas syringe:



The pressure of the 1.0 mole of $H_2$ gas is twice as high when the volume of the syringe is reduced to 5.0 litres because the $H_2$ molecules are more tightly packed together (more concentrated) so they make a greater number of collisions with the inner walls of the syringe.

## Worked Example 1

A 2.0 L bottle containing $N_2$ is at a pressure of 2.50 atm. A second 2.0 L bottle contains 5.0 moles of Argon gas. The pressure of the gas in this bottle is 1.25 atm. How many moles of $N_2$ are present in the first 2.0 L bottle of gas? Both bottles are at the same temperature.

## Worked Example 1 Solutions

As both bottles of gas have the same temperature and volume, the only variable that can account for the difference in pressure is the moles of gas. If the second bottle contains 5.0 moles of Argon gas at 1.25 atm, then the first bottle containing $N_2$ at a pressure of 2.50 atm must have twice the moles of gas. Therefore the moles in the first bottle is equal to 5.0 x 2 = 10 moles of gas. The fact that each bottle contains a different type of gas does not affect the pressure in each bottle.

Or using the universal gas equation:

Remove the constant variables of volume and temperature and make $n_1$ the unknown.

$$\frac{P_1\cancel{V_1}}{\cancel{T_1}n_1} = \frac{P_2\cancel{V_2}}{\cancel{T_2}n_2}$$

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

$$n_1 = \frac{P_1 n_2}{P_2}$$

$P_1$ = 2.5 atm		$P_2$ = 1.25 atm
$n_1$ = ? mol		$n_2$ = 5.0 mol

$$n_1 = \frac{2.5 \text{ x } 5.0}{1.25} = 10 \text{ mol}$$

## Worked Example 2

0.25 mol of He gas is drawn into a gas syringe at a temperature of 35 $^0$C and 2.0 atm pressure. The volume of the gas is at 5.0 mL. If the temperature is reduced to 25 $^0$C and the pressure decreased to 1.30 atm, what will be the new volume of this gas?

## Worked Example 2 Solutions

Remove the moles from the equation as they remain constant.

$$\frac{P_1V_1}{T_1\cancel{n_1}} = \frac{P_2V_2}{T_2\cancel{n_2}}$$

$P_1$ = 2.0 atm		$P_2$ = 1.3 atm
$V_1$ = 5.0 mL		$V_2$ = ?
$T_1$ = 35$^0$C + 273 = 308 K		$T_2$ = 25 $^0$C + 273 = 298 K

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$V_2 = \frac{2.0 \text{ x } 5.0 \text{ x } 298}{308 \text{ x } 1.3} = 7.4 \text{ mL}$$

# The Ideal Gas Equation

The ideal gas equation is

**PV = nRT**    *This equation is given on page 5 of the end of year exam data book.*

This equation shows the relationship between the moles, pressure, volume and temperature of any gas. This equation can be used to calculate the moles, volume, temperature and pressure of all the bottles of gas described on pages 41 to 45. *Unlike the universal gas equation, this equation is not used for calculations where one or more of the variables are changing.*

P = pressure in KPa
V = volume in Litres
n = moles
R = Gas constant = 8.31
T = temperature in K

## Worked Example 3

Prove that the gas bottle on the left hand side of page 45 has a pressure of 2.4 atm.

## Worked Example 3 Solutions

First of all make sure that the units are appropriate for the ideal gas equation.

V = 10.0 L
T = 298 K
n = 1.0 mole
R = 8.31

PV = nRT

$$P = \frac{nRT}{V}$$

$$= \frac{1.0 \text{ x } 8.31 \text{ x } 298}{10.0} = 247.638 \text{ KPa}$$

247.638 ÷ 101.3 = 2.4446 = 2.4 atm

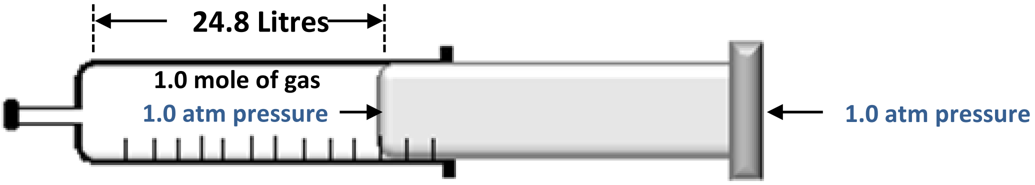
# Molar volume of a gas

<u>The term molar volume refers to the volume of 1.0 mole of a gas at a specific set of conditions of temperature and pressure.</u>

## Molar volume of a gas at standard laboratory conditions (SLC)

SLC conditions are 0.987 atm pressure and 25 $^0$C (298 K) temperature. **At SLC conditions 1.0 mole of any gas will occupy a volume of exactly 24.8 L.** So if 1.0 mole of a gas was drawn into a gas syringe at SLC conditions, the plunger would adjust itself so that the volume of the gas was exactly 24.8 L.

- In labs as is the case with most rooms, the average air pressure is 0.987 atm which is slightly less than the average air pressure of 1 atm in the outside environment at sea level.



The pressure of the gas inside the syringe (1.0 atm) is pushing the plunger outwards. The pressure of the surrounding air pushing the plunger in the opposite direction (inwards) is also equal to 1.0 atm. Since these 2 opposing forces are equal the plunger stays in the same position and the volume of the gas remains at a constant 24.8 L.

The volume of any gas at SLC conditions can be calculated by: **V = n x 24.8 L**

*On page 5 of the end of year exam data book this equation is expressed is*

$n = \frac{V}{Vm}$ *Vm represents the molar volume of a gas at SLC (24.8 L)*

**0.987 atm = 750 mmHg = 100KPa**

↑

*This information is provided on page 6 of the end of year exam data book.*

## Worked Example 4

Calculate the volume occupied by 2.5 moles of air at SLC conditions.

## Worked Example 4 Solutions

At SLC: V = n x 24.8
= 2.5 x 24.8 = 62 L

## Worked Example 5

If a gas syringe containing $O_2$ gas at a temperature of 25 $^{0}$C and 0.987 atm pressure occupies a volume of 750 mL, calculate

**a.** the moles of gas
**b.** the mass of the gas

## Worked Example 5 Solutions

**a.** At SLC: $n = \frac{v}{24.8}$

$$= \frac{0.750}{24.8} = 0.030242 = 0.0302 \text{ mol}$$

**b.** m = n x M
= 0.030242 x 32.0 = 0.967744 = 0.968 g

In summary,

**Molar volume ($V_m$) of a gas at 298 K and 100 KPa (SLC) = 24.8 L mol$^{-1}$**

*This information is provided on page 5 of the end of year exam data book.*

# CHAPTER 3 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
If a gas is at a pressure of 200 KPa, the equivalent pressure in mmHg is

**A.** 760
**B.** 1.97
**C.** 2.0 x $10^5$
**D.** 1.5 $10^3$

*Use the following information to answer questions 2 and 3.*

Some important information about 2 gases, A and B is shown below.

| Gas A | Gas B |
|---|---|
| 2.0 atm pressure | 4.0 atm pressure |
| 5 $^{0}$C temperature | 10 $^{0}$C temperature |
| 5.0 L of volume | 2.5 L of volume |

**Question 2**
The greater pressure of Gas B is mainly due to

**A.** its greater temperature.
**B.** its lower volume.
**C.** its lower volume and greater temperature to an equal extent.
**D.** Unable to be determined unless the identity of Gases A and B is known.

**Question 3**
The moles of gas A is closest to

**A.** 0.44 mol
**B.** 0.219 mol
**C.** 0.877 mol
**D.** Unable to be determined unless the identity of Gases A and B is known.

**Question 4**
Which of the following gases has a density of 1.78 g L$^{-1}$ at SLC conditions?

**A.** $O_2$
**B.** $N_2$
**C.** $CH_4$
**D.** $CO_2$

**Question 5**
20 grams of He gas is blown into a rubber balloon. If the same mass of Ar gas is blown into another balloon at the same temperature and pressure, it is correct to say that the balloon containing Ar will be

**A.** at a volume equal to the balloon containing He.
**B.** at a volume greater than the balloon containing He.
**C.** at a pressure that is greater than the balloon containing He.
**D.** at a volume that is less than the balloon containing He.

**Question 6**
A gas syringe contains 100 mL of Ne gas at a pressure of 1.0 atm and temperature of 25 $^{0}$C. If the temperature of the gas is raised to 50 $^{0}$C then

**A.** the volume of the gas will increase.
**B.** the volume of the gas will decrease.
**C.** the volume and pressure of the gas will decrease.
**D.** the volume and pressure will both increase.

**Question 7**
Two bottles of gas, bottle Y and bottle Z are at the same temperature and volume.

Bottle Y contains 20 g of $O_2$
Bottle Z contains 20 g of $N_2$

When comparing the moles and pressure of each gas it is correct to say that

**A.** Bottle Y has more moles and a lower pressure.
**B.** Bottle Z has more moles and a greater pressure.
**C.** Bottle Y has less moles and a greater pressure.
**D.** Bottles Y and Z have the same pressure but Z has the greater number of moles.

**Question 8**
If 5.0 g of ethene gas ($C_2H_4$) has a pressure of 200 KPa, then the pressure of the same mass of butene gas ($C_4H_8$) at the same conditions of volume and temperature would be

**A.** 400 KPa
**B.** 200 KPa
**C.** 100 KPa
**D.** 300 KPa

**Question 9**
The molar volume of a gas in mL, that is at a temperature of 50 $^0$C and a pressure of 2.0 atm is

**A.** $1.32 \times 10^4$
**B.** $6.1 \times 10^3$
**C.** $5.9 \times 10^4$
**D.** $2.45 \times 10^4$

**Question 10**
What is the pressure exerted by 24.5 g of argon gas that has been placed in a 2.0 Litre container at a temperature of 125 $^0$C ?

**A.** 1.0 atm
**B.** 2.0 atm
**C.** 10 atm
**D.** 20 atm

## Short Answer Questions

**Question 1**

Calculate the mass of 10.0 L of $O_2$ gas at SLC conditions.

**Question 2**

How many Litres of argon gas will fill up a gas syringe at SLC conditions if the mass of the gas is equal to 20.0 g?

**Question 3**

An incandescent light globe of 50.0 mL volume operates at a temperature of 3,300 K. How many moles of inert gas will such a light bulb contain if the pressure within the bulb is to be maintained at 80.0 % of atmospheric pressure?

**Question 4**

A glass flask contains 16.0 g of oxygen gas at 30.0 $^0$C temperature and 2.00 atm pressure. What would be the molar mass of 15.0 g of a gas in a second identical flask that was at the same conditions of temperature and pressure?

# Chapter 4 – Acids, Bases, pH and Important reaction types

Only a basic knowledge of acids and bases is required for year 12 chemistry.

An **acid** is a substance that donates hydrogen ions ($H^+$) to a base. When an acid is placed in water, the acid donates $H^+$ to $H_2O$ molecules resulting in the production of hydronium ions ($H_3O^+$). The equation below shows hydrochloric acid (HCl) reacting with water.

$HCl\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

A simplification of this reaction is

$HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

$H^+$ ions are often referred to as protons. The reaction of an acid with water is often referred to as an ionisation reaction because the products of the reaction are always ions.

- So when in solution (dissolved in water) an acid will produce $\mathbf{H_3O^+}$ ions which are more simply referred to as $\mathbf{H^+}$ ions or **protons**.

You should know the names and formulae of the following acids:

| | | | |
|---|---|---|---|
| Hydrochloric acid | **HCl** | *strong acid* | *monoprotic acid* |
| Nitric acid | $\mathbf{HNO_3}$ | *strong acid* | *monoprotic acid* |
| Sulfuric acid | $\mathbf{H_2SO_4}$ | *strong acid* | *diprotic acid* |
| Ethanoic acid | $\mathbf{CH_3COOH}$ | *weak acid* | *monoprotic acid* |
| Phosphoric acid | $\mathbf{H_3PO_4}$ | *weak acid* | *triprotic acid* |
| Carbonic acid | $\mathbf{H_2CO_3}$ | *weak acid* | *diprotic acid* |

A **strong acid** is completely or almost completely ionised in water. So when a strong acid such as HCl is placed in water, nearly every HCl molecule will donate its $H^+$ ion to a $H_2O$ molecule. The resultant mixture will contain a very small number of HCl molecules but a much larger number of $Cl^-$ and $H_3O^+$ ions.

A **weak acid** is only partially (partly) ionised in water. So when a weak acid such as $CH_3COOH$ is placed in water, only a very small number of $CH_3COOH$ molecules will donate their $H^+$ ions to water. The resultant mixture will contain a large number of $CH_3COOH$ molecules but a very small number of $CH_3COO^-$ and $H_3O^+$ ions.

A **monoprotic acid** has 1 $H^+$ ion that it can donate. The reaction between HCl and $H_2O$ at the top of the page shows that the monoprotic acid, HCl, has donated 1 $H^+$ ion to a $H_2O$ molecule.

A **polyprotic acid** is one that can donate 2 or more $H^+$ ions. A **diprotic** acid is a polyprotic acid that can donate 2 $H^+$ ions. When the diprotic acid, $H_2SO_4$, reacts with water, the 2 $H^+$ ions are donated in 2 stages as can be seen in the equation below.

$H_2SO_4\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ HSO_4^-\ (aq)\ +\ H_3O^+\ (aq)$
$HSO_4^-\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ SO_4^{2-}\ (aq)\ +\ H_3O^+\ (aq)$

A **triprotic** acid is a polyprotic that can donate 3 $H^+$ ions. When the triprotic acid, $H_3PO_4$, reacts with water, 3 $H^+$ ions are donated in 3 stages as can be seen in the equation below.

$H_3PO_4\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ H_2PO_4^-\ (aq)\ +\ H_3O^+\ (aq)$
$H_2PO_4^-\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ HPO_4^{2-}\ (aq)\ +\ H_3O^+\ (aq)$
$HPO_4^{2-}\ (aq)\ +\ H_2O\ (l)\ \rightarrow\ PO_4^{3-}\ (aq)\ +\ H_3O^+\ (aq)$

A **base** is a substance that receives $H^+$ ions from an acid. When a base is placed in water, the base receives $H^+$ ions from $H_2O$ molecules to produce hydroxide ions ($OH^-$). The equation below shows the base ammonia ($NH_3$), reacting with water.

$NH_3\ (aq) + H_2O\ (l) \rightarrow NH_4^+\ (aq) + OH^-\ (aq)$

Many bases are **metal hydroxides.** That is, they are ionic compounds that contain $OH^-$ ions joined to a metal ions. Some examples of metal hydroxides are NaOH, KOH, $Ba(OH)_2$ etc. When placed in water these bases dissociate into ions:

$NaOH\ (aq) \rightarrow Na^+\ (aq)\ +\ OH^-\ (aq)$

$Ba(OH)_2\ (aq) \rightarrow Ba^{2+}\ (aq)\ +\ 2OH^-\ (aq)$

Another common base is sodium carbonate ($Na_2CO_3$). When the base $Na_2CO_3$ is placed in water, it first of all dissociates into $Na^+$ and $CO_3^{2-}$ ions:

$Na_2CO_3\ (aq) \rightarrow\ 2Na^+\ (aq) +\ CO_3^{2-}\ (aq)$

The $CO_3^{2-}$ ions act as a base and accept $H^+$ ions from $H_2O$ molecules.

$CO_3^{-2}\ (aq) +\ H_2O\ (l)\ \rightarrow HCO_3^-\ (aq)\ +\ OH^-\ (aq)$

- So when in solution bases produce **$OH^-$**.
- The term **alkali** is used to describe a base that dissolves in water.

## pH scale

The pH scale is used to show how acidic or basic a solution is. It is a number scale between -1 and 15.

-1 0 1 2 3 4 5 6 **7** 8 9 10 11 12 13 14 15

**NEUTRAL**

ACIDIC BASIC

- Solutions with a pH of 7 are neutral (Eg. pure water).

- Solutions with a pH under 7 are acidic. The lower the pH value the more acidic the solution. For example, a solution with a pH of 0 is more acidic than one with a pH of 3. On this scale the most acidic solution has a pH of -1.

- Solutions with a pH above 7 are basic. The higher the pH value the more basic the solution. For example, a solution with a pH of 12 is more basic than one with a pH of 9. On this scale the most basic solution has a pH of 15.

- As the $H_3O^+$ / $H^+$ concentration of a solution increases the pH decreases and the solution is more acidic / less basic (less alkaline).

- As the $OH^-$ concentration of a solution increases the pH increases and the solution is more basic (more alkaline) / less acidic.

## Important Reaction Types

In the end of year exam you may have to write out balanced equations for or show an understanding of the following types of reactions involving acids. Having a knowledge of the valency table in appendix 3 would be very useful.

**reactive metal + acid → salt and hydrogen gas ($H_2$)**

- Examples of reactive metals include metals in groups 1 and 2 and other metals such as Fe, Al and Zn.

Some examples of this type of reaction:

magnesium + hydrochloric acid → magnesium chloride + hydrogen gas
$Mg\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$

calcium + sulfuric acid → calcium sulfate + hydrogen gas
$Ca\ (s) + H_2SO_4\ (aq) \rightarrow CaSO_4\ (aq) + H_2\ (g)$

**acid + metal hydroxide → salt + water ($H_2O$)**

hydrochloric acid + sodium hydroxide → sodium chloride + water
$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (l)$

phosphoric acid + barium hydroxide → barium phosphate + water
$2H_3PO_4\ (aq) + 3Ba(OH)_2\ (aq) \rightarrow Ba_3(PO_4)_2\ (aq) + 6H_2O\ (l)$

- The reaction between an acid and a base is referred to as a **neutralisation reaction**. So the reaction between metal hydroxides and acids are neutralisation reactions.

**acid + metal oxide → salt + water ($H_2O$)**

nitric acid + magnesium oxide → salt + water
$2HNO_3\ (aq) + MgO\ (s) \rightarrow Mg(NO_3)_2\ (aq) + H_2O\ (l)$

hydrochloric acid + sodium oxide → sodium chloride + water
$2HCl\ (aq) + Na_2O\ (s) \rightarrow 2NaCl\ (aq) + H_2O\ (l)$

- Metal oxides are bases so the reaction between metal oxides and acids are neutralisation reactions.

**acid + metal hydrogen carbonate → salt + water + carbon dioxide gas**

ethanoic acid + sodium hydrogen carbonate → sodium ethanoate + water + carbon dioxide gas
$CH_3COOH\ (aq) + NaHCO_3\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l) + CO_2\ (g)$

**acid + metal carbonate → salt + water + carbon dioxide gas**

phosphoric acid + magnesium carbonate → magnesium phosphate + water + carbon dioxide gas
$2H_3PO_4\ (aq) + 3MgCO_3\ (s) \rightarrow Mg_3(PO_4)_2\ (aq) + 3H_2O\ (l) + 3CO_2\ (g)$

hydrochloric acid + sodium carbonate → sodium chloride + water + carbon dioxide gas
$2HCl\ (aq) + Na_2CO_3\ (aq) \rightarrow 2NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)$

# Chapter 5 – Stoichiometry

**Stoichiometry** shows the relationship between the reactants and products in a chemical reaction as described by a balanced equation.

The coefficients (numbers used to balance the equation) in a balanced equation show a number ratio that can be used to calculate the quantity of products from a given amount of reactants or vice versa. Let's use a simple balanced equation to illustrate how stoichiometry works.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

According to the coefficients in this balanced equation, **2 molecules of $H_2$** react with **1 molecule of $O_2$** to produce **2 molecules of $H_2O$**. The $O_2$ did not have a coefficient so its coefficient is understood to be 1.

Whenever $H_2$ and $O_2$ react, exactly twice the number of molecules of $H_2$ must be present compared to the number of $O_2$ molecules for a complete reaction to occur. A complete reaction means that after the reaction has occurred, all of the $H_2$ and $O_2$ present have been used up. The number of $H_2O$ molecules produced will always be twice the number of $O_2$ molecules that reacted and exactly the same as the number of $H_2$ molecules that reacted.

As the coefficients in the balanced equation show a number ratio, they must also show a mole ratio. Remember that moles represent very large numbers. So it can also be said that according to the above equation,

**2 moles of $H_2$** react with **1 mole of $O_2$** to produce **2 moles of $H_2O$.** The table below shows how this ratio can be applied to various amounts of $H_2$, $O_2$ and $H_2O$.

| $2\,H_2$ | + | $O_2$ | → | $2\,H_2O$ |
|---|---|---|---|---|
| 2 moles | | 1 mole | | 2 moles |
| 4 moles | | 2 moles | | 4 moles |
| 5 moles | | 2.5 moles | | 5 moles |
| 9 moles | | 4.5 moles | | 9 moles |
| 0.10 mole | | 0.050 mole | | 0.10 mole |

This table clearly shows that a during a complete reaction, the number of moles of $H_2$ reacting is always exactly double the number of moles of $O_2$ reacting. The number of $H_2O$ molecules produced is equal to the number of $H_2$ molecules that reacted and double the number of moles of $O_2$ molecules that reacted.

Here is a simple question using stoichiometry.

**$SO_3$ gas can be produced according to the following equation.**

**$2SO_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2SO_3\ (g)$**

**How many moles of $SO_3$ can be produced if 0.50 mole of $SO_2$ reacts?**

According to the ratio given by the balanced equation:

$n\ (SO_3) = n\ (SO_2)$
$= 0.50$

- *Ratio of $SO_2$ to $SO_3$ is 2 : 2 or 1 : 1*

**How many moles of $O_2$ must be present if all of the 0.50 mole of $SO_2$ is to react?**

According to the equation, the moles of $O_2$ present must be exactly half the number of moles of $SO_3$ produced for a complete reaction. So if 0.50 moles of $SO_2$ are to react, there must be AT LEAST 0.25 mole of $O_2$ present: $n\ (O_2) = ½ \times n\ (SO_2)$
$= ½ \times 0.50 = 0.25$ mol

So there can be exactly 0.25 mole of $O_2$ or greater than 0.25 mole of $O_2$ for all of the 0.50 mole of $SO_2$ to react. If there is more than 0.25 mole of $O_2$ present, then all of the $SO_2$ will react but there will be some unreacted $O_2$ left over. The amount of $O_2$ present at the start of the reaction would be described as EXCESS.

EXCESS MEANS TO HAVE MORE THAN ENOUGH.

So the wording in the first question was too simple. It only mentioned that 0.50 mole of $SO_2$ reacted. A better wording of this question is:

**"How many moles of $SO_3$ can be produced if 0.50 mole of $SO_2$ reacts with EXCESS $O_2$?**

Here is another simple question involving stoichiometry.

**How many grams of $H_2O$ can be produced if 5.0 g of $H_2$ reacts with excess $O_2$ according to the following equation:**

**$2H_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2H_2O\ (g)$**

A rookie error often made with this question is to apply the ratio in the equation to the 5.0 g of $H_2$. The ratio of $H_2$ to $H_2O$ is 2 : 2 or 1 : 1. So if 5.0 g of $H_2$ reacts does this mean that 5.0 g of $H_2O$ will be produced?

The answer is no because the ratio can only be applied to MOLES not MASSES. A molecule of $H_2O$ can be said to contain a $H_2$ molecule plus an O atom. So a $H_2O$ molecule must be heavier than a $H_2$ molecule because of the extra mass due to the O atom. So if 5.0 g of $H_2$ completely reacted to produce $H_2O$, the $H_2O$ will contain all of the 5.0 g of the $H_2$ molecules plus the extra mass from the O atoms. The mass of $H_2O$ produced will be greater than the mass of $H_2$ that reacted.

Here is the correct way to answer the question.

First of all convert the mass of $H_2$ into moles:

$$n\ (H_2) = \frac{m}{M}$$

$$= \frac{5.0}{2.0} = 2.5\ \text{mol}$$

Now use the ratio to find the moles of $H_2O$ produced:

$$n\ (H_2O) = n\ (H_2)$$
$$= 2.5\ \text{mol}$$

Finally convert the moles of $H_2O$ into a mass.

$$m\ (H_2O) = n \times M$$
$$= 2.5 \times 18.0 = 45\ \text{g}$$

As was expected the $H_2O$ produced weighs much more than the mass of $H_2$ that reacted because of the extra mass due to the O atoms. An oxygen atom weighs much more than a hydrogen atom.

Below is list of steps that should be followed when completing stoichiometry questions.

**Step 1 –** Write out the balanced equation.

**Step 2 –** On the equation underline the chemical species whose quantity is unknown and mark it with an ***X.*** Underline the species whose quantity is known.

**Step 3 –** Find the moles of the **"known"** species.

**Step 4 –** Use the ratio to find the moles of the species whose quantity is **"unknown".**

**Step 5 –** Convert the moles of the unknown into the required quantity – mass, volume, concentration etc.

Here is an example of how to use these steps to solve a stoichiometric problem.

**What mass, in grams, of hydrogen is required to produce 1.0 Kg of water. The equation for the reaction is**

$$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$$

**Step 1 –** Write out a balanced equation.

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

**Step 2 –** On the equation underline the chemical species whose quantity is unknown and mark it with an ***X.*** Underline the species whose quantity is known.

$\underline{2H_2} (g) + O_2 (g) \rightarrow \underline{2H_2O (l)}$

***X*g** **1.0 Kg**

**Step 3 –** Find the moles of the "known" species ($H_2O$).

1.0 Kg x 1,000 = 1,000 g

$n (H_2O) = \frac{m}{M}$

$n (H_2O) = \frac{1,000}{18.0} = 55.5556$ mol

**Step 4 –** Use the ratio to find the moles of the "unknown" species ($H_2$).

$n (H_2) = n (H_2O)$

$= 55.5556$ mol

**Step 5 –** Convert the moles of the unknown into the required quantity – mass, volume, concentration etc. (in this example grams)

$m (H_2) = n \times M$

$= 55.5556 \times 2.0$

$= 111.1112 = 1.1 \times 10^2$ g

If you have difficulty working out the ratio just by looking at the coefficients in the equation, try this formula:

$$\mathbf{n (unknown)} = \frac{\textbf{coefficient of known}}{\textbf{coefficient of unknown}} \mathbf{\times n (known)}$$

For this example:

$n (H_2) = \frac{2}{2} \times 55.5556 = 55.5556$ mol

## Worked Example 1

Octane ($C_8H_{18}$) burns in excess oxygen in the internal combustion engine of a car. The equation for the complete combustion of octane is

$2C_8H_{18}\ (l) + 25O_2\ (g) \rightarrow 16CO_2\ (g) + 18H_2O\ (l)$

If 500.0 g of $O_2$ has fully reacted,

**a.** What mass of octane is required to fully react with the $O_2$ gas?
**b.** What volume of $CO_2$ gas, in litres, would be collected at 2.0 atm pressure and a temperature of 100.0 $^0$C?

## Worked Example 1 Solutions

$$\begin{array}{lllllll}
\underline{2C_8H_{18}\ (l)} & + & \underline{25O_2\ (g)} & \rightarrow & \underline{16CO_2\ (g)} & + & 18H_2O\ (l) \\
\boldsymbol{X}\text{ g} & & 500.0\text{ g} & & \boldsymbol{X}\text{ L} & & \\
 & & & & 2.0\text{ atm} & & \\
 & & & & 100.0\ ^0\text{C} & &
\end{array}$$

**a.** $n\ (O_2) = \frac{500.0}{32.0} = 15.625$ mol

$n\ (C_8H_{18}) = n\ (O_2) \times \frac{2}{25}$

$= 15.625 \times \frac{2}{25} = 1.25$ mol

$m\ (C_8H_{18}) = 1.25 \times 114.0$

$= 142.5 = 143$ g

**b.** $n\ (CO_2) = n\ (O_2) \times \frac{16}{25}$

$= 15.625 \times \frac{16}{25} = 10$ mol

$PV = nRT$

$V = \frac{nRT}{P}$

$P = 2.0 \text{ atm} \times 101.3 = 202.6$ KPa
$R = 8.31$
$T = 100.0 + 273 = 373$ K

$V = \frac{10 \times 8.31 \times 373}{202.6} = 152.9926 = 1.5 \times 10^2$ L

## Worked Example 2

A 10.0 mL volume of a HCl solution is placed into a conical flask. It is found that 25.00 mL of a 0.250 M $Ba(OH)_2$ solution is exactly enough to react with all of the HCl in the flask. Calculate the molar concentration of the HCl solution.

## Worked Example 2 Solutions

Sometimes you will have to work out the equation yourself. This is why you have to learn all of the reaction types from chapter 4.

$\underline{2HCl\ (aq)}\ +\ \underline{Ba(OH)_2}\ (aq) \rightarrow BaCl_2\ (aq)\ +\ 2H_2O\ (l)$

10.0 mL 0.250 M

***X*** M 25.00 mL

$n\ (Ba(OH)_2) = c \times v$

$= 0.250 \times 0.02500 = 0.00625$ mol

$n\ (HCl) = n\ (Ba(OH)_2) \times 2$

$= 0.00625 \times 2 = 0.0125$ mol

$C\ (HCl) = \frac{n}{v} = \frac{0.0125}{0.010} = 1.25$ M

## Reactants In excess

So far the stoichiometry questions we have looked at have stated a known quantity of just one of the reactants. This reactant has always totally reacted. The second reactant has been described as either in excess (more than enough for a complete reaction) or as having an amount that is exactly enough for a complete reaction with the other reactant

Now we will have questions where there is data to calculate the moles of both reactants. You will not be told which reactant has been totally used up and which one is in excess. Consider the example below.

**A pure strip of magnesium ribbon containing 0.25 mole of atoms has been exposed to 0.50 mole of $O_2$ gas. How many moles of MgO are produced? The equation for the reaction is**

**$2Mg\ (s) + O_2\ (g) \rightarrow 2\ MgO\ (s)$**

If we approach this question like the others we would underline the Mg and $O_2$ and give the moles of each reactant. The MgO would be underlined as the unknown quantity.

$\underline{2Mg}\ +\ \underline{O_2} \rightarrow \underline{2MgO}$

0.25 mol 0.50 mol ***X*** mol

According to the ratio, the moles of Mg present must be exactly double the moles of $O_2$ if there is to be a complete reaction. Clearly the moles of Mg and $O_2$ supplied are not in the 2 to 1 ratio required for a complete reaction.

If we calculate the moles of MgO by applying the ratio to the moles of Mg:

n (MgO) = n (Mg)
= 0.25 mol

If we calculate the moles of MgO by applying the ratio to the moles of $O_2$:

n (MgO) = n ($O_2$) x 2
= 0.50 x 2 = 1.0 mol

So we get 2 different answers for the moles of MgO produced, 0.25 mole if we work with the 0.25 mole of Mg or 1.0 mole if we work with the 0.50 mole of $O_2$. They can't both be right!

One of these reactants will have totally reacted. The moles of this reactant can be used to calculate the moles of the unknown MgO. The other reactant will be **in excess,** meaning that only some of it reacted with the rest remaining unreacted after the reaction has finished. If the moles of the excess reactant are used, the calculation of the moles of the MgO produced will be higher than the true value because not all of this reactant was consumed (used up) during then reaction. The following table can be used to work out which reactant fully reacted and which one was in excess.

| | **2 Mg (s)** | + | **$O_2$ (g)** | → | **2 MgO (s)** |
|---|---|---|---|---|---|
| *n (supplied)* | 0.25 mol | | 0.50 mol | | |
| *n (required) using ratio* | 0.50 x 2 = 1.0 mol | | 0.25 x ½ = 0.125 mol | | |

The **n (supplied)** row simply shows the number of moles of each reactant that is present for the reaction. The **n (required)** row shows how many moles of each reactant is required to react with the supplied amount of the other one according to the stoichiometric ratio. So if 0.50 mol of $O_2$ is present, according to the ratio twice that number of moles of Mg is required to react with it (0.50 x 2 = 1.0 mol).

This shows that the number of moles of Mg supplied is not enough to react with the $O_2$. There is only 0.25 mole of Mg present but the supplied 0.50 mol of $O_2$ requires 1.0 mole of Mg. Therefore all of the 0.25 mole of Mg supplied will react. The moles of the MgO produced can be calculated by applying the ratio to the supplied mole of Mg.

n (MgO) produced = n (Mg) supplied
= 0.25 mol

The reactant that was totally used up (in this case the Mg) is referred to as the **LIMITING REACTANT**. This is because the number of moles of product that can be produced is limited by the quantity of this reactant that is present.

Now looking at the $O_2$. If 0.25 mole of Mg is present, exactly half that number of moles of $O_2$ is required to react with it (0.25 x ½ = 0.125 mol). Of the 0.50 mol of the $O_2$ that is supplied, only 0.125 mole of it will react with the 0.50 mole of the Mg. Therefore the $O_2$ is **IN EXCESS** because the moles supplied is greater than the moles required for the reaction. Remember that the word EXCESS means to have more than is required. As was discussed earlier, the moles of the excess reactant can't be used to calculate the moles of a product because not all of it reacts.

The moles of the ***reactant in excess*** or moles of ***excess reactant that remains unreacted*** can be calculated by using the following formula:

**n (reactant in excess) = n (excess reactant supplied) – n (required or reacts)**

So in this example:

n ($O_2$ in excess) = n ($O_2$) supplied – n ($O_2$) required/reacted
= 0.50 – 0.125 = 0.375 = 0.38 mol

- *As the final answer involves subtraction, the answer must be rounded off to the number of decimal places present in the piece of data containing the least number of decimal places – refer to appendix 1).*

This means that of the 0.50 mole of $O_2$ that was present at the start of the reaction, only 0.125 mole reacted resulting in 0.38 mole of $O_2$ remaining unreacted or in excess.

In summary,

**Limiting reactant :** n (supplied) is less than n (required)

- All of the moles of this reactant present or supplied at the start of the reaction will react.
- The moles of the limiting reactant supplied can be used to calculate the moles of the products.

**Excess reactant :** n (supplied) is greater than n (required)

- Only some of the moles of this reactant supplied will react. The rest will remain unreacted or be in excess.
- n (reactant in excess) = n (excess reactant supplied) – n (required or reacts)

## Worked Example 3

10.0 g of magnesium powder is placed into 200.0 mL of 0.10 M nitric acid.

**a.** Which reactant is in excess?
**b.** How many grams of the excess reactant will remain after the reaction has ended?
**c.** What is the molar concentration of the magnesium nitrate produced? Assume that the volume of the nitric acid solution is unchanged during the reaction.

## Worked Example 3 Solutions

| | $Mg$ (s) | + | $2HNO_3$ (aq) | → | $Mg(NO_3)_2$ (aq) | + | $H_2$ (g) |
|---|---|---|---|---|---|---|---|
| ***n (supplied)*** | $n = \frac{10.0}{24.3}$<br>= 0.4115<br>= 0.412 mol | | n = c x v<br>= 0.10 x 0.2000<br>= 0.020 mol | | | | |
| ***n (required)*** | 0.020 x ½<br>= 0.010 mol | | 0.4115 x 2<br>= 0.823<br>= 0.823 mol | | | | |

**a.** Mg is in excess because n (supplied) is greater than n (required)

**b.** n (Mg) in excess = n (Mg) supplied) – n (Mg) required
= 0.4115 – 0.010 = 0.4015 = 0.40 mol

m (Mg) unreacted or in excess = 0.4015 x 24.3
= 9.75645 = 9.76 g

**c.** n ($Mg(NO_3)_2$) = ½ x n ($HNO_3$) supplied
= ½ x 0.0200 = 0.0100 mol

The $Mg(NO_3)_2$ produced will be dissolved in 200.0 mL of water which is equal to the volume of the $HNO_3$ at the start of the reaction. All of the $HNO_3$ has reacted as it is the limiting reactant but the volume of the solution is unchanged. This is because the volume of the solution is due to water. All of the dissolved $HNO_3$ reacts but the water in which it was dissolved in DID NOT TAKE PART in the reaction so there is still 200 mL of water present.

$$C\ (Mg(NO_3)_2) = \frac{n}{v}$$

$$= \frac{0.0100}{0.2000} = 0.050\ M$$

# Stoichiometry involving gases at the same temperature and pressure

One of the golden rules of stoichiometry is that the ratio given by the balanced equation can only be applied to moles. The ratio can however, be applied to reactions that have reactants and products in the gaseous state at constant temperature and pressure. That is, the temperature and pressure of the gases at the start of the reaction is the same as at the end of the reaction. Let's investigate this further.

When 2 gases are at the same temperature and pressure their volumes will show the same relationship as their moles. Consider the following example:

| **Gas 1** | **Gas 2** |
|---|---|
| Moles = **2.0 mol** | Moles = **4 .0 mol** |
| Pressure = 101.3 KPa | Pressure = 101.3 KPa |
| Temperature = 298 K | Temperature = 298 K |

The volume of each of these gases can be calculated using PV=nRT.

$$V\ \textbf{(Gas 1)} = \frac{nRT}{P} = \frac{2.0 \times 8.31 \times 298}{101.3} = 48.89\ L$$

$$V\ \textbf{(Gas 2)} = \frac{nRT}{P} = \frac{4.0 \times 8.31 \times 298}{101.3} = 97.78\ L$$

When calculating the volumes of these 2 gases using PV=nRT, R, T and P are the same. The only difference is the value of their moles. So if the moles of gas 2 (4.0 moles) is twice the value of the moles of gas 1 (2.0 moles), then the calculated volume of gas 2 (97.78 mL) must also be twice the value of gas 1 (48.89 L). So the volumes of these gases at the same temperature and pressure show the same relationship as their moles.

**So the mole ratio given by the coefficients in a balanced equation can be applied to the volumes of gases provided the temperature and pressure remain constant.**

## Worked Example 4

5 mL of $H_2$ gas is allowed to react with excess $O_2$ gas at 1.0 atm pressure and 25 $^0$C temperature. What will be the volume of the water vapour produced if the temperature and pressure remains constant during the reaction?

## Worked Example 4 Solutions

$$2H_2\,(g) + O_2\,(g) \rightarrow \underset{V = ?}{\underline{2H_2O\,(g)}} \qquad V\,(H_2O) = V\,(H_2) = 5\ mL$$

# CHAPTER 5 REVIEW QUESTIONS

## Multiple Choice

**Question 1**

During a chemical reaction 2 moles of A completely reacts with 3 moles of B to produce 1.5 moles of C. This reaction is represented by which equation?

**A.** $A + B \rightarrow C$
**B.** $2A + 3B \rightarrow C$
**C.** $4A + 6B \rightarrow 2C$
**D.** $4A + 6B \rightarrow 3C$

**Question 2**

Hydrogen gas reacts explosively with oxygen to produce water and a large amount of heat. The equation for this reaction is given below.

$2\,H_2\,(g) + O_2\,(g) \rightarrow 2\,H_2O\,(g)$

A chemist mixes some hydrogen and oxygen gas together in a gas bottle and ignites the mixture with a spark. When the reaction is complete 5.0 mol of hydrogen gas remains unreacted and 10 mol of water are produced. Select the statement below which is consistent with the above information.

**A.** The hydrogen is the limiting reactant and the oxygen is in excess.
**B.** 5.0 mole of hydrogen has completely reacted.
**C.** 15 mol of hydrogen has completely reacted with 5.0 mole of oxygen.
**D.** 15 mol of hydrogen is mixed with 5.0 mole of oxygen.

**Question 3**

The dissociation of $KNO_3$ in water is described by the following equation.

$KNO_3\,(s) \rightarrow K^+\,(aq) + NO_3^-\,(aq)$

What is the concentration of $K^+$ ions when 1.0 g of $KNO_3$ dissociates on 2.0 L of water?

**A.** $1.0 \times 10^{-3}$ M
**B.** 1.0 g $L^{-1}$
**C.** $4.9 \times 10^{-3}$ M
**D.** 39.1 g $L^{-1}$

**Question 4**

What is the concentration of hydroxide ions remaining in solution when 25.0 mL of 0.30 M $Ba(OH)_2$ is mixed with 25 mL of 0.10 M $HNO_3$?

**A.** 0.050 M
**B.** 0.075 M
**C.** 0.250 M
**D.** 0.125 M

**Question 5**

28 g of calcium carbonate are reacted in a solution containing excess sulfuric acid. What volume of carbon dioxide gas will be collected at SLC conditions after the reaction has reached completion.

**A.** 0.24 L
**B.** 6.3 L
**C.** 2.7 L
**D.** 6.9 L

**Question 6**
Sulfur dioxide and oxygen react according to the following equation.

$2SO_2 (g) + O_2 (g) \rightarrow 2SO_3 (g)$

If 1.0 mole of $O_2$ and 0.50 mole of $SO_2$ are mixed together and allowed to react completely there will be

**A.** no reactants remaining.
**B.** no $O_2$ remaining and 1.0 mole of $SO_3$.
**C.** 0.75 mole of $O_2$ and 0.50 mole of $SO_3$.
**D.** 0.75 mole of $O_2$ and 1.0 mole of $SO_3$.

**Question 7**
When 5.0 L of $H_2$ gas is allowed to react with 5.0 L of $O_2$ gas, $H_2O$ gas is produced according to the following equation.

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (g)$

If the conditions of the reaction are kept at a constant 25 $^{0}$C and 760 mm Hg pressure, the resultant gaseous mixture will contain

**A.** 5.0 L of $H_2O$ and 2.5 L of $H_2$.
**B.** 2.5 L of $O_2$ and 5.0 L of $H_2O$.
**C.** 2.5 L of $H_2O$ only.
**D.** 5.0 L of $H_2$, 5.0 L of $O_2$ and 5.0 L of $H_2O$.

## Short Answers

**Question 1**
When exposed to heat calcium carbonate will decompose into calcium oxide and carbon dioxide gas.

$CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$

**a.** What mass of CaO will be produced from the decomposition of 3.4 g of $CaCO_3$?

**b.** What mass of $CaCO_3$ would have been decomposed if 25 mL of $CO_2$ was collected in a balloon with a pressure of 760 mm Hg at a temperature of 35 $^{0}$C?

**Question 2**
5.0 g of Al metal is placed in a 2.0 L flask containing $Cl_2$ gas at a pressure of 2.0 atm and temperature of 25 $^{0}$C. The product of the reaction is aluminium chloride.

**a.** Which reactant is inexcess?

**b.** How many grams of the excess reactant will remain after the reaction?

**c.** What mass, in grams, of $AlCl_3$ will be produced?

**Question 3**
What volume of 1.0 M NaOH in mL, would be required to completely react with a 50.0 mL solution containing 1.31 x $10^{23}$ molecules of HCl?

**Question 4**
$Cl_2$ gas was used as a chemical weapon during World War 1. Soldiers protected themselves from this poisonous gas by breathing through handkerchiefs that were soaked in urine. It is believed that the $NH_3$ in the urine reacted with the $Cl_2$ according to the equation:

$4NH_3 + 3Cl_2 \rightarrow NCl_3 + 3NH_4Cl$

If 5.0 L of $Cl_2$ is passed through a solution containing excess $NH_3$, what would be the change in pressure, in atm, of the 5.0 L of $Cl_2$ gas if the temperature throughout the reaction remained at 27 $^{0}$C ? The initial pressure of the $Cl_2$ gas was 2.0 atm.

# Chapter 6 – Chemical Energy

## Chemical Energy

Chemical energy is a type of potential energy (stored energy) that is found in the bonds that hold the atoms together in a substance. For example there is chemical energy in the covalent bonds that hold the atoms together in the molecules of covalent compounds and in the ionic bonds that hold the ions together in ionic compounds. The chemical energy in these bonds can be transformed into either heat energy or electrical energy. This chapter is only dealing with the transformation of **chemical energy into heat energy and vice versa.** Chapter 11 will be dealing with the transformation of chemical energy into electrical energy.

The **chemical energy** of a substance is also known as its **heat content (H)** or **enthalpy (H)**. These 3 terms can be used interchangeably.

The units used for measuring energy are **Joules (J), Kilojoules (KJ) and Megajoules (MJ).**

$$\begin{tikzcd}
\textbf{MJ} \arrow[r, bend left, "\times 10^{3}"] & \textbf{KJ} \arrow[l, bend left, "\times 10^{-3}"] \arrow[r, bend left, "\times 10^{3}"] & \textbf{J} \arrow[l, bend left, "\times 10^{-3}"]
\end{tikzcd}$$

## Exothermic reactions

An **exothermic reaction** is a chemical reaction that produces heat energy. Some examples of exothermic reactions that you might be familiar with are

- Combustion (burning) reactions, eg. the combustion of octane in a car engine.
- Acid/base neutralisation reactions.
- The burning of magnesium metal.

Since exothermic reactions release heat energy, they will always result in an **increase in the temperature of the environment surrounding the reaction.** The environment could be the surrounding air or water if the reaction is taking place in a solution.

In terms of enthalpy, **exothermic reactions result in products that have a LOWER enthalpy than the reactants.** Let's use the combustion of octane to show how this works.

$$\mathbf{2\ C_8H_{18}\ (l)\ +\ 25\ O_2\ (g)\ \rightarrow\ 16\ CO_2\ (g)\ +\ 18\ H_2O\ (g)}$$

$H = 30{,}466\ \text{KJ mol}^{-1}$ $H = 20{,}358\ \text{KJ mol}^{-1}$

The combined enthalpy of the reactants is 30,466 KJ mol$^{-1}$. The units, **kJ mol$^{-1}$**, refer to the enthalpy in KJ, of an amount of moles of reactants and products that is equal to the coefficients in the balanced equation. That is, 2 moles of $C_8H_{18}$ and 25 moles of $O_2$ have a combined enthalpy of 30,466 KJ. In a similar way, the combined enthalpy of the products is 20,358 KJ mol$^{-1}$. That is, 16 moles of $CO_2$ and 18 moles of $H_2O$ have a combined enthalpy of 20,358 KJ.

An important law in science is the **LAW OF CONSERVATION OF ENERGY.** This law states that energy can be neither created nor destroyed, just transformed (changed) from one form into another. In the chemistry context, this law states that the energy present at the start of a chemical reaction must equal the energy present at the end of a chemical reaction when the products have been formed.

It appears as though this law is not being obeyed as the chemical energy of the products is 10,108 KJ less than the chemical energy of the reactants. So what has happened to the missing energy? The missing 10,108 KJ of chemical energy has been transformed into **heat energy**. When the 16 moles of $CO_2$ and 18 moles of $H_2O$ were formed, the bonding in the molecules only required 20,358 KJ of the 30,466 KJ of chemical energy present in the 2 moles of $C_8H_{18}$ and 25 moles of $O_2$. As a consequence the excess (not needed) 10,108 KJ of chemical energy in the reactants was changed into **heat energy.** Now the energy on both sides of the equation is equal and the equation can be rewritten as

$$\mathbf{2\,C_8H_{18}\,(l) + 25\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g)}$$
H = 30,466 KJ mol$^{-1}$ H = 20,358 KJ mol$^{-1}$ + 10,108 KJ of heat

- *Please note that the enthalpy values of 30,466 KJ mol$^{-1}$ and 20,358 KJ mol$^{-1}$ are not the real enthalpy values of the reactants and products during the combustion of octane. These values are just intended to help you understand how the chemical energy of the reactants and products are involved in the production of heat energy during an exothermic reaction.*

The heat energy released by this reaction is due to the **difference in enthalpy** between the reactants and products. The difference in enthalpy is known as **ΔH**:

**ΔH = H (products) – H (reactants)**

For the above example,

$\Delta H = 20{,}358 - 30{,}466 = -10{,}108$ KJ mol$^{-1}$

For an exothermic reaction the value of ΔH will always be negative because **the enthalpy of the products is always less than the enthalpy of the reactants.** So the calculation will always involve the subtraction of a larger number from a smaller one which will obviously always produce a negative value.

The units for ΔH, **KJ mol$^{-1}$**, are the same as the units that were used for the enthalpy of the reactants and products. A balanced equation accompanied by its ΔH value is known as a **thermochemical equation.** The thermochemical equation for the combustion of octane is

**$2\ C_8H_{18}\ (l)\ +\ 25\ O_2\ (g) \rightarrow 16\ CO_2\ (g)\ +\ 18\ H_2O\ (g)$ ΔH = -10,108 KJ mol$^{-1}$.**

This thermochemical equation tells us that:

If 2 moles of octane is completely combusted in oxygen, 10,108 KJ of heat energy is released.
If 25 moles of oxygen completely reacts with octane , 10,108 KJ of heat energy is released.
If 16 moles of carbon dioxide are produced, 10,108 KJ of heat energy is released.
If 18 moles of water are produced, 10,108 KJ of heat energy is released.

So the units KJ mol$^{-1}$ have a similar meaning to when they were used to show the enthalpy of the reactants and products. The units, **kJ mol$^{-1}$**, when used for ΔH refer to the heat energy in KJ, released when the moles of reactant used up or product made are present in an amount, in mole, that is equal to their coefficients in the balanced equation.

- *The units KJ mol$^{-1}$ can be confusing for some students because in chemistry when the last part of units are raised to the power of - 1 it refers to a unit (1) amount of that particular quantity. For example, mol L$^{-1}$ means the moles in a 1 litre volume. The units KJ mol$^{-1}$ can have this more conventional meaning when used to represent what is known as the heat of combustion. In this case the units KJ mol$^{-1}$, represent the KJ of heat energy released by 1 mole of a substance. This will be explored further in chapter 7.*

- **ΔH is also known as heat of reaction**

## Combustion Reactions

The reaction between octane and oxygen is an example of **combustion.** Combustion is an exothermic reaction between a substance and oxygen that releases heat in the form of a flame (fire). Whenever something burns such as a piece of paper, a forest etc., combustion is occurring. There are 2 main types of combustion – **complete combustion** and **incomplete combustion**.

### Complete Combustion:

Complete combustion occurs if a compound burns in a plentiful excess supply of oxygen. If the compound contains C and H the products are water ($H_2O$) and carbon dioxide gas ($CO_2$).

For example, the complete combustion of octane.

$C_8H_{18}\ (l)\ +\ 12.5\ O_2\ (g) \rightarrow 8\ CO_2\ (g)\ +\ 9\ H_2O\ (g)$ *It is acceptable to balance equations with decimals/fractions*

OR

$2\ C_8H_{18}\ (l)\ +\ 25\ O_2\ (g) \rightarrow 16\ CO_2\ (g)\ +\ 18\ H_2O\ (g)$

Another example is the complete combustion of ethanol.

$C_2H_5OH (l) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (g)$

## Incomplete combustion:

Incomplete combustion occurs when a substance burns in a low or limited supply of oxygen. . If the substance contains carbon and hydrogen the products of the reaction are either water and carbon monoxide (CO) or water and black soot (C) if the supply of oxygen is extremely low.

For example, the incomplete combustion of octane.

$2C_8H_{18} (l) + 17O_2 (g) \rightarrow 16CO (g) + 18H_2O (g)$

$2C_8H_{18} (l) + 9O_2 (g) \rightarrow 16C(s) + 18H_2O (g)$

Another example is the incomplete combustion of ethanol.

$C_2H_5OH (l) + 2O_2 (g) \rightarrow 2CO (g) + 3H_2O (g)$

$C_2H_5OH (l) + O_2 (g) \rightarrow 2C (s) + 3H_2O (g)$

- The heat of reaction ($\Delta H$) of a combustion reaction is often referred to as **molar enthalpy of combustion.**

# Endothermic reactions

An **endothermic reaction** is a chemical reaction that absorbs heat energy from the surrounding environment. The surrounding environment can include air and water if the reaction is occurring in an aqueous solution. Some examples of endothermic reactions that you might familiar with are

- Cold packs used to treat injuries such as sprains and bruises. When the endothermic reaction within the cold pack is activated, the reaction absorbs heat from surrounding water. This lowers the temperature of the water, which cools down the site of the injury.
- A more common example is the evaporation of water, however this is a physical change not a chemical reaction as only a change in state is involved. Liquid water absorbs heat energy from the surrounding air causing it to change into water vapour.

Since endothermic reactions absorb heat energy from their surrounding environment, they will **lower the temperature of the surrounding environment.** *If an endothermic reaction is taking place in water, the reaction will absorb heat from the water and its temperature will decrease. If the reaction is taking place in air, the reaction will absorb heat from the surrounding air and its temperature will decrease.*

In terms of enthalpy, **endothermic reactions result in products that have a GREATER enthalpy than the reactants.** Let's look at the reaction between carbon dioxide and carbon as an example of how this works.

**$CO_2(g) + C(s) \rightarrow 2CO(g)$**
$H = 300\ KJ\ mol^{-1}$ $\qquad$ $H = 461\ KJ\ mol^{-1}$

As was the case with the example of the exothermic reaction, the units **$kJ\ mol^{-1}$**, refer to the enthalpy in KJ, of an amount of moles of reactants and products that is equal to their coefficients in the balanced equation. So the combined enthalpy of 1 mol of $CO_2$ and 1 mole of C is 300 KJ. On the product side of the equation, the enthalpy of 2 mol of CO is equal to 461 KJ.

This time it is the chemical energy of the products that is greater than the chemical energy of the reactants. The 300 KJ of enthalpy present in the reactants is insufficient to produce the products as they require 461 KJ of chemical energy. This missing 161 KJ of chemical energy is absorbed as heat by the $CO_2$ and C. When the product, $CO_2$ is made, this 161 KJ of heat is transformed into chemical energy and becomes part of the 461 KJ of chemical energy of the products.

**$CO_2(g) + C(s) \rightarrow 2CO(g)$**
$H = 300\ KJ\ mol^{-1}$ $\qquad$ $H = 461\ KJ\ mol^{-1}$
+ 161 KJ heat

$\Delta H = H\ (products) - H\ (reactants)$

$\Delta H = 461 - 300 = +161\ KJ\ mol^{-1}$

For an endothermic reaction, the ΔH will always be a positive value. This is because the calculation will always involve the subtraction of a lower enthalpy value (reactants) from a greater enthalpy value (products).

The thermochemical equation for the reaction between $CO_2$ and C can be written as

**$CO_2(g) + C(s) \rightarrow 2\ CO(g) \qquad \Delta H = +161\ KJ\ mol^{-1}$**

This equation tells us that:

When 1 mole of $CO_2$ completely reacts with C, 161 KJ of heat energy are absorbed.
When 1 mole of C completely reacts with $CO_2$, 161 KJ of heat energy are absorbed.
When 2 moles of CO are produced, 161 KJ of heat energy are absorbed by the reactants.

- As was mentioned earlier, ΔH refers to the heat energy in KJ, released (exothermic reaction) or absorbed (endothermic reaction) when the moles of reactant or product are present in an amount equal to their coefficients in the balanced equation. So if the coefficients in the balanced equation are changed, the ΔH will change by a proportionate amount. Let's use the thermochemical equation for the combustion of octane as an example.

  $2\ C_8H_{18}\ (l) + 25\ O_2\ (g) \rightarrow 16\ CO_2\ (g) + 18\ H_2O\ (g) \qquad \Delta H = -10{,}108\ KJ\ mol^{-1}$.

  If the coefficients in the balanced equation are DOUBLED the ΔH will also DOUBLE.

  $4\ C_8H_{18}\ (l) + 50\ O_2\ (g) \rightarrow 32\ CO_2\ (g) + 36\ H_2O\ (g) \qquad \Delta H = -10{,}108\ KJ\ mol^{-1} \times 2$
  $= -20{,}216\ KJ\ mol^{-1}$

  Doubling the coefficients means that double the moles of reactants have reacted so double the amount of heat energy must be produced.

  If the coefficients are HALVED the ΔH will also HALVE.

  $C_8H_{18}\ (l) + 12.5\ O_2\ (g) \rightarrow 8CO_2\ (g) + 9H_2O\ (g) \qquad \Delta H = -10{,}108\ KJ\ mol^{-1} / 2$
  $= -5{,}054\ KJ\ mol^{-1}$

  If the equation is REVERSED the ΔH sign will CHANGE.

  $16\ CO_2\ (g) + 18\ H_2O\ (g) \rightarrow 2\ C_8H_{18}\ (l) + 25\ O_2\ (g) \quad \Delta H = +10{,}108\ KJ\ mol^{-1}$.

  If a reaction is reversed, the products will become the reactants and the reactants will become the products. This also means that if the original equation was exothermic, the reversed equation will be endothermic. So the sign of the ΔH must change when a thermochemical equation is reversed.

# SUMMARY

- Heat of reaction (ΔH) = H (products) – H (reactants)
- ΔH has the units KJ $mol^{-1}$ or KJ/mol
- Exothermic reactions: H (products) < H (reactants). ΔH = – value.
- With exothermic reactions, the difference in enthalpy between the reactants and products is released as heat into the surrounding environment. As a consequence the surrounding environment has an increase in temperature. The heat energy released by the reaction is due to some of the chemical energy in the reactants (the difference between the chemical energy of the reactants and products) transforming into heat energy when the products are made.
- With endothermic reactions: H (products) > H (reactants). ΔH = + value.
- With endothermic reactions, the difference in enthalpy between the reactants and products is absorbed as heat from the surrounding environment. As a consequence the surrounding environment has a decrease in temperature. The heat energy absorbed by the reactants (the difference between the chemical energy of the reactants and products) is transformed into the chemical energy of the products when they are made.
- Energy transformation in exothermic reactions: **Chemical energy → Heat energy**
- Energy transformation in endothermic reactions: **Heat energy → Chemical energy**

## Worked Example 1

The petrol tank of a motor vehicle holds 60.0 Litres of octane fuel. When the octane in this tank undergoes complete combustion the thermochemical equation is

$$2\ C_8H_{18}\ (l)\ +\ 25\ O_2\ (g)\ \rightarrow\ 16\ CO_2\ (g)\ +\ 18\ H_2O\ (g) \qquad \Delta H = -10{,}108\ KJ\ mol^{-1}$$

How many kilojoules of heat energy are released when all the octane in this tank is combusted?
The density of octane is 0.703 g/mL

## Worked Example 1 Solutions

Convert 60.0 Litres of octane into mL: 60 x 1000 = 60,000 mL

Now convert 60,000 mL of octane into a mass in grams.

$$d = \frac{m}{V}$$

$$m = d \times v$$
$$= 60{,}000 \times 0.703 = 42{,}180 \text{ g}$$

$$n(C_8H_{18}) = \frac{42{,}180}{114.0} = 370 \text{ mol}$$

Now use cross multiplying to calculate the KJ of heat energy released by 370 mol of octane. Start from the thermochemical equation which shows us that 2 mol of octane releases 10,108 KJ of heat energy.

2 mol $C_8H_{18}$ → 10,108 KJ
370 mol $C_8H_{18}$ → **X** KJ

**X** x 2 = 10,108 x 370

$$\mathbf{X} = \frac{10{,}108 \times 370}{2} = 1{,}869{,}980 \text{ KJ} = 1.87 \times 10^6 \text{ KJ}$$

- *Some students make the mistake of giving the final answer using the units KJ mol$^{-1}$. This is not correct as we have not calculated the ΔH. As the coefficient of octane in the thermochemical equation is 2, the units KJ mol$^{-1}$ can only be used to show the KJ of heat released by 2 mol of $C_8H_{18}$. In this question we calculated the KJ of heat released by 370 mol of $C_8H_{18}$ so the only appropriate units are KJ.*

## Activation Energy ($E_A$)

Recall that particles (atoms, ions and molecules) that make up a substance are constantly vibrating and moving. If the substance is a solid the particles are just vibrating in fixed positions. If the substance is a liquid or a gas the particles are vibrating and moving through space. Particles are able to vibrate and move through space because they possess KINETIC ENERGY (energy of movement). The kinetic energy of particles can be increased when they absorb HEAT ENERGY.

Since particles are constantly vibrating and moving around, the particles that make up reactants are able to collide with each other. At conditions of relatively low temperature such as 25 $^{0}$C (room temperature), these collisions might be weak and the particles just bounce off each other. These reactant particles will not react with each other because before a chemical reaction can occur, whether it be an exothermic or an endothermic one, the reactant particles must collide with a force that is great enough to break the bonds that hold their atoms together. When the bonds in the reactants have broken, the atoms that made up the reactants can fully separate from each other and then rejoin to make the products. If weakly colliding particles absorb some heat energy, their kinetic energy may increase to the point where the reactant particles are moving fast enough to have collisions with sufficient force to break their bonds. That is, the reactant particles are able to react with each other and form products.

**Activation energy ($E_A$)** is the minimum amount of energy that reactant particles need to absorb in order to have kinetic energy that is high enough to cause collisions with sufficient force to break their bonds and cause a chemical reaction.

There are many different ways of wording this definition of activation energy. Here are some variations of the above definition that are less "wordy".

**Activation energy** is the minimum amount of energy required to initiate (start) a chemical reaction.

**Activation energy** is the minimum amount of energy required to break the bonds in the reactants and start a chemical reaction.

**Activation energy** is the minimum amount of kinetic energy that reactant particles need to possess in order to have collisions strong enough to break their bonds and cause a reaction.

- ❖ *Each one of these definitions emphasised "minimum amount" of energy to cause a chemical reaction. This means that it is just enough energy to break bonds and cause a reaction. The reactant particles may absorb an amount of energy that is greater than the activation energy and they will obviously still be able to react. So for a reaction to occur, REACTANT PARTICLES MAY ABSORB AN AMOUNT OF ENERGY THAT IS EITHER EQUAL TO OR GREATER THAN THE ACTIVATION ENERGY REQUIRED FOR THE REACTION TO OCCUR.*

- Sometimes the energy that reactants need to absorb in order to start a reaction is referred to as an **ACTIVATION ENERGY BARRIER.**

- Even reactions that occur at room temperature have an activation energy barrier that needs to be overcome. These reactions have a low activation energy and the heat in the surrounding environment at 25 $^0$C is sufficient to start the reaction. That is, the reactant particles can absorb enough heat from the surroundings at 25 $^0$C to increase their kinetic energy to the point where their collisions are strong enough to break bonds and cause a chemical reaction.

- All of the above discussion about activation energy is part of COLLISION THEORY. This will be explored more in the next chapter.

- Combustion reactions like many exothermic reactions will keep reacting even after the source of their activation energy has been removed. Let us look at the combustion of butane gas in a barbecue as an example:

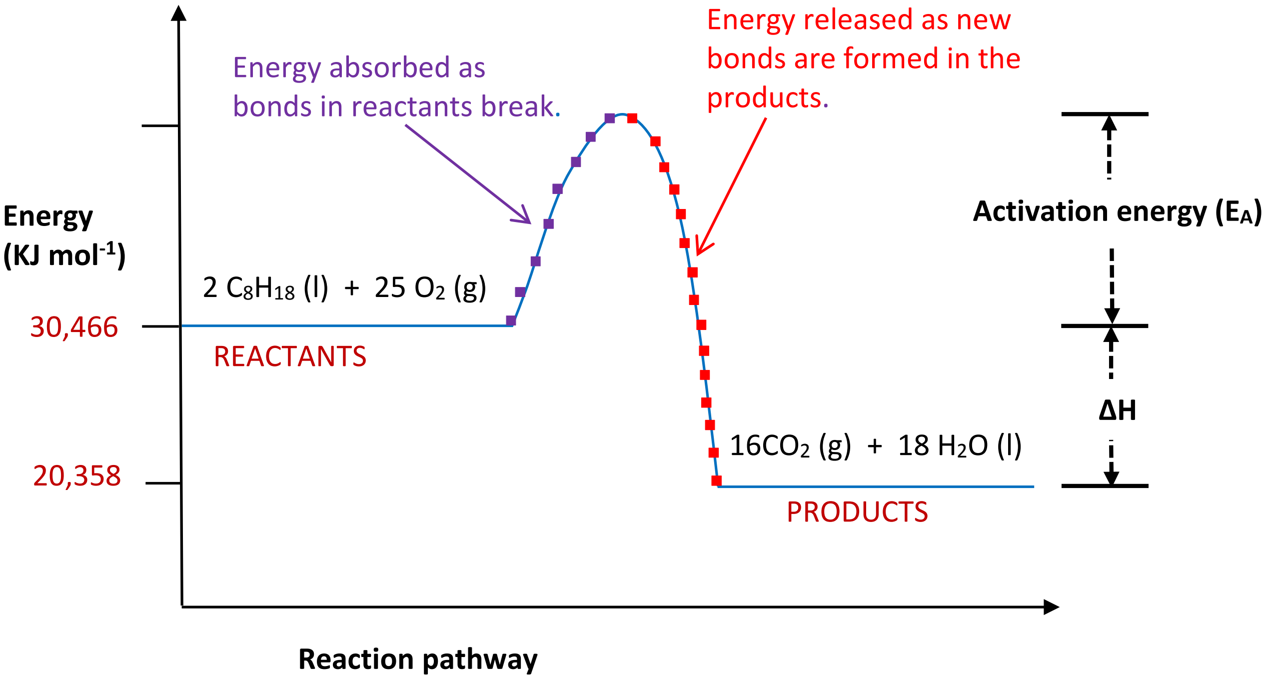
  $C_4H_{10}$ (g) + $6.5O_2$ (g) → $4CO_2$ (g) + $5H_2O$ (g)    $\Delta H = -$

  Most barbecues have a mechanism that will produce a spark in order to get the gas burning (combusting). This spark provides the activation energy for the reaction between the gas and oxygen. After the initial spark has gone the butane gas keeps on combusting even though the source of activation energy (the spark) is no longer there. The spark is needed just to provide the activation energy for the small number of $C_4H_{10}$ and $O_2$ molecules that are close to the spark. Once these molecules react, the heat released by the exothermic reaction can be absorbed by other $C_4H_{10}$ and $O_2$ molecules that are nearby providing them with the activation energy that they need to react. The heat energy released by these reacting molecules can be absorbed by other molecules and so on. It is like a big chain reaction. This is why candles keep burning after they have been lit, gas stoves keep burning after they have been lit and so on.

## Energy Profile Diagrams

The changes in enthalpy that occur during exothermic and endothermic reactions can be shown in ENERGY PROFILE DIAGRAMS / ENERGY PROFILES. The energy profile diagram shown below is for the **exothermic reaction** of the combustion of octane. The energy profile not only shows the changes in enthalpy when reactants are converted into products but it also shows the activation energy required for the reaction to occur. The energy profile diagram for the reaction between octane and oxygen is shown below.

**$2\ C_8H_{18}\ (l)\ +\ 25\ O_2\ (g) \rightarrow 16\ CO_2\ (g)\ +\ 18\ H_2O\ (g)$ $\Delta H = -10{,}108\ KJ\ mol^{-1}$**



Energy profile diagrams are graphs with energy on the vertical axis and reaction pathway on the horizontal axis. Reaction pathway doesn't have any units. It just shows the reaction proceeding from reactants to products.

The horizontal line at energy of 30,466 KJ mol$^{-1}$ represents the chemical energy of the 2 moles of $C_8H_{18}$ and 25 moles of $O_2$. When the reactants possess this chemical energy there is no reaction. This is because the $C_8H_{18}$ and $O_2$ molecules have insufficient kinetic energy to react. That is the collisions occurring between the molecules are not strong enough to break the bonds between their atoms.

The line rising up from the enthalpy of the reactants (30,466 KJ mol$^{-1}$) towards the "top of the hill" shows the reactant molecules gaining energy from an external heat source such as a flame, spark etc. Once the reactant molecules have absorbed a quantity of energy that has taken their energy value right to the top of the hill, the activation energy required for the reaction has been reached.

So right at the top of the hill on the graph the reactants have just enough kinetic energy to collide with sufficient force to cause a reaction.

- *With the combustion of octane the activation energy comes from an external heat source such as a spark or a flame. With some reactions however, the activation energy is much lower and the heat from the surrounding environment at room temperature or even lower can be enough to start the reaction.*

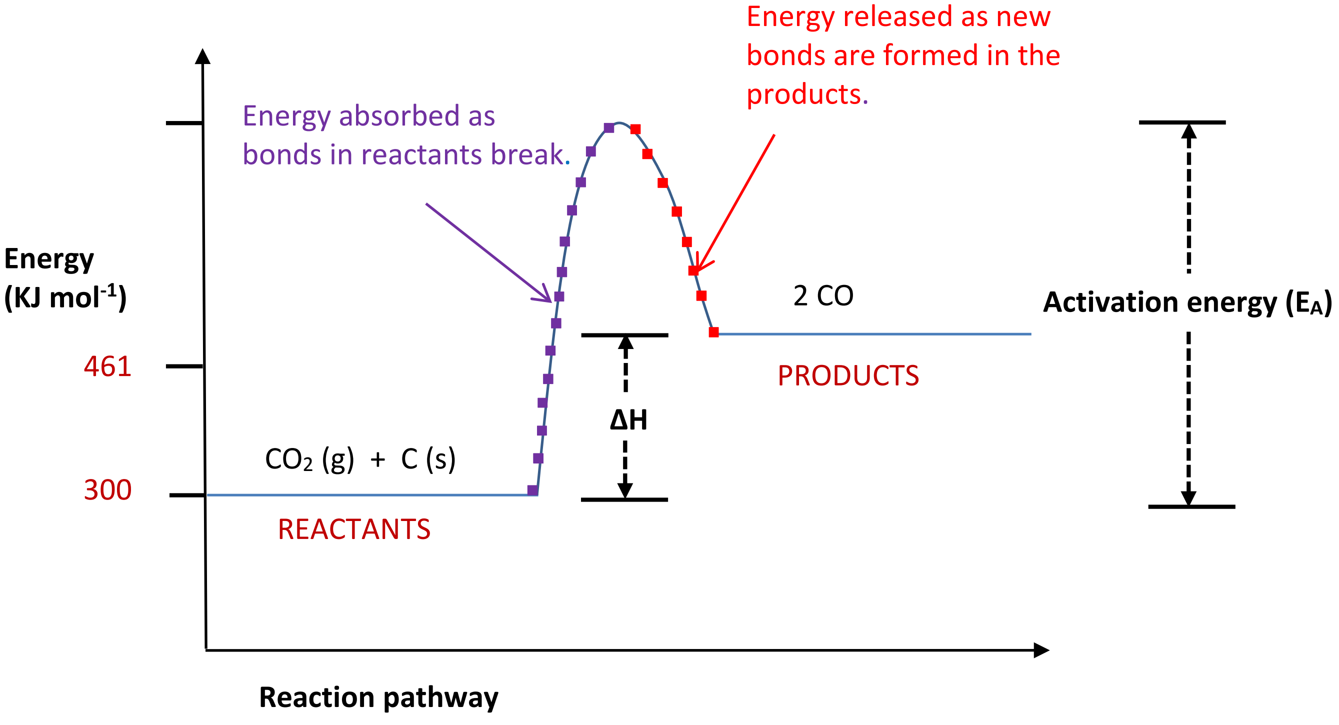
The line going down and away from the top of the hill shows energy released as the reactant atoms which have just been pulled apart, come together to form new bonds in the product molecules.

It is important to realise that the difference in enthalpy between the reactants and products (ΔH) does not represent all of the heat energy released by an exothermic reaction. As can be seen on the graph it is the whole line going down from the top of the hill to the enthalpy of the products that shows the heat energy released by the reaction. The ΔH is only represented by the part of that line that is between the enthalpy of the reactants and the products.

- Exothermic reactions don't just release heat energy. They also ABSORB heat energy. An exothermic reaction will release more heat energy than it absorbs. That is, there is a net release of heat energy. This can be seen on the graph – the line going up from the H (reactants) to the top of the hill (activation energy) is shorter than the line going down from the top of the hill to the H (products).

An energy profile diagram can also be drawn for the **endothermic reaction** between $CO_2$ and C.

**$CO_2(g) + C(s) \rightarrow 2\,CO(g) \quad \Delta H = +161\ KJ\ mol^{-1}$**

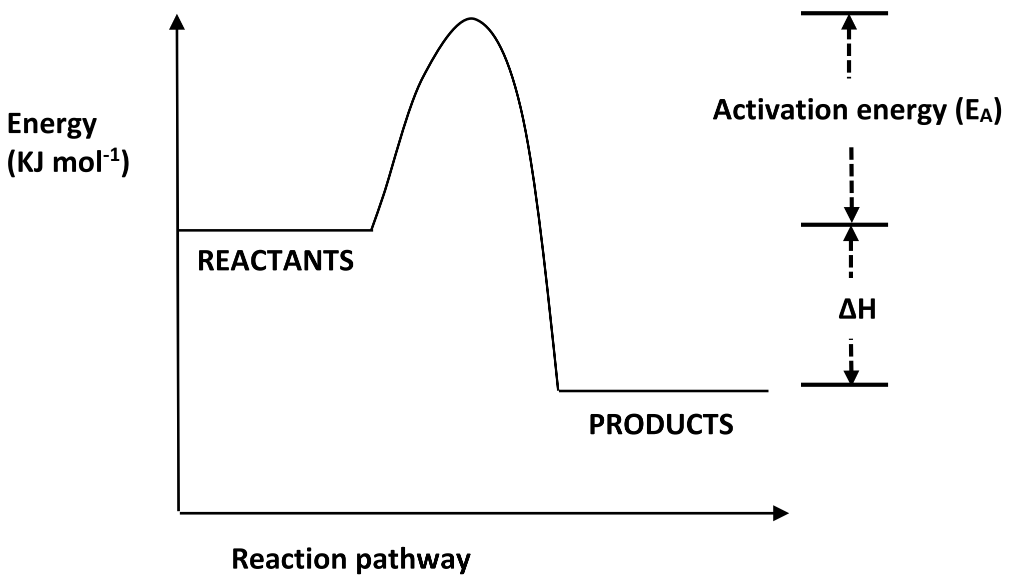


The major difference between this energy profile and the one for the combustion of octane is the relative positions of the reactants and the products. That is, this profile diagram has the reactants at lower enthalpy than the products because it represents an endothermic reaction.

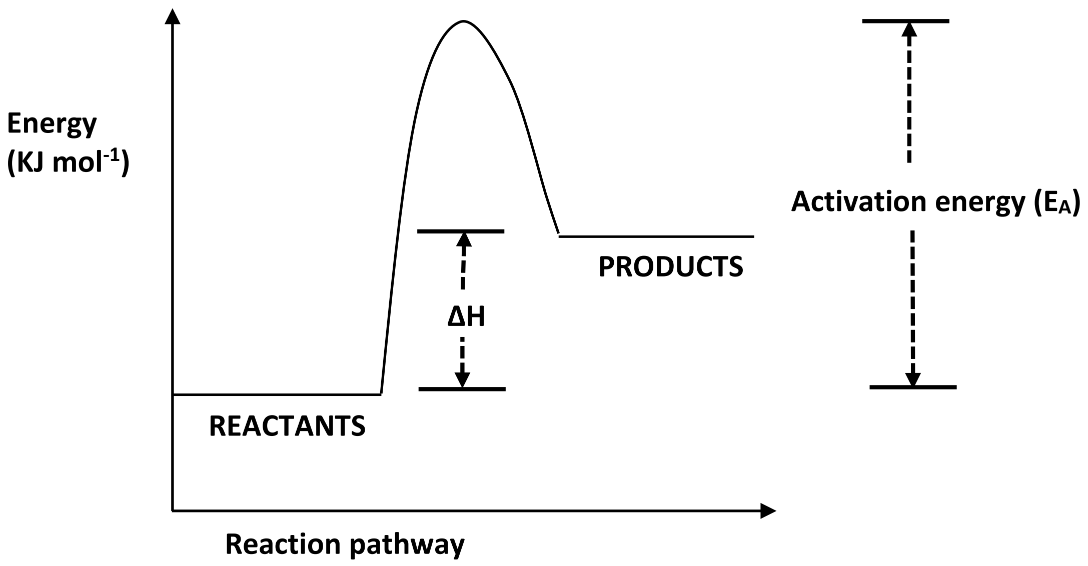
- Endothermic reactions don't just absorb energy. They also RELEASE energy. An endothermic reaction will absorb more energy than it releases. That is, there is a net absorbing of energy. This can be seen on the graph – the line going up from the H (reactants) to the top of the hill (activation energy) is longer than the line going down from the top of the hill to the H (products).

# SUMMARY

## Exothermic energy profile



## Endothermic energy profile

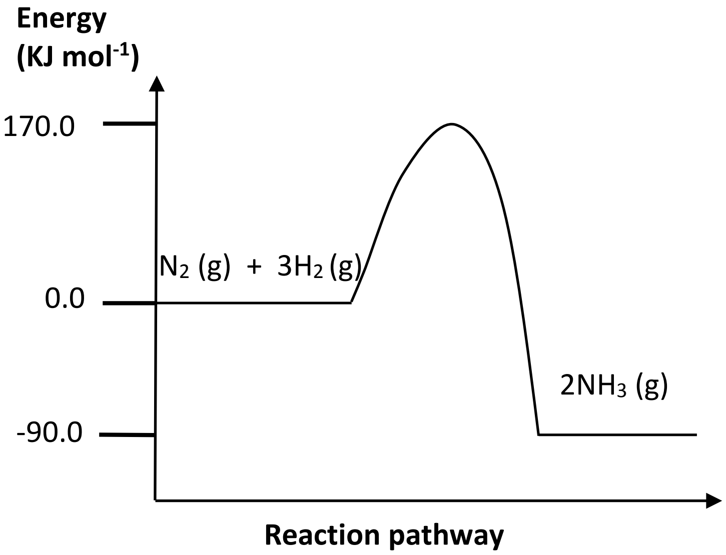


## Worked Example 3

Ammonia gas ($NH_3$) can be produced by the following reaction:

$N_2$ (g) + $3H_2$ $\rightarrow$ $2NH_3$ (g)

The energy profile diagram for this reaction is shown below.



**a.** What is the heat of reaction for the production of $NH_3$?

**b.** What is the activation energy for this reaction?

**c.** What is the activation energy for the reverse reaction?

## Worked Example 3 Solutions

**a.** The heat of reaction (ΔH) = H (products) – H (reactants)
= -90 – 0.0 = -90.0 KJ mol$^{-1}$

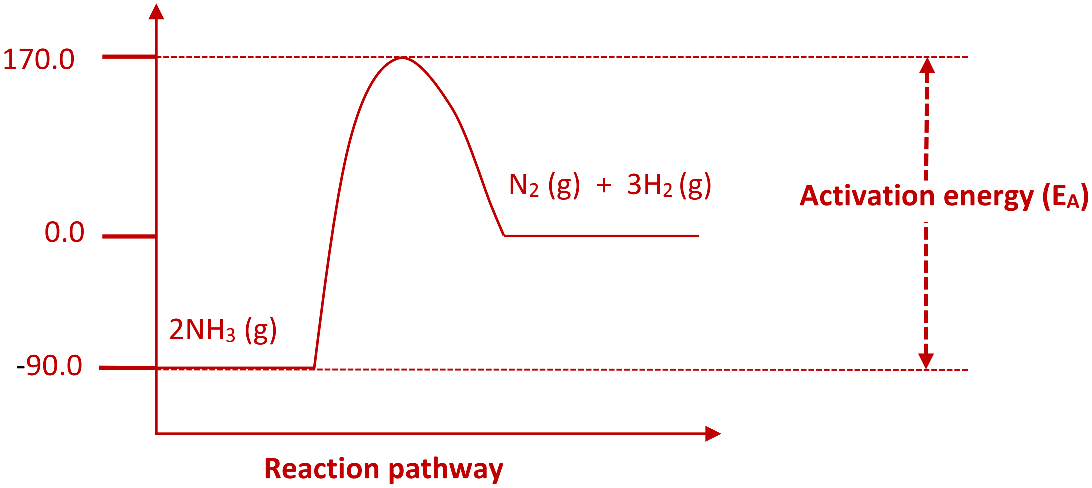
**b.** $E_A$ = 170.0 – 0.0 = +170.0 KJ mol$^{-1}$

- *The activation energy always has a POSITIVE VALUE, regardless of whether the reaction is exothermic or endothermic.*

- *The enthalpy of the reactants, $N_2$ + $3H_2$, is given as 0.0. This suggests that the reactants have zero chemical energy which of course is not the case. The actual enthalpy values given on the vertical axis are not important. The only important thing is the difference between the values which are used to calculate* ΔH and activation energy. *An infinite number of values could be used for the vertical axis that would give a heat of reaction of -90.0 KJ mol$^{-1}$ and an activation energy of +170.0 KJ mol$^{-1}$.*

**c.** *To calculate the activation energy of the reverse reaction it is best to redraw the energy profile for the reverse reaction. This means flipping the graph around. The equation for the reverse reaction is*

$2NH_3\ (g) \rightarrow N_2\ (g) + 3H_2\ (g)$



*Now it can be clearly be seen that on the vertical axis the activation energy for the reverse reaction is the difference between 170.0 and -90.0.*

$E_A = 170.0 - (-90.0) = +260.0$ *KJ* $mol^{-1}$

# CHAPTER 6 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
Which of the following reactions is exothermic?

**A.** $2CO \rightarrow CO_2 + C \quad \Delta H = -161\ KJ\ mol^{-1}$
**B.** $2H_2O \rightarrow 2H_2 + O_2 \quad \Delta H = +570\ KJ\ mol^{-1}$
**C.** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
$\Delta H = +2800\ KJ\ mol$
**D.** $FeCl_2 \rightarrow Fe + Cl_2 \quad \Delta H = +341.8\ KJ\ mol$

**Question 2**
One mole of benzoic acid can be combusted to produce 1600 KJ of heat energy. What is the ΔH for this reaction if the balanced equation is

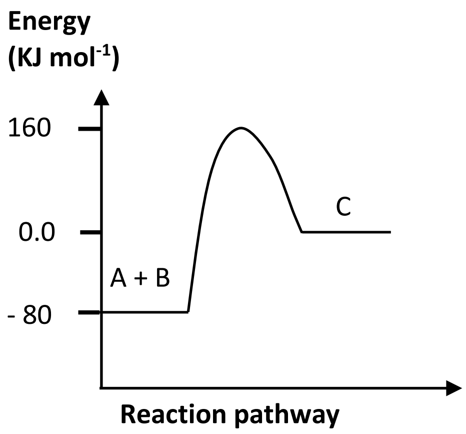
$2C_6H_5COOH + 15O_2 \rightarrow 14CO_2 + 6H_2O$

**A.** -1600 KJ/mol
**B.** - 3200 KJ/ $mol^{-1}$
**C.** 3200 KJ $mol^{-1}$
**D.** -3200 KJ/mol

**Question 3**
When 1.0 mol of methane gas undergoes complete combustion it releases 889 KJ of heat energy. At SLC conditions, what volume of methane gas would release twice this amount of heat energy?

**A.** 49.6 L
**B.** 2.0 L
**C.** 44.8 L
**D.** 24.8 ?

**Question 4**
This energy profile shows the changes in energy that occur when the reactants A and B are converted into the product C.



If C is converted into A and B, the activation energy required for this reaction is equal to

**A.** +160 KJ $mol^{-1}$
**B.** +80 KJ $mol^{-1}$
**C.** -80 KJ $mol^{-1}$
**D.** +240 KJ $mol^{-1}$

**Question 5**
When bonds are formed in the products of a chemical reaction, energy is released

**A.** during exothermic reactions only.
**B.** during exothermic and endothermic reactions.
**C.** during endothermic reactions only.
**D.** only if the activation energy of the reaction is less than the difference in enthalpy between the reactants and products.

## Short Answers

**Question 1**

Water can be produced from an explosive reaction between hydrogen gas and oxygen gas. The thermochemical equation for this reaction is shown below.

$2H_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2H_2O\ (g)$

$\Delta H = -572\ KJ\ mol^{-1}$

**a.** How many Kilojoules of heat energy would be released if 25.0 g of oxygen gas completely reacted?

**b.** How many Kilojoules of heat energy would be released if 1.0 Kg of water was produced?

**c.** How many kilojoules of heat energy would be released if 50.0 mL of $H_2$ gas was mixed with 100.0 mL of $O_2$ gas at SLC conditions?

**d.** Rewrite the above thermochemical equation if the heat of reaction was +286 KJ mol$^{-1}$.

**e.** Draw the energy profile diagram for the reaction described by the original equation if the activation energy of the reverse reaction is 1,950 KJ mol$^{-1}$. You must show and label the enthalpy of the reactants and products, the ΔH and the activation energy.

**f.** How would the ΔH of the reaction,

$2H_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2H_2O\ (l)$

compare with the ΔH for the above (original) equation? You must explain your answer by referring to the equation showing the condensation of steam into liquid water:

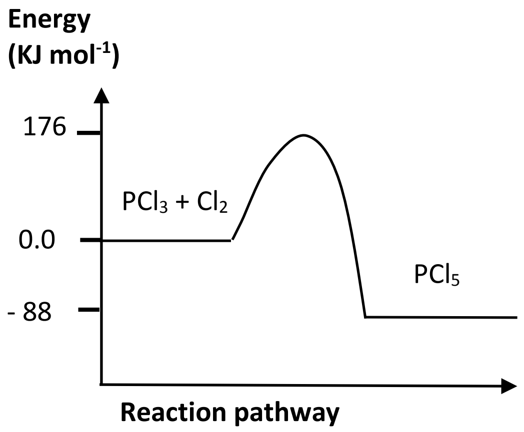
$H_2O\ (g)\ \rightarrow\ H_2O\ (l)\qquad \Delta H = -$

**Question 2**

When Mg is dissolved into excess hydrochloric acid, the change in enthalpy is equal to 58.8 KJ mol$^{-1}$. How many mL of hydrogen gas would be produced at 405 $^0$C and pressure 2.0 atm if the reaction produced 215 KJ of heat energy?

**Question 3**

The energy profile shown below is for the formation of $PCl_5$ from $PCl_3$ and $Cl_2$.



**a.** What is the activation energy for the formation of $PCl_5$?

**b.** What is the ΔH for the formation of $PCl_5$?

**c.** What is the activation energy for the formation of $PCl_3$ and $Cl_2$?

**d.** What is the ΔH for the decomposition of $PCl_5$?

**e.** Are the covalent bonds stronger in 1 mol of $PCl_5$ or 1 mol of $PCl_3$ and 1 mol of $Cl_2$? Discuss.

**Question 4**

The gas used in stoves is mainly comprised of methane gas. A spark or flame is used to provide the activation energy for the combustion of methane gas to produce the heat that is needed for cooking food. The thermochemical equation for the combustion of methane gas is shown below.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \quad \Delta H = -803 \text{ KJ mol}^{-1}$$

Use this thermochemical equation to explain why the methane gas keeps burning even after the ignition source, the flame or spark, is taken away from the gas.

**Question 5**

When X and Y react to produce Z,

$X + Y \rightarrow Z$,

the energy produced during the formation of bonds in Z is equal to 540 KJ mol$^{-1}$ and the energy absorbed to break the bonds in X and Y is equal to 310 KJ mol$^{-1}$.

**a.** Draw the energy profile for this reaction. You must show the enthalpy of the reactants and products (give values) and the activation energy for the reaction. The **ΔH** and **activation energy** must be clearly labeled on your diagram.

**b.** Write out the thermochemical equation for this reaction.

**Question 6**

Give the thermochemical equation for the combustion of butane if one mole of butane produces 2874 KJ of heat energy when completely combusted in oxygen.

**Question 7**

How does the activation energy for the reaction,

$N_2 + 3H_2 \rightarrow 2NH_3$

compare with the activation energy for the reaction

$\frac{1}{2} N_2 + 1.5\, H_2 \rightarrow NH_3$.

Discuss your answer.

**Question 8**

Write out equations, including states, for the following:

**a.** the complete combustion of $C_7H_{16}$ (l)

**b.** The incomplete combustion of $C_5H_{12}$ (l) producing carbon monoxide.

**c.** The incomplete combustion of $C_4H_9OH$ (l) producing soot (C).

# Chapter 7 – Fuels

## Fuels

A **Fuel** is a substance that can be used to release energy in a form that it is useful to society. The fuels that this chapter covers can be classified as **fossil fuels** and **biofuels / biochemical fuels**. <u>The chemical energy of these fuels is converted into heat energy through combustion.</u> Recall that combustion is a heat releasing exothermic reaction involving oxygen.

## Fossil Fuels

**Fossil fuels** are fuels produced from the slow decomposition of the remains of dead plants and animals. Fossil fuels take millions of years to form and are found under the earth's crust on both land and sea. All fossil fuels are **non-renewable.** If a fuel is **non-renewable** it is used at a rate that is much faster than the rate at which it can be replaced by nature. As a consequence non-renewable energy resources are running out. They are described as "finite" which means that there is only a fixed amount of these fuels in the Earth and once they are used up they will not be replaced in our lifetime. Since nature takes millions of years to make fossil fuels, there is no way that they can be replaced at a rate that is equivalent to the rate at which society uses them up.

Some examples of fossil fuels are **coal**, **crude oil**, **petroleum gas (derived from crude oil)** and **natural gas**.

### <u>Coal</u>

Coal contains carbon and other substances such as water. It is the carbon part of coal that can act as a fuel so the greater the carbon content of coal the better its quality as a fuel. Black coal has a higher carbon content but lower water content than brown coal so it is a better fuel. The main use of coal is to provide electricity for use in homes and industry.

**The energy content of coal**

The energy content of a fuel refers to the amount of heat energy that is released when the fuel is combusted. Energy content can be measured in many ways. Some common examples are:

**Kilojoules per mole (KJ mol$^{-1}$ or KJ/mol):** This refers to the KJ of heat energy released when1 mole of a fuel is combusted.

- Don't confuse this with **ΔH** which has the same units **KJ mol$^{-1}$.** In ΔH, the units KJ mol$^{-1}$ refers to the KJ of heat energy released by a number of moles of a substance that is equivalent to the coefficient of that substance in a balanced chemical equation (refer to page 72 of chapter 6). When referring to energy content, the units KJ mol$^{-1}$ refer to the KJ of heat energy released from the combustion of one mole of a fuel.

**KJ per gram (KJ g$^{-1}$ or KJ/g):** This refers to the KJ of heat energy released when 1 g of a fuel is combusted.
**MJ per gram (MJ g$^{-1}$ or MJ/g):** This refers to the MJ of heat energy released when 1 g of a fuel is combusted.
**MJ per tonne (MJ T$^{-1}$ or MJ/T)**: This refers to the MJ of heat energy released when 1 tonne of a fuel is combusted.
**KJ per litre (KJ L$^{-1}$ or KJ/L):** This refers to the KJ of heat energy released when 1 litre of a gaseous or liquid fuel is combusted.

The energy content of black coal is approximately **35 KJ g$^{-1}$.** This means that 1 g of black coal releases 35 KJ of heat energy when combusted.

The energy content of brown coal is approximately **28 KJ g$^{-1}$.** The lower energy content of brown coal when compared to black coal is due to the fact that brown coal has a lower carbon content but higher water content than black coal.

The energy content of coal is never given using the units **KJ mol$^{-1}$.** This is because coal is an impure substance containing varying proportions of carbon, water and other substances. As a result it is not possible to convert a given mass of coal into moles as there is no molar mass to divide the mass by.

- Energy content can also be referred to as **heat of combustion.**

- The heat of combustion in KJ mol$^{-1}$ is often referred to as **molar heat of combustion.** *Don't confuse this with the* heat of reaction ($\Delta H$) of a combustion reaction which is often referred to as **molar enthalpy of combustion.**

When coal is combusted it is the carbon part that reacts with oxygen to produce energy. The complete combustion of coal can be described by:

$C (s) + O_2 (g) \rightarrow CO_2 (g)$

Coal can be incompletely combusted as if the level of oxygen available is low. The equation for the incomplete combustion of coal is:

$2C (s) + O_2 (g) \rightarrow 2CO (g)$

The incomplete combustion of coal as is the case with all incomplete combustion reactions, does not release as much heat energy as the complete combustion of coal. That is, during incomplete combustion not all of the chemical energy of the fuel is converted into heat energy.

**Energy conversions (transformations) for when coal is used to make electricity**
As was mentioned earlier, coal is mainly used to make electricity. The heat released from the combustion of coal is converted into heat energy which is converted into mechanical energy (kinetic energy) which is converted into electrical energy:

*Chemical Energy → Thermal (Heat energy) → Mechanical energy (kinetic) → Electrical energy*

- ❖ *These conversions occur in a coal fired power station. The details of how a coal fired power station works are not required for unit 3 chemistry.*

The efficiency of the conversion of the chemical energy in coal into electrical energy is approximately 30%.

The term **efficiency** refers to the proportion or percentage of the total energy present at the start of an energy conversion that is transformed into useful energy. Let's assume that the chemical energy present in a sample of coal is 100 KJ. After this chemical energy is converted into heat energy, mechanical energy and finally electrical energy, only 30 KJ of the original 100 KJ of chemical energy in the coal, is present as electrical energy. The missing 70 KJ of chemical energy has been lost along the way. Most of this energy would have been lost as heat leaving only a small proportion of the heat energy produced available to be converted into mechanical energy. <u>It is important to note that any energy conversion involving heat is always very inefficient. This is because it is very easy for heat energy to be lost from a system that is converting energy into different forms. A system or device that converts energy into different forms is known as an **energy converter.**</u>

The efficiency of an energy converter or system involving energy conversions can be calculated using the formula:

$$\text{Efficiency} = \frac{\text{Useful energy}}{\text{Total available energy}} \times 100$$

Useful electrical energy

$$\text{The efficiency of the conversion of chemical energy in coal into electricity} = \frac{30}{100} \times 100 = 30\ \%$$

Chemical energy at the start.

$$\textit{Chemical Energy} \rightarrow \boxed{\textit{Heat energy} \rightarrow \textit{Mechanical energy}} \rightarrow \textit{Electrical energy}$$

100 KJ 70 KJ lost 30 KJ

- ❖ When coal is combusted, some of the heat energy released is absorbed by the water found within it causing the water to vaporise into steam. This heat absorbed by the water is not available to be converted into any other useful form of energy. *So the higher the water content of coal the lower its efficiency.*

**The sourcing (obtaining it from under the ground) of coal**

Coal is obtained through open cut mining where heavy machinery is used to dig huge pits into the surface of the earth where coal deposits are found. Huge vehicles are used to bring the coal to the surface.

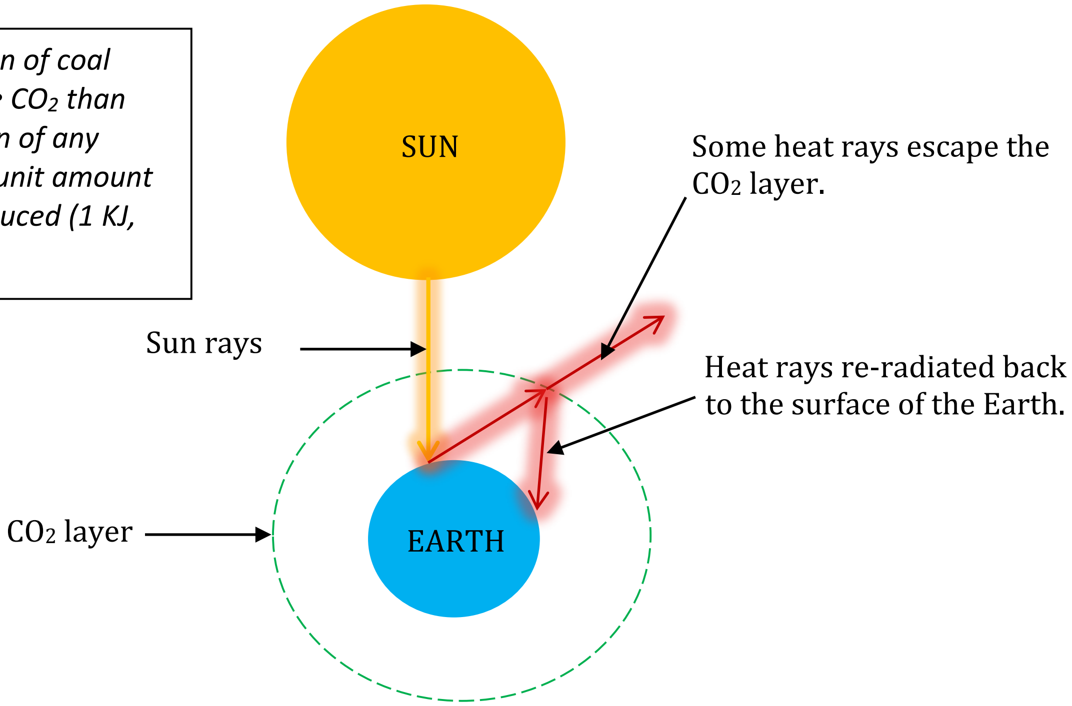
**Environmental impact of mining coal**

The mining of coal results in the clearing of many natural habitats such as forests. This results in the death and displacement of the native animals that live there. When the earth is dug up during coal mining, heavy metals found in the ground are brought up to the surface. These heavy metals can mix with the waste water produced by the mining process and seep into the water table. The term water table refers to the flow of water that occurs under the ground. The water table can transport these heavy metals into the soil of farms and the habitats of animals resulting in the contamination of these environments. Heavy metals brought to the surface can be washed into streams and rivers by rain resulting in water pollution that can destroy aquatic plants and animals. This water pollution can also destroy the local fishing industry. If a coal mine catches fire large amounts of ash, smoke and carbon dioxide gas are produced. The ash and the smoke can make it difficult for people and animals to breathe. The carbon dioxide gas can contribute to global warming which is explained below.

**Environmental impact of the combustion of coal**

Natural processes such as the cellular respiration of organisms, bushfires and activity from volcanoes all release carbon dioxide gas ($CO_2$) into the Earth's atmosphere. The $CO_2$ forms a layer around the Earth. Sunlight is able to penetrate this layer of $CO_2$ and heat up the surface of the Earth. The heat produced rises up back towards the layer of $CO_2$. Some of this heat passes straight through the layer of $CO_2$ and leaves the Earth's atmosphere. A large amount of the heat however, is absorbed by the $CO_2$ which re-radiates it or pushes it back towards the surface of the Earth. This re-radiation of heat back to the surface of the Earth is necessary to keep the temperature of the Earth at a level that is appropriate for the survival of all organisms. The re-radiation of heat by the $CO_2$ back to the Earth is known as the **greenhouse effect.** This is an appropriate term as the layer of $CO_2$ acts like the glass in a greenhouse. The glass in a greenhouse allows sunlight to pass through it . When the sunlight is absorbed by the contents of the greenhouse – plants, soil etc. it is converted into heat rays. These heat rays are not able to pass through the glass. Consequently the heat stays trapped in the greenhouse causing its temperature to be much warmer than the temperature outside.

*The combustion of coal produces more $CO_2$ than the combustion of any other fuel per unit amount of energy produced (1 KJ, 1 MJ etc.)*



When fossil fuels such as coal are completely combusted, the $CO_2$ produced adds to the layer of the $CO_2$ in the atmosphere. This increased amount of $CO_2$ in the atmosphere leads to an increased amount of re-radiation of heat rays back to the surface of the Earth which has caused the temperature of the Earth to rise above levels considered to be natural. The re-radiation of heat due to the increase in the concentration of $CO_2$ in the atmosphere by the combustion of fossil fuels is referred to as the **enhanced greenhouse effect.** The term "enhanced" is appropriate as the human activity of burning fossils fuels has enhanced or increased the impact of the greenhouse effect which occurs naturally. The increase in global temperatures due to the enhanced greenhouse effect is known as **global warming.** Global warming is believed to be responsible for rising sea levels, extreme storms and the death and extinction of many plant and animal species. When fossil fuels such as coal are incompletely combusted, carbon monoxide (CO) is produced. CO is not considered to be a major greenhouse effect causing gas but it is poisonous to humans and other animals. CO can kill people and animals at high concentrations. The poisonous nature of carbon monoxide will be covered in greater detail in chapter 9.

- The combustion of coal produces more greenhouse producing $CO_2$ than any other fuel.

Many fossil fuels such as coal contain small amounts of sulfur (S). When the fossil fuels are combusted the sulfur reacts with oxygen to produce sulfur dioxide gas ($SO_2$). The equation for this reaction is given below.

$S(s) + O_2(g) \rightarrow SO_2(g)$

$SO_2$ is a respiratory irritant (makes breathing difficult) and causes the production of acid rain which can damage buildings and plants.

When fossil fuels like coal are combusted a great amount of heat is produced. This heat can cause the oxygen ($O_2$) and nitrogen ($N_2$) in the air to react with each other to produce nitrous oxides such as NO and $NO_2$. That is, the heat from the combustion reaction provides the activation energy for the reaction between $N_2$ and $O_2$ . NO and $NO_2$ are often referred to as $NO_x$. The "x" represents the number of oxygen atoms in the nitrous oxide. The equations for the production of these gases are shown below.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$

The NO produced can react with oxygen to produce $NO_2$.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

NO and $NO_2$ can produce acid rain and act as respiratory irritants.

# Crude oil

Crude oil is a thick black liquid which is a mixture of high molecular mass (large molecules) alkanes. The largest alkane found in crude oil has the formula $C_{70}H_{142}$. Alkanes are a group of hydrocarbons that you most likely would have learnt about in year 11. They will be covered in Unit 4 Chemistry Tutor. The different alkanes from crude oil can be separated into components of similar molecular mass. The separated components from crude oil can be referred to as petroleum. A major component of crude oil **is petrol** which has **octane ($C_8H_{18}$)** as its main constituent. Petrol is used as a transport fuel in cars, buses, trucks etc.

### The energy content of some of the components of crude oil

Crude oil is not used as a fuel, rather the different alkanes that are separated from it can be used as a fuel. Two fuels derived from crude oil are petrol (mainly octane) and diesel (a mixture of high molecular mass alkanes, eg. $C_{12}H_{26}$).
The energy content of octane ($C_8H_{18}$) is **47.9 KJ $g^{-1}$**
The energy content of diesel is **45.0 KJ $g^{-1}$**

- The diesel sourced from crude oil is often referred to as PETRODIESEL.

### The efficiency of petrol and diesel when used as a transport fuel

When used as a transport fuel, the heat from the combustion of petrol and diesel is converted into mechanical energy. The energy transformation is:

*Chemical energy* → *Heat energy* → *Mechanical energy*
100 KJ 75 KJ to 80 KJ lost 20 to 25 KJ (petrol engine)

As is the case with all combustion engines, the efficiency of the conversion of the chemical energy in petrol and diesel into mechanical energy is approximately 20 to 25 %. In reality a diesel engine is more efficient than a petrol engine. This is due to factors such as different engine design in diesel powered cars.

### The sourcing of crude oil

As crude oil is a liquid, the open cut mining method used for obtaining coal is not appropriate for crude oil. Holes are drilled into the Earth's surface where the oil deposits are and the oil is forced up to the surface through a series of pipes.

### Environmental impact of obtaining crude oil

The sourcing of crude oil is not as intrusive on the natural environment as the sourcing of coal. The open cut mining used to obtain coal produces huge holes in the Earth's crust which can be kilometers wide. The holes drilled into the crust to obtain crude oil may be numerous in number but they are only a few centimetres wide. Crude oil is highly flammable so there is always the potential for fires and explosions which harm people and animals in the immediate vicinity of the drilling area. The carbon dioxide produced from the burning oil contributes to global warming.

Oil rigs are used to extract crude oil under the ocean. If these rigs malfunction huge amounts of crude oil can be released into the sea. Oil can also be released into the sea from the huge ships used to transport crude oil. Crude oil is less dense than water so it floats on the surface of the sea and can kill fish and other marine animals. If the oil gets swept onto the shore it can destroy even more organisms. An oil spill can destroy the fishing industry in the affected area.

**Environmental impact of obtaining octane and petrodiesel from crude oil**

Octane and petrodiesel are separated from the other components in crude oil by a process known as fractional distillation. The actual process of fractional distillation is not covered in units 3 and 4 chemistry. During fractional distillation some of the hydrocarbon molecules are released into the atmosphere as gases and become a part of air pollution. During fractional distillation some of the gases produced must be burnt off. This produces CO and $CO_2$. As crude oil is a mixture of highly flammable liquids and gases, there is always the potential for fires and explosions during fractional distillation.

**Environmental impact of the combustion of octane and petrodiesel**

The $CO_2$ released from the combustion of octane and diesel produces carbon monoxide (CO) gas which is toxic to humans and carbon dioxide gas ($CO_2$) which causes global warming. The combustion of diesel releases slightly more $CO_2$ than the combustion of octane. Crude oil contains traces of sulfur and sulfur containing compounds. As a consequence the combustion of octane and petrodiesel will produce $SO_2$. As is always the case with combustion, $NO_x$ will be produced due the release of large amounts of heat which allows $N_2$ and $O_2$ from the air to react with each other.

- The water vapour produced when hydrocarbon fuels such as octane and petrodiesel are combusted is a greenhouse gas. However carbon dioxide gas has a much greater impact on global warming than water vapor – $H_2O$ (g).

## Petroleum gas

Sometimes low molecular mass gaseous alkanes become trapped in crude oil. These low molecular mass gaseous alkanes can be separated from the crude oil to form **petroleum gas. Liquefied petroleum gas (LPG)** is a mixture of gases mainly comprising of propane ($C_3H_8$) and butane ($C_4H_{10}$). The gases are stored in tanks at very high pressure which causes them to become liquids. LPG is mainly used as a transport fuel for cars, trucks and buses.

**Energy Content of petroleum gas**

The most widely used type of petroleum gas is LPG. The energy content of lpg can vary greatly depending on its composition. The energy content of the major components of lpg are:

| | |
|---|---|
| Propane ($C_3H_8$) | **50.5 KJ $g^{-1}$** |
| Butane ($C_4H_{10}$) | **49.7 KJ $g^{-1}$** |

### Efficiency of LPG when used as a transport fuel

When LPG is combusted in the engine of a transport vehicle, the energy transformations involved are:

*Chemical energy → Thermal energy → Mechanical energy*
100 KJ 80 KJ lost 20 KJ

The efficiency of this energy transformation is approximately 20 %. Most of the original chemical energy in the LPG molecules is converted into heat but only a fraction of the heat is converted into the mechanical energy of the car. Heat is always very easily lost from an energy converter such as an engine. The efficiency of an LPG powered car is less than a petrol or diesel powered car.

### Environmental impact of obtaining petroleum gas from crude oil

Petroleum gas is separated from the other components in crude oil by a process known as fractional distillation. The hazards involved with fractional distillation were discussed earlier.

### Environmental impact of the combustion of petroleum gas such as LPG

The $CO_2$ released from the combustion of petroleum gas such as LPG produces carbon monoxide (CO) gas which is toxic to humans and carbon dioxide gas ($CO_2$) which causes global warming. The combustion of LPG produces less $CO_2$ than the combustion of coal but more than the combustion of natural gas. The amount of $CO_2$ released from the combustion of LPG is less than that released from the combustion of octane and diesel. Crude oil contains traces of sulfur and sulfur containing compounds. As a consequence the combustion of petroleum gas will produce $SO_2$. As is always the case with combustion, $NO_x$ will be produced due the release of large amounts of heat which allows $N_2$ and $O_2$ from the air to react with each other.

## Natural gas

Natural gas is a mixture of low molecular mass alkanes such as methane ($CH_4$), ethane ($C_2H_6$) and propane ($C_3H_8$). It usually contains about 95% $CH_4$ and low quantities of $C_2H_6$ and $C_3H_8$ and even smaller amounts of other gases. Natural gas is mainly used for heating and cooking (the gas in stoves).

***Coal seam gas (CSG) –*** Coal seam gas is natural gas that is found in coal deposits under the ground. The coal contains pores (tiny holes) that trap and hold the gas.

### Energy Content of natural gas

The energy content of natural gas is approximately **54.0 KJ $g^{-1}$** depending on its composition. The energy content of the components of natural gas are:

| | |
|---|---|
| Methane ($CH_4$) | **55.6 KJ $g^{-1}$** |
| Ethane ($C_2H_6$) | **51.9 KJ $g^{-1}$** |
| Propane ($C_3H_8$) | **50.5 KJ $g^{-1}$** |

### Efficiency of the combustion of natural gas into heat

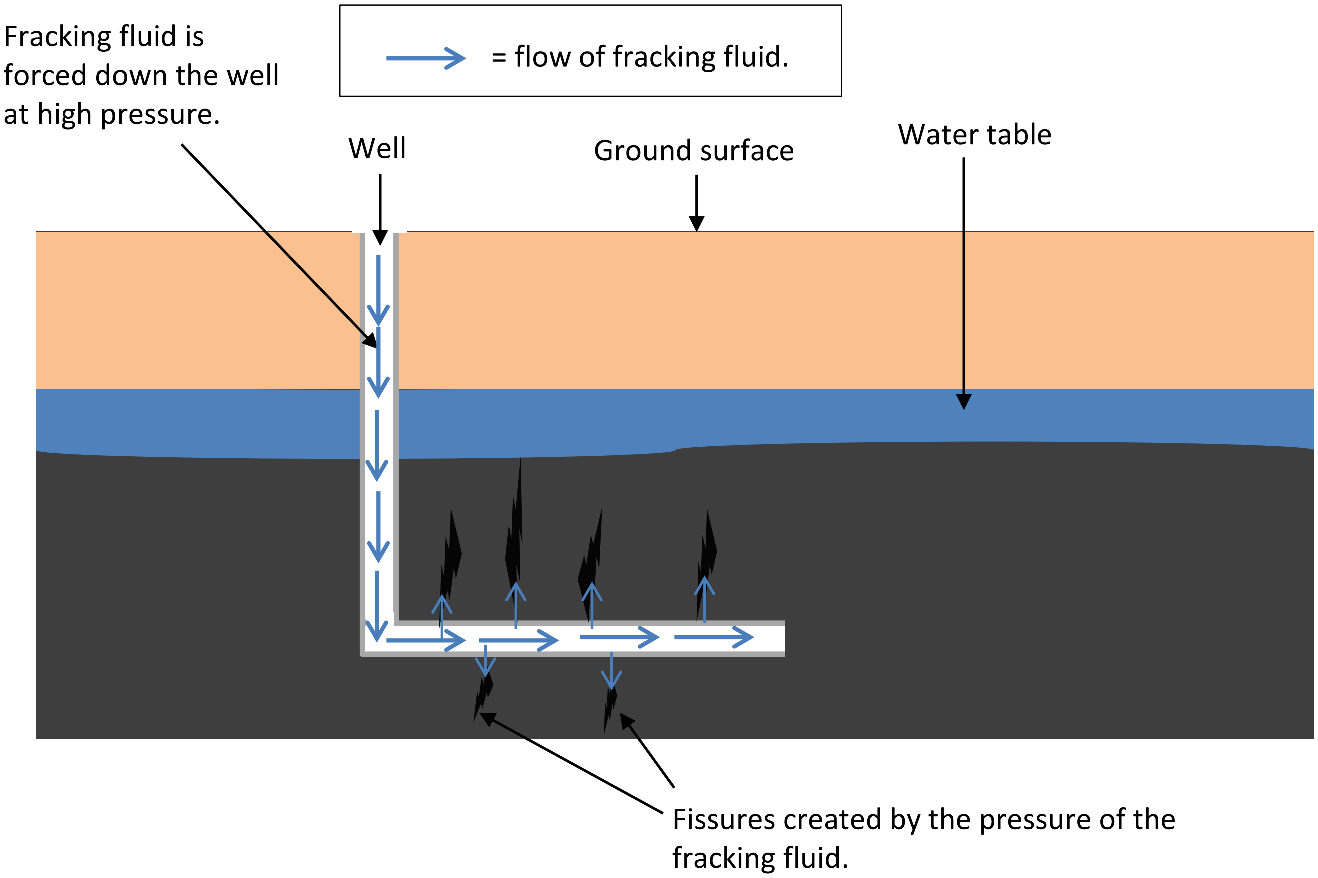
When natural gas is combusted in a gas heater or gas stove the energy transformation involved is:

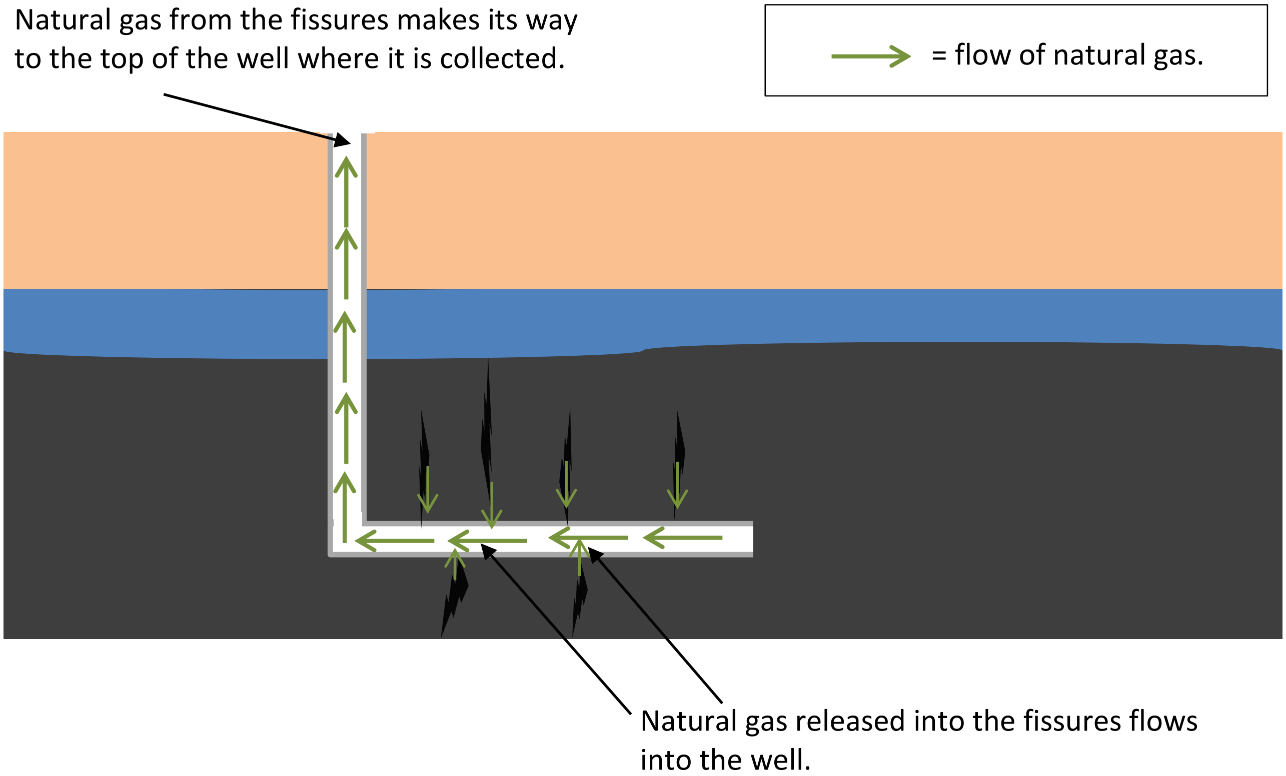
Chemical energy → Heat energy

The efficiency of this energy conversion is very high, approximately 85%. That is, approximately 85% of the chemical energy in the natural gas is converted into heat. It is worth noting however, that when considering how much of the heat actually gets used for its intended purpose, the efficiency will be much less than 85%. For example, much of the heat released from a gas heater will escape through the walls, ceiling and windows of a room leaving only a fraction of the total heat released available for heating up the contents of the room. When heat is produced in a gas stove only a fraction of the total heat released is transferred into the pan, pot etc. that is holding the food. Much of the heat will be lost to the surrounding air.

### The sourcing of coal seam gas

Coal seam gas is extracted from under the ground by a process known as **fracking.** Fracking involves drilling wells into the coal deposits where natural gas is trapped. The wells will often run both vertically and horizontally through the coal deposit (refer to the diagram on the next page). These coal deposits are usually quite deep and lie below the water table. The wells are encased in cement and/or steel. Fracking liquid is forced down the wells at very high pressure. This liquid contains mainly water, sand and other chemicals such as hydrocarbons. When the fracking fluid is forced through the well at high pressure, it hits the coal with great force causing it to crack and form fissures. Fissures are a series of thin cracks that spread throughout the coal. The lower parts of the well that are in contact with the coal contain holes that allow the high pressure fracking fluid to contact and penetrate the coal. The natural gas locked inside the pores of the coal will now flow into the fissures. When the water pressure is reduced or completely stopped, the gas inside the fissures is able to flow up through the wells where it is collected at the surface. The sand in the fracking fluid prevents the fissures from closing. It keeps the fissures open without totally blocking them so the natural gas is able to escape. The hydrocarbons act as a lubricant, making it easier for the flow of materials such as sand through the wells.


Fracking fluid is forced down the well at high pressure.
= flow of fracking fluid.
Well
Ground surface
Water table
Fissures created by the pressure of the fracking fluid.


Natural gas from the fissures makes its way to the top of the well where it is collected.
= flow of natural gas.
Natural gas released into the fissures flows into the well.

#### Environmental impact of obtaining natural gas by fracking

Chemicals in the fracking fluid such as hydrocarbons are toxic to humans and other organisms and pose many health risks. These chemicals can leach into the water table which can transport them to rivers and streams killing plants and animals and contaminating human drinking water. The chemicals can also contaminate soil used for the farming of crops. Heavy metals in the ground can be forced into the water table by the fracking process. Heavy metals are toxic and can be carcinogenic (cause cancer). The natural gas itself can also get forced into the water table. Methane is a greenhouse gas so any methane lost to the air during fracking will contribute to the greenhouse effect.

#### Environmental impact of the combustion of natural gas

The $CO_2$ released from the combustion of natural gas is a greenhouse gas. The carbon monoxide (CO) gas from the incomplete combustion of natural gas is toxic to humans . The combustion of natural gas produces less $CO_2$ than the combustion of coal, octane, diesel and LPG. The combustion of natural gas produces negligible (insignificant) amounts of $SO_2$. Inevitably however, the combustion of natural gas does produce NO and $NO_2$ ($NO_x$). As natural gas is highly flammable, there is always the risk of fire and explosion during its use and storage.

## Biofuels / Biochemical fuels

**Biofuels** or **biochemical fuels** are fuels that have been derived from living things such as plants and animals. Biochemical fuels are also said to be made from **biomass** or **organic material**. Biomass/organic material is any material, living or dead, derived from living things. Some examples of biomass are plants and animals (living or dead) and their waste. This chapter will be dealing with 3 biofuels – **bioethanol, biogas** and **biodiesel**.

All biofuels are **renewable**. If a fuel is renewable, it is used at a rate that is equivalent to the rate at which it can be replaced by nature. For example, a plant may take a few weeks or months to grow to a maturity where it can be used to obtain a fuel. So when a biofuel is used up, only a short period of time is required for nature to replace it. Biofuels are continually replaced by nature whereas fossil fuels, which are non-renewable, take millions of years to be replaced.

### Bioethanol

Bioethanol is derived from plants which includes crops like sugar cane, corn and maize. The glucose ($C_6H_{12}O_6$) produced in these plants during photosynthesis is converted into ethanol ($C_2H_5OH$). Bioethanol is mainly used as a fuel for cars and buses.

#### Energy content of bioethanol

The energy content of bioethanol is **29.6 KJ $g^{-1}$.** This is less than the energy content of all of the fossil fuels covered so far.

## The efficiency of bioethanol when used as a transport fuel

When used as a transport fuel, the heat from the combustion of ethanol is converted into mechanical energy. The energy transformation is:

*Chemical energy → Heat energy → Mechanical energy*
100 KJ 80 KJ lost 20 KJ

As is the case with most combustion engines, the efficiency of the conversion of the chemical energy in bioethanol into mechanical energy is approximately 20 %.

## Environmental impact of the sourcing of bioethanol

Bioethanol is derived from plants and plants need space and water to grow. If bioethanol is to be used on a wider scale as a transport fuel, huge amounts of land, fertiliser and water would be needed to grow the plants. This could result in the clearing of forests resulting in the destruction of native plants and animals. The clearing of forests can result in soil erosion where top soil is driven away by wind and rain. As a consequence the remaining soil is less fertile.

## Environmental impact of the combustion of bioethanol

When $C_2H_5OH$ is combusted, $CO_2$ is produced as is the case with the combustion of all fuels containing carbon. The $CO_2$ produced by the combustion of bioethanol however, *does not result in an increase in the level of $CO_2$ in the atmosphere.* The carbon present in the ethanol molecule came from the carbon in the glucose ($C_6H_{12}O_6$) that was made by plants during photosynthesis. All of the carbon in glucose comes from $CO_2$. During photosynthesis plants absorb $CO_2$ from the air to make glucose:

Photosynthesis equation
$6CO_2\,(g) + 6H_2O\,(l) \rightarrow C_6H_{12}O_6\,(aq) + 6O_2\,(g)$

During the production of bioethanol, The $C_6H_{12}O_6$ produced during photosynthesis is converted into $C_2H_5OH$. When the ethanol is combusted:

$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(l)$

The amount of $CO_2$ produced from the combustion of ethanol is the same as the amount of $CO_2$ that was removed from the atmosphere during photosynthesis. So overall there is no addition or subtraction of $CO_2$ from the atmosphere. It must be noted however, that $CO_2$ releasing energy resources such as coal are used to make bioethanol. For example, electricity produced from the burning of coal may be involved in the manufacture of bioethanol and trucks running on petrodiesel may be used in its transportation, so there is a small increase in the amount of $CO_2$ released into the atmosphere associated with the use of bioethanol as a fuel. *This is the case with the other biofuels covered in this chapter – biogas and biodiesel.* This release of $CO_2$ is significantly less than that released from the combustion of fossil fuels.

There is no significant quantity of sulfur in bioethanol so its combustion does not produce any significant amount of $SO_2$ gas. When bioethanol is combusted $NO_x$ is produced.

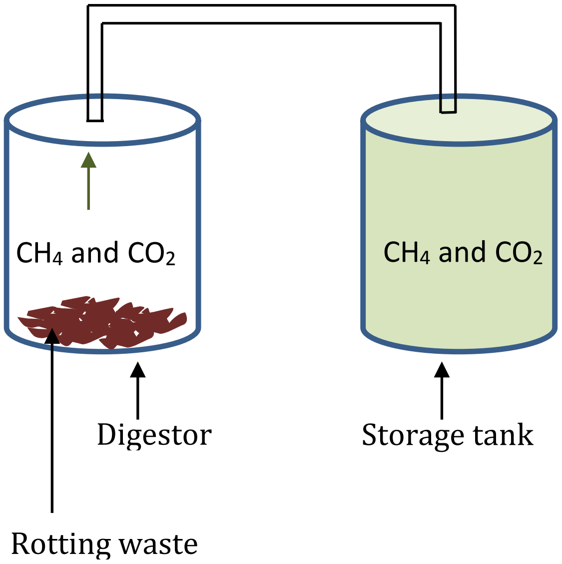
Highly toxic carbon monoxide (CO) is produced when ethanol is incompletely combusted.

## Biogas

Biogas is gaseous mixture of methane ($CH_4$) and carbon dioxide ($CO_2$). The volume of biogas is approximately 60 % $CH_4$ and 30% $CO_2$. The remaining volume is made up of small amounts of other gases. Biogas is produced from the decomposition (rotting) of waste material from plants and animals. Biogas can be combusted to produce heat for homes. The heat produced from the combustion of biogas can also be used to generate electricity.

### Obtaining biogas

In order to produce $CH_4$ (the part of the biogas that acts as a fuel), anaerobic bacteria are used to decompose the waste material in the absence of oxygen. The waste material is decomposed in a tank known as a digestor. The $CH_4$ and $CO_2$ produced in the digestor are allowed to pass through a pipe and into a storage tank.



### Energy content of biogas

The energy content of biogas depends on the proportion of $CH_4$ it contains as this is the only component that contains any significant amount of energy. Methane ($CH_4$) has an energy content of **55.6 KJ g$^{-1}$.** If one gram of biogas was combusted however, the release of heat energy would be lower than this as large proportion of the one gram would contain gases such as $CO_2$ which cannot be combusted. The energy content of biogas containing 60 % $CH_4$ by volume at SLC conditions is approximately **20 KJ g$^{-1}$**

### Energy conversions (transformations) for when biogas is used to make electricity

If the heat from the combustion of $CH_4$ is used to make electricity, the efficiency of the transformation of chemical energy into electrical energy is about 30%.

*Chemical Energy → Heat energy → Mechanical energy → Electrical energy*
100 KJ 70 KJ lost 30 KJ

### Environmental impact of the sourcing of biogas

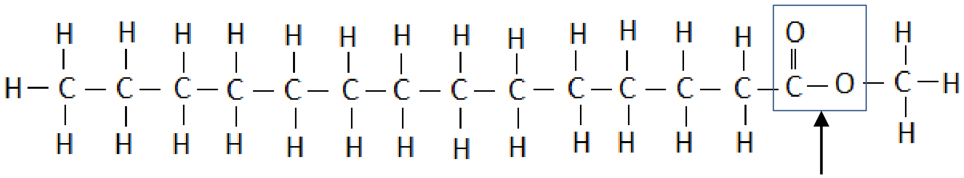
If biogas was to be used to generate electricity on a large scale, the supply of waste such as animal manure and rotting vegetation would be difficult to maintain in the large quantities required. A large amount of land would need to be cleared to meet this demand. The clearing of land results in the destruction of native plants and animals and soil erosion which renders land infertile.

### Environmental impact of the combustion of biogas

As biogas is made from biomass, the $CO_2$ emissions associated with its use are quite low as the $CO_2$ released from the combustion of the $CH_4$ is equivalent to the $CO_2$ absorbed during the production of the plant and animal material during photosynthesis. Animals may not photosynthesis but they eat plant material which supplies them with carbon atoms to build up their tissues. So the animal waste used to make biogas contains carbon atoms that were derived from photosynthesis. There is only a small amount of sulfur containing compounds in biogas so its combustion does not produce a significant amount of $SO_2$. $NO_x$ is produced during the combustion of biogas. Toxic CO is produced when biogas is incompletely combusted.

## Biodiesel

Biodiesel is a biofuel derived from either animal fat or vegetable oil. The fat/oil is converted into a long ester. Esters will be covered in more detail in Unit 4 Chemistry Tutor. The ester produced from the fat/oil is known as **biodiesel.** An example of a biodiesel molecule with molecular formula, $C_{13}H_{27}COOCH_3$, is shown below.



*Ester group (COO)*

### Energy content of biodiesel

Biodiesel is not a pure substance. The molecule shown above is just an example of what a biodiesel molecule might look like. A sample of biodiesel could contain a large mixture of molecules of various sizes. It would also contain unreacted fat and oil. The energy content of biodiesel is approximately **41 KJ $g^{-1}$**.

**The efficiency of biodiesel when used as a transport fuel**
When used as a transport fuel, the heat from the combustion of biodiesel is converted into mechanical energy. The energy transformation is:

*Chemical energy → Heat energy → Mechanical energy*
100 KJ 75 to 80 KJ lost 20 to 25 KJ

**Environmental impact of the sourcing of biodiesel**
Biodiesel is mainly derived from the oils of plants. Only a small amount of biodiesel is currently derived from the fat of animals. Animals and plants need space and water to grow. If biodiesel is to be used on a wider scale as a transport fuel, huge amounts of land, fertiliser and water would be needed to grow the plants. The animals would need a large amount of food, water and land for grazing. This could result in the clearing of forests resulting in the destruction of native plants and animals. The clearing of forests can result in soil erosion where top soil is driven away by wind and rain. As a consequence the remaining soil is less fertile.

Biodiesel like all biofuels does not cause a significant increase in the level of $CO_2$ in the atmosphere. The carbon in the fats and oils used to make biodiesel ultimately comes from glucose produced from photosynthesis. So when biodiesel is combusted, the amount of carbon dioxide released into the atmosphere is equivalent to the amount of carbon dioxide that was removed from the atmosphere during photosynthesis. Since $CO_2$ releasing energy resources such as coal are used to make biodiesel, there is a small increase in the amount of $CO_2$ released into the atmosphere associated with the use of biodiesel as a fuel.

There is no significant quantity of sulfur in biodiesel so its combustion does not produce any significant amount of $SO_2$ gas. When biodiesel is combusted CO and $NO_x$ are produced.

## Comparison of Biodiesel and Petrodiesel

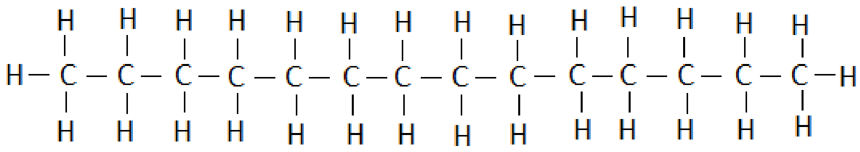
As we have just seen, biodiesel is derived from animal fat/plant oil and petrodiesel is derived from crude oil. Both forms of diesel can be used as transport fuels, however petrodiesel is currently used much more than biodiesel. In order to compare the suitability of biodiesel and petrodiesel as transport fuels, we need to look at 2 properties that have not been addressed yet. They are **hydroscopy** and **viscosity.**

### Hydroscopy

Hydroscopy refers to the ability of a substance to absorb water from the surrounding air. In order to understand why some substances are more **hydroscopic** than others we need to know a few basic things about polar and non-polar molecules.

A polar molecule is able to make bonds with water. These bonds are relatively strong and can be either dipole-dipole bonds or hydrogen bonds. Dipole-dipole bonds and hydrogen bonds are examples of intermolecular bonding (bonding between molecules). Non-polar molecules are unable to make bonds with water.

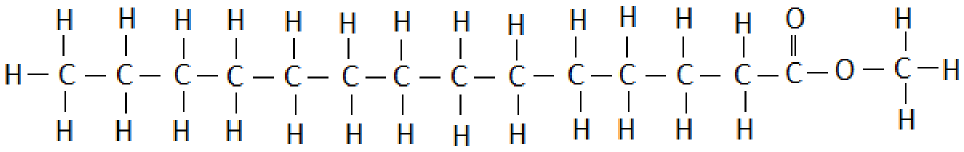
Petrodiesel molecules are hydrocarbons as is the case with all molecules found in crude oil. Hydrocarbons only contain C and H and are non-polar. An example of a petrodiesel molecule ($C_{14}H_{30}$) is shown below.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

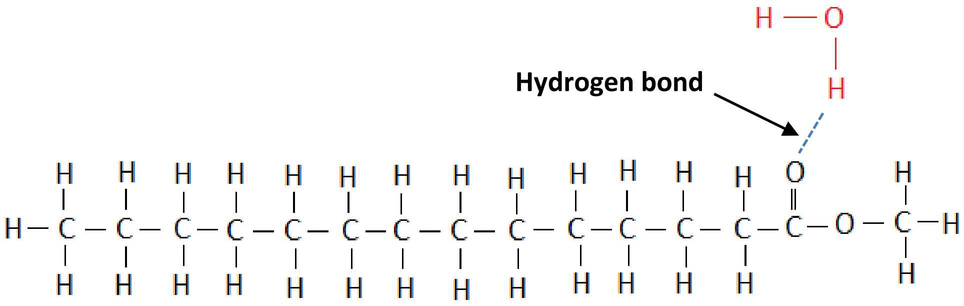
As petrodiesel molecules are non-polar they are unable to make any intermolecular bonds with water molecules. So petrodiesel molecules are not a very hydroscopic.

Now let's consider the biodiesel molecule ($C_{13}H_{27}COOCH_3$) shown below.



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\underset{H}{\overset{H}{C}}-H$$

The structure of this molecule is very similar to the petrodiesel one. It is mainly hydrocarbon (C and H) in structure. A major difference between the 2 molecules however, is the presence of the ester group (COO) in biodiesel. The ester group is polar. So the biodiesel molecule can be seen as being mainly non- polar (C and H part) with a small polar part (COO). The ester group can make hydrogen bonds with water as can be seen in the diagram below.



As a consequence biodiesel has high hydroscopy. There are always $H_2O$ molecules floating around in the air in the form of a gas (water vapour). If a sample of biodiesel is exposed to the air, the molecules at the surface will randomly collide with $H_2O$ molecules. The biodiesel molecules will make hydrogen bonds with the $H_2O$ from the air. These $H_2O$ molecules will eventually move deeper into the biodiesel liquid.

The water present in biodiesel can cause corrosion (rust) in the engine and other components of a motor vehicle. The water also allows microorganisms such as mold to grow in some of the components of the car. The presence of water in the fuel makes it more difficult for combustion to occur. The presence of water in biodiesel can also produce rust and mold in the tanks used to store biodiesel. <u>These problems do not occur with petrodiesel as it is not hydroscopic.</u>

## Viscosity

Viscosity is a measure of how difficult it is for a liquid to flow. The higher the viscosity of a liquid the more difficult it is for the liquid to flow. Liquids with high viscosity move slowly. Some examples of highly **viscous** liquids are honey and maple syrup. Liquids with low viscosity are water and ethanol. These liquids flow very quickly and easily.

Some of the factors that affect the viscosity of a liquid are:

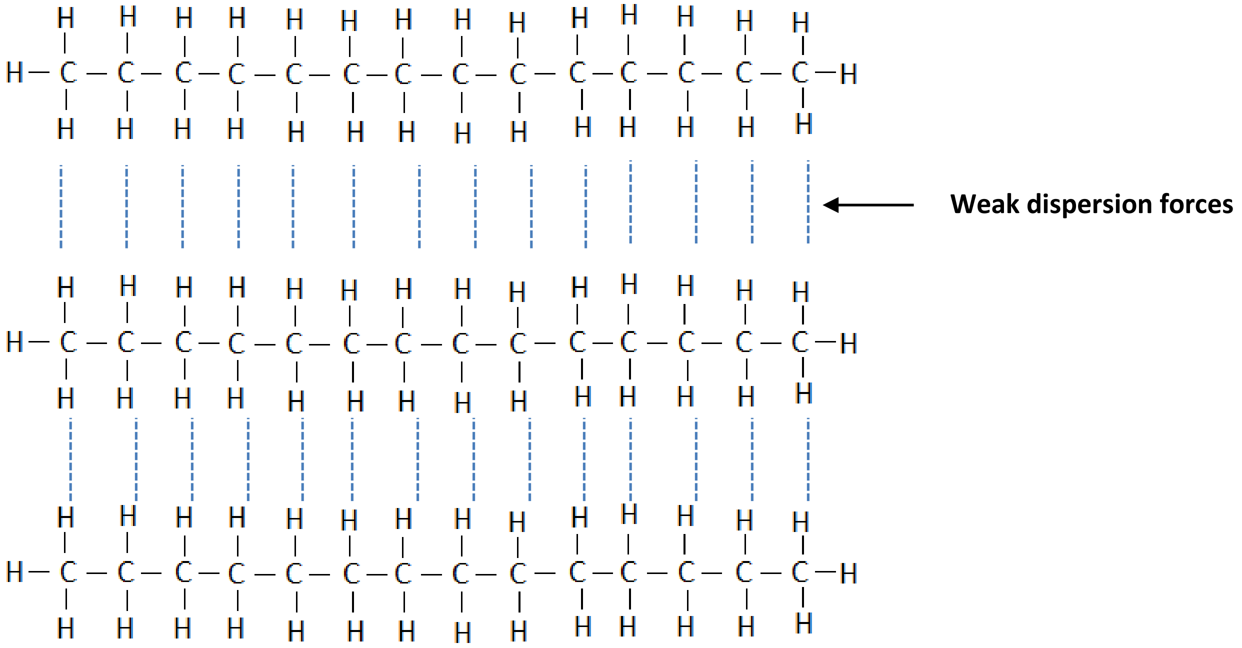
- Molecular size. *The greater the size the molecules in a liquid the higher the viscosity.*
- Strength of intermolecular forces. *The stronger the intermolecular forces the higher the viscosity.*
- The density of the liquid or how tightly packed the molecules are. *The more tightly packed together the molecules are in a liquid the stronger the intermolecular forces and the higher the viscosity.*
- Temperature. *The lower the temperature of a liquid, the less kinetic energy the molecules have and the tighter they join together. As a consequence the lower the temperature of a liquid the higher its viscosity.*

Biodiesel **has a higher viscosity** than petrodiesel. Generally the molecules in biodiesel are larger and as a consequence move more slowly. The fact that the molecules are larger also means that they will be able to form stronger intermolecular forces which will increase the viscosity even further.

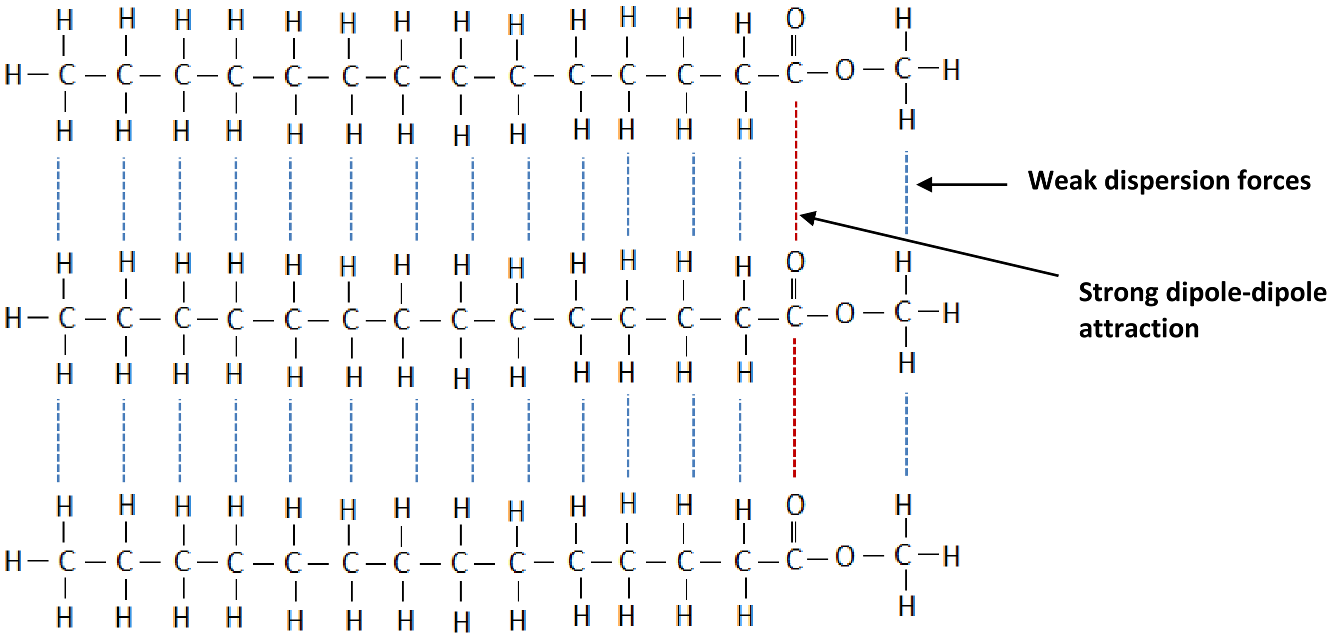
As petrodiesel molecules are fully non-polar, the intermolecular forces between adjacent petrodiesel molecules are only weak dispersion forces. The hydrocarbon part (non-polar part) of biodiesel molecules are also attracted by weak dispersion forces. The polar ester groups however, are able to form stronger dipole-dipole bonds between adjacent molecules. As a consequence the biodiesel molecules are held together more tightly and strongly making it more difficult for the liquid to flow.

- ❖ The stronger attraction between biodiesel molecules makes it more difficult for the molecules to move over and around each other. As a consequence the liquid is unable to flow as freely as the less viscous petrodiesel molecules which have weaker attraction between molecules.

The diagram below shows the presence of only weak dispersion forces between adjacent petrodiesel molecules.



The diagram below shows weak dispersion forces and strong dipole-dipole attraction holding adjacent biodiesel molecules together.



The higher viscosity of biodiesel means that it is more difficult for it to move through fuel lines than petrodiesel. A fuel line is simply a hose that connects the fuel tank of a motor vehicle to the engine. The fuel pump, which is the mechanism that pumps the fuel from the tank through the fuel line and into the engine, will need to use more energy to pump a highly viscous liquid. The high viscosity of biodiesel makes it a problematic fuel in cold weather. In colder weather, the increased viscosity of biodiesel can make it even more difficult for the fuel to move through a fuel line.

- The efficiency of a biodiesel powered engine is approximately the same as the efficiency of a petrodiesel powered engine.

## Using Stoichiometry to compare the $CO_2$ emissions of different fuels

When the $CO_2$ emissions of different fuels are compared, it is often done by comparing the quantity of $CO_2$ that is produced for the production of a given amount of energy from the fuel. For example, mass of $CO_2$ produced per MJ of energy produced. This can be calculated using **stoichiometry**.

As an example, let's compare the mass of $CO_2$ in grams produced per MJ (1 MJ) of energy from the combustion of octane ($C_8H_{18}$) with the mass in grams of $CO_2$ produced per MJ of energy from the combustion of ethanol ($C_2H_5OH$).

To do this calculation we need 2 important things. A balanced combustion equation for each fuel and some information about how much energy a given quantity of each fuel can produce (energy content or heat of reaction for each fuel):

$2C_8H_{18}\,(l) + 25O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(g) \qquad \Delta H = -\ 10{,}928\ KJ\ mol^{-1}$

$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(g) \qquad \Delta H = -\ 1{,}364\ KJ\ mol^{-1}$

Starting with the thermochemical equation for the combustion of octane, calculate the mass of $CO_2$ produced per 1 MJ of energy produced:

Convert the $\Delta H$ of octane into MJ: 10,928 divided by 1000 = 10.928 MJ

16 mol of $CO_2$ → 10.928 MJ
***X*** *mol of* $CO_2$ *→ 1 MJ*

***X*** x 10.928 = 16 x 1

$$\boldsymbol{X} = \frac{16 \text{ x } 1}{10.928} = 1.46413 \text{ mol of } CO_2$$

*So 1.46413 mol of* $CO_2$ *are produced for the production of 1 MJ of energy.*

*Convert this number of moles into a mass:*

*m* $(CO_2) = 1.46413 \text{ x } 44.0 = 64.422$ *g*

***Therefore 64.422 g of*** $CO_2$ ***are produced per MJ of energy produced from the combustion of octane.***

Now do the same calculation for the combustion of ethanol.

Convert the ΔH of ethanol into MJ: 1364 divided by 1000 = 1.364 MJ

2 mol of $CO_2 \rightarrow$ 1.364 MJ
***X** mol of $CO_2 \rightarrow$ 1 MJ*

**X** x 1.364 = 2 x 1

$$X = \frac{2 \text{ x } 1}{1.364} = 1.46628 \text{ mol of } CO_2$$

*So 1.466628 mol of $CO_2$ are produced for the production of 1 MJ of energy.*

*Convert this number of moles into a mass:*

*m ($CO_2$) = 1.46628 x 44.0 = 64.52 g*

***Therefore 64.52 g of $CO_2$ are produced per MJ of energy produced from the combustion of ethanol.***

Note that this calculation only takes into account the mass of $CO_2$ directly produced from the combustion reactions, not the overall increase in the $CO_2$ in the atmosphere. For this we need to consider whether or not the ethanol was sourced from plants (a biofuel) in which case the increase in $CO_2$ would be very low.

A similar calculation can be performed for gaseous fuels at a given temperature and pressure. For example:

Compare the volume (L) of $CO_2$ produced per MJ of energy from the combustion of methane ($CH_4$) at a temperature of 100 $^0$C and pressure of 1.5 atm with the combustion of propane at the same temperature and pressure.

$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (g)$ ΔH = - 889 KJ $mol^{-1}$

$C_3H_8 (g) + 3.5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (l)$ ΔH = - 2217 KJ $mol^{-1}$

Start with thermochemical equation for the combustion of $CH_4$.

889 KJ divided by 1000 = 0.889 MJ

1 mol of $CO_2 \rightarrow$ 0.889 MJ
***X** mol of $CO_2 \rightarrow$ 1 MJ*

**X** x 0.889 = 1 x 1

***X*** = $\frac{1 \text{ x } 1}{0.889}$ = *1.12486 mol of* $CO_2$

Convert the moles of $CO_2$ into a volume (L) using PV = nRT
Convert pressure into KPa:  1.5 x 101.3 = 151.95 KPa
Convert temperature into Kelvin: 100 + 273 = 373 K

V ($CO_2$) = $\frac{nRT}{P}$

V ($CO_2$) = $\frac{1.12486 \text{ x } 8.31 \text{ x } 373}{151.95}$ = 22.9 L

***Therefore 22.9 L of $CO_2$ are produced per MJ of energy produced from the combustion of methane.***

Now do the same for propane:

2217 KJ divided by 1000 = 2.217 MJ

3 mol of $CO_2$ → 2.217 MJ
***X*** *mol of* $CO_2$ *→ 1 MJ*

***X*** x 2.217 = 1 x 3

***X*** = $\frac{1 \text{ x } 3}{2.217}$ = *1.35318 mol of* $CO_2$

V ($CO_2$) = $\frac{1.35318 \text{ x } 8.31 \text{ x } 373}{151.95}$ = 27.6035 = 28 L

***Therefore 28 L of $CO_2$ are produced per MJ of energy produced from the combustion of propane.***

# Using the specific heat capacity of water to determine the energy released from a fuel

The **specific heat capacity** of a substance refers to the joules of heat energy that 1 g of the substance needs to absorb in order to have its temperature increase by 1 $^{0}$C or 1 K.

The specific heat capacity of water is **4.18 J g$^{-1}$ $^{0}$C$^{-1}$** or **4.18 J g$^{-1}$ K$^{-1}$.** This means that 1.0 g of water needs to absorb 4.18 J of heat energy in order to have its temperature rise by 1.0 $^{0}$C or 1.0 K.

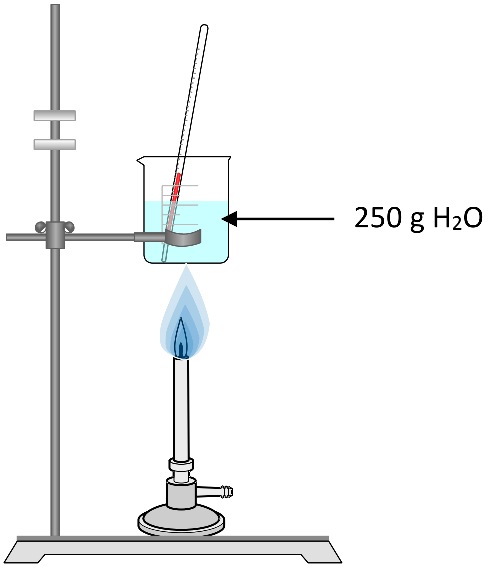
- The density of water is 0.997 g mL$^{-1}$. So 1.0 mL of water has a mass of 0.997 g
  *The density of water is given on page 5 of the end of year exam data book.*

**Energy absorbed by water (J) = mass of water (g) x 4.18 x ΔT**

- *On page 5 of the end of year exam data book this equation is expressed as*
  **q = mc ΔT**

This equation can be used to calculate how many joules of heat energy a given mass of water needs to absorb in order to have its temperature increase by a certain number of degrees. Consider the following question as an example.

How many joules of heat energy does 250 g of water need to absorb from the blue flame of a Bunsen burner in order to have its temperature increase from 21.0 $^{0}$C to its boiling temperature (100.0 $^{0}$C)?

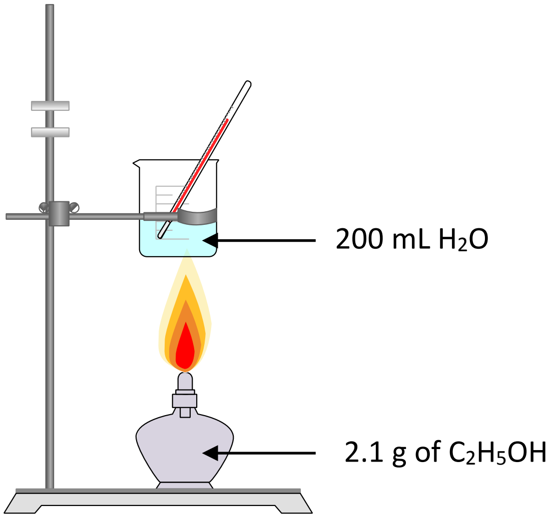


E = m ($H_2O$) x 4.18 x ΔT
= 250 x 4.18 x 79 (100 – 21.0)
= 82,555 J
= 8.3 x 10$^{4}$ J

So according to this calculation, 250 g of water needs to absorb 8.3 x $10^4$ J of heat in order to have its temperature increase by 79 $^0$C.

This principle can be used to calculate the energy released by a fuel. Consider the following example.

The 2.1 grams of $C_2H_5OH$ in a spirit burner is completely combusted. The heat released is used to heat a beaker containing 200 mL of water. The temperature of the water increases by 72 $^0$C. Calculate the energy content of the ethanol in KJ/g.



First of all calculate the heat energy in Joule, absorbed by the water.

m ($H_2O$) in the beaker = d ($H_2O$) x v ($H_2O$)
= 0.997 x 200
= 199.4 g

E = m ($H_2O$) x 4.18 x $\Delta$T
= 199.4 x 4.18 x 72
= 60,011.424 J
= 60.011.424 KJ

If the water absorbed 60.011424 KJ of heat from the burning $C_2H_5OH$ then it must be assumed that the combustion of 2.1 g of $C_2H_5OH$ released 60.011424 KJ.

2.1 g $C_2H_5OH \rightarrow$ 60.011424 KJ KJ
1 g $C_2H_5OH \rightarrow$ ***X*** KJ

***X*** x 2.1 = 1 x 60.011424 KJ

$$X = \frac{1 \text{ x } 60.011424}{2.1} = 28.57686 \text{ KJ} = 29 \text{ KJ g}^{-1}$$

In reality, the calculation of the energy content of the ethanol using this method will be much less than the true value because most of the heat will not reach the water in the beaker. It is likely that more than 50 % of the heat released from the burning ethanol will be lost to the surrounding air. Even if all of the heat did get absorbed by the water, the calculated energy content will still be a bit lower than the true value. This will be discussed further in Unit 4 Chemistry Tutor. Using the specific heat capacity of water will only give an approximation of the heat energy released by a fuel. *This approximation will always be lower than the true value.*

## Comparison of the energy contents of fuels / $CO_2$ emissions of fuels

- *These fuels were at SLC conditions (25 $^0$C and 100 KPa) when their heats of combustion and $CO_2$ emissions were calculated. They were completely combusted to produce $CO_2$ and $H_2O$.*

| **Fuel** | **Heat of combustion ($KJ\ g^{-1}$)** | **Heat of combustion ($KJ\ mol^{-1}$)** | **$CO_2$ emissions ($g\ CO_2$ / MJ)** |
|---|---|---|---|
| Black coal (~90 % C) | 35 | - | 100 |
| Brown coal (~70 % C) | 28 | - | 78.0 |
| Octane ($C_8H_{18}$) | 47.9 | 5460 | 64.4 |
| Petrodiesel (mixture of high molecular mass alkanes) | 45.0 | - | 69.0 |
| LPG ($C_3H_8$ & $C_4H_{10}$) | 46.0 | - | 55.0 |
| Propane ($C_3H_8$) | 50.5 | 2220 | 59.5 |
| Butane ($c_4H_{10}$) | 49.7 | 2880 | 61.2 |
| Natural gas ($CH_4$ , $C_2H_6$ & $C_3H_8$) | 54.0 | - | 51.0 |
| Methane ($CH_4$) | 55.6 | 890 | 49.5 |
| Ethane ($C_2H_6$) | 51.9 | 1560 | 56.7 |
| Kerosene ($C_{10}H_{22}$ to $C_{16}H_{34}$) | 46.2 | - | |
| Bioethanol ($C_2H_5OH$) | 29.6 | 1360 | Very low as fuel made by photosynthesis |
| Biogas ($CH_4$ & $CO_2$) | 20.0 | - | Very low as fuel made by photosynthesis |
| Biodiesel | 41.0 | - | Very low as fuel made by photosynthesis |

- Note that the values in this table should not be taken as definitive exact values. Fuels such as coal, petrodiesel, biodiesel, natural gas, LPG and biogas are mixtures and have varying compositions depending on where they were sourced and processed. As a consequence the energy contents and $CO_2$ emissions of these fuels can vary significantly between different sources. Use this table as a way of making general comparisons between different fuels.

- This table shows that black coal and brown coal produce the most $CO_2$ of all the fuels shown and natural gas and its main constituent $CH_4$, produce the least amount of $CO_2$.

- Petrodiesel, biodiesel, LPG, kerosene (mixture of alkanes ranging from $C_{10}H_{22}$ to $C_{16}H_{34}$) and natural gas are **blended fuels.** A blended fuel is a mixture of compounds. Each compound can act as a fuel. Not all fuels that exist as a mixture are blended fuels. For example, biogas is not a blended fuel because it is only the methane part of it that can act as a fuel. The other main constituent of biogas, carbon dioxide, cannot act as a fuel as it cannot be combusted to produce energy. The ratio of the compounds in these fuels can vary so it is not appropriate to assign them $\Delta H$ or molar heat of combustion values. Their heat of combustions can vary depending on the ratio of the compounds in the fuel.

- *Page 10 from the end of year exam data book has the heat of combustion of some common fuels.*

# CHAPTER 7 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
Which of the following fuels produces the largest quantity of greenhouse gases ($CO_2$)?

**A.** petrodiesel
**B.** coal
**C.** natural gas
**D.** octane

**Question 2**
An environmental problem associated with the extraction of coal seam gas is

**A.** the release of heavy metals into the water table
**B.** the clearing of large amounts of forests.
**C.** the production of acid rain.
**D.** the release of $CO_2$ into the atmosphere.

**Question 3**
Which fuel releases the most energy per gram of fuel combusted?

**A.** natural gas
**B.** coal
**C.** petrodiesel
**D.** LPG

**Question 4**
Biofuels are less polluting than fossil fuels because they

**A.** are renewable.
**B.** are made from biomass.
**C.** don't produce $CO_2$ gas when combusted.
**D.** are made either directly or indirectly from photosynthesis.

**Question 5**
A similarity between biodiesel and petrodiesel is that

**A.** they are both made from fats and oils.
**B.** they are both derived from crude oil.
**C.** they are both highly hydroscopic.
**D.** they both have dispersion forces acting between adjacent molecules.

**Question 6**
Most of the electricity produced in Australia is from the conversion of the enthalpy in coal into electricity. During this conversion

**A.** chemical energy (enthalpy) is converted directly into electrical energy.
**B.** approximately 70% of the heat produced from the combustion in coal is converted directly into electricity.
**C.** about 30% of the chemical energy in coal is converted into heat.
**D.** None of the above are correct.

**Question 7**
The COMPLETE combustion of all fossil fuels and biofuels produces

**A.** significant amounts of $CO_2$ and CO
**B.** significant amounts of sulfur dioxide.
**C.** NO and $NO_2$.
**D.** CO.

## Short Answers

**Question 1**
Compare coal seam gas and biogas in terms of renewability, energy content and impact on the environment.

**Question 2**
Butane ($C_4H_{10}$) has a heat combustion of 2874 KJ $mol^{-1}$. That is, the combustion of 1 mole of butane produces 2874 KJ of heat energy. Using this information calculate

**a.** the heat of reaction ($\Delta H$) of butane.
**b.** the heat of combustion of butane in KJ/g.
**c.** the energy content of butane in KJ $L^{-1}$ at SLC conditions.

**Question 3**
Calculate the % of carbon present in a 50.0 g sample of brown coal if it produces 90.0 g of $CO_2$ when completely combusted.

**Question 4**
The energy content of ethane ($C_2H_6$) is 51.9 KJ $g^{-1}$. Express this as

**a.** KJ $mol^{-1}$
**b.** J $g^{-1}$
**c.** MJ $Kg^{-1}$

**Question 5**
Why are the combustion engines of motor vehicles so inefficient at converting chemical energy into kinetic energy?

**Question 6**
When the $CO_2$ emissions of fuels are compared, it is usually done by comparing the mass of $CO_2$ produced per unit amount of energy produced. For example the grams of $CO_2$ produced per MJ of energy produced. Why is this better than comparing the mass of $CO_2$ produced per gram of fuel combusted? You should support your answer with calculations by referring to the following data:
*Heat of combustion of* $C_4H_{10} = 49.6$ *KJ* $g^{-1}$
*Heat of combustion of* $C_{12}H_{22}O_{11} = 16.5$ *KJ* $g^{-1}$

**Question 7**
Express the greenhouse gas emissions of propanol as Kg $CO_2$ / MJ if the combustion of 1 mole of propanol produces 2016 KJ of heat energy.

**Question 8**
The molecular formulae shown below are of fuels that can be used to power buses.

$C_{14}H_{30}$
$C_{17}H_{35}COOCH_2CH_3$

These buses are going to transport tourists to the snow fields in Victoria's alpine region during winter. Give the formula of the fuel which is best suited for the transportation needs described in this question. Discuss why this fuel is best suited.

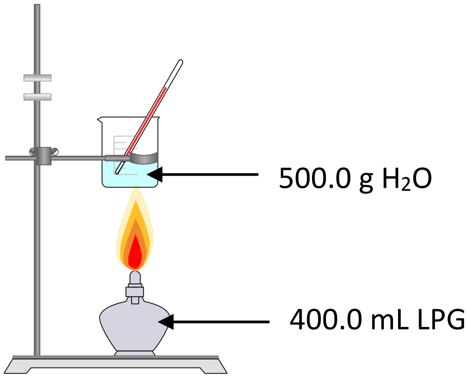
**Question 9**
Compare petrodiesel and biodiesel in terms of

**a.** the impact their sourcing and combustion has on the environment.
**b.** long term storage.
**c.** the ease of movement of the fuels through fuel lines.

**Question 10**
Explain why the combustion of all fuels produces nitrous oxides such as NO and $NO_2$.

**Question 11**
A 2.5 gram sample of glucose ($C_6H_{12}O_6$) is completely combusted. The heat released from the reaction causes the temperature of 100 mL of water to increase from 10 $^0$C to 80 $^0$C. Calculate the energy content of the glucose in KJ $g^{-1}$.

**Question 12**
LPG is a mixture of propane and butane gas. 400.0 mL of LPG is combusted and the heat released by this reaction made the temperature of 500.0 g of water rise by 17.9 $^0$C. The apparatus used is shown below.



**a.** Calculate the number of KJ of heat absorbed by the 500.0 g of water.
**b.** Most of the heat energy released by the LPG does not get absorbed by the water. Where does this heat go to?
**c.** If 35.0 % of the heat released is absorbed by the water, calculate the heat of combustion of the LPG in KJ/L.
**d.** If 90.0 % of the volume of the LPG is propane, calculate the heat of combustion of the LPG in KJ/g if the 400.0 mL of LPG gas was at standard laboratory conditions before it was combusted.
**e.** Calculate the Kg of $CO_2$ produced per KJ of heat released (Kg $CO_2$ / KJ) from the combustion of the 400.0 mL of LPG.

**Question 13**
Bioethanol is produced from the fermentation of the glucose that is produced by plants during photosynthesis. The equations showing the formation of bioethanol are shown below.

<u>photosynthesis</u>
$6CO_2\ (g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (aq) + 6O_2\ (g)$

<u>Fermentation</u>
$C_6H_{12}O_6\ (aq) \rightarrow 2CO_2\ (g) + 2C_2H_5OH\ (aq)$

When the bioethanol is used as a fuel it is combusted in oxygen:

$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g)\ 3H_2O\ (g)$

**a.** Use the stoichiometry shown in these equations to show that the combustion of bioethanol is a **carbon neutral process.** That is, show that the combustion of bioethanol does not increase the levels of $CO_2$ in the Earth's atmosphere.
**b.** Explain why in practice, using bioethanol as a fuel does slightly increase the level of $CO_2$ in the atmosphere.

**Question 14**
Discuss the impact that the activation energy of the combustion of a fuel has on the net (overall) amount of energy it can release.

**Question 15**
Write out the thermochemical equation for the complete combustion of hydrogen gas.

# Chapter 8 – Rates of Reaction

This chapter is focussed on looking at how chemical reactions can be made to occur more quickly / at a faster rate. Before we can get into this it is necessary to understand **COLLISION THEORY**.

## Collision Theory

Collision theory states that the particles (atoms, ions or molecules) taking part in a reaction are moving randomly and will eventually collide. A reaction will only occur if the particles collide with a force that is either equal to or greater than the activation energy for the reaction. In other words a reaction will only occur if the particles collide with sufficient force to break the bonds holding the atoms together in a substance. Reactant particles must also collide at the correct angle/orientation in order for the bonds to break and cause a reaction.

The speed/rate of a chemical reaction can be increased in 2 main ways:

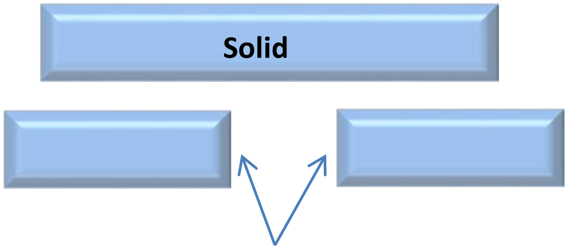
1. **By increasing the frequency (number of) of successful collisions that occur between reactant particles**. *Increasing the frequency of collisions means increasing the number of collisions that reactant molecules can make in a given amount of time (Eg. Per second or per minute etc.).* This can be achieved by *increasing the surface area of reacting solids or liquids, increasing the concentration of reactants that are in solution or the gaseous state (increase in pressure) and increasing the temperature. All of these actions will **increase the frequency of total collisions** (this includes collisions that are strong enough to cause a reaction and those that are not). It is just the increase in the collisions that are strong enough to cause a reaction that result in an increase in the rate of reaction. A catalyst will increase the frequency of successful collisions but not the frequency of total collisions. This will be clarified later in this chapter.*

2. **By increasing the proportion / fraction / % of reactant particles that have enough energy to produce a chemical reaction.** This can be achieved by *increasing the temperature or adding a catalyst.*

Let us start off by looking at the factors involved in increasing the rate of a reaction using the first way mentioned, *increasing the frequency of collisions that occur between reactant particles that already have sufficient energy to react.*

## Increasing the surface area of solids

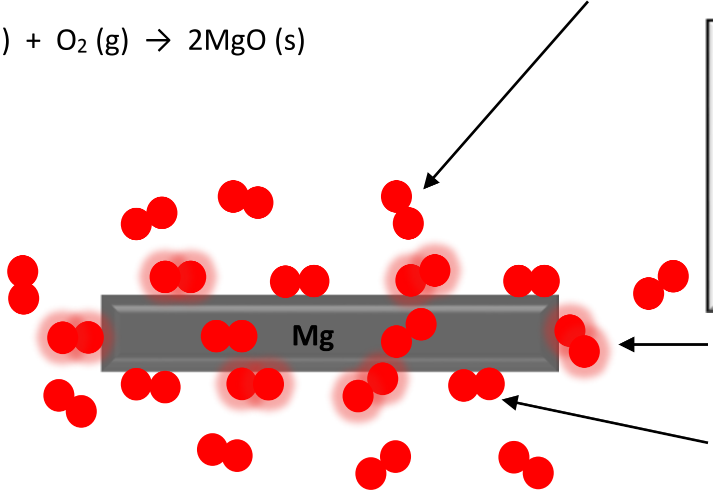
The surface area of a solid simply refers to the surface that is exposed. When a solid reacts with a solution or a gas it is only its exposed surface that is able to react at any given time. If a solid is broken into 2 pieces its surface area is increased because 2 new surfaces have been created at the point of the break. For example:



*2 new surfaces created at the point of the break. Therefore the surface area of the solid is greater than what it was before it was broken up into 2 pieces.*

The diagram below shows a single piece of solid magnesium metal (Mg) reacting with oxygen ($O_2$) gas. The equation for this reaction is

$2Mg\ (s)\ +\ O_2\ (g)\ \rightarrow\ 2MgO\ (s)$



$O_2$ molecule that is yet to collide with Mg.

*This diagram shows that in a given amount of time, eg 1 second, **there are 12 collisions** in total. **6 of them are successful.***

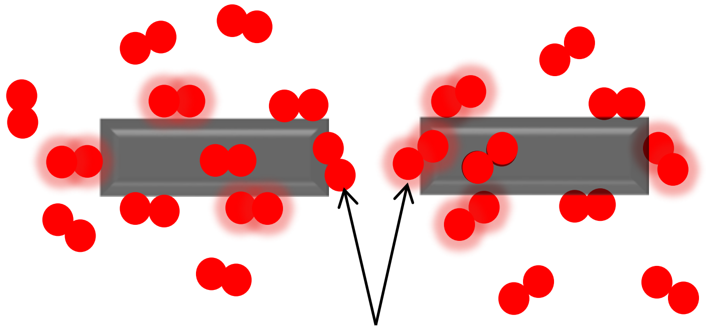
***% successful collisions = 6/12 x 100***
***= 50 %***

$O_2$ molecule making a SUCCESSFUL COLLISION with Mg.

$O_2$ molecule making an UNSUCCESSFUL COLLISION with Mg.

When a solid reacts with a gas, liquid or solution, it is only the surface of the solid that is able to react at any given time. That's because it is only the atoms on the surface that are exposed and able to make direct contact with the other reactant particles. The surface of the Mg metal is currently colliding with 12 $O_2$ molecules. However, not every collision between the Mg atoms and the $O_2$ molecules is **successful** (strong enough to cause a reaction). That is, not every collision between the Mg atoms and $O_2$ molecules is strong enough to break the bonds and result in a chemical reaction. *Another way of stating this is that not every collision between an Mg atom and an $O_2$ molecule has the activation energy required for a reaction*. <u>This is because at any given temperature, not all of the reactant particles are moving with the same kinetic energy.</u> Some particles are colliding with enough force to break their bonds where as other slower moving particles are just bouncing off each other. This will be explored further later on in the chapter. Of the 12 collisions occurring between the Mg atoms and $O_2$ molecules, only 6 are resulting in a chemical reaction (the $O_2$ molecules shown with a red glow are colliding with sufficient force to react).

If the Mg is broken into 2 pieces, its surface area that is exposed to the $O_2$ molecules will increase as can be seen in the diagram below. The 12 collisions that were occurring before the piece of Mg was broken, are still occurring as the original surface is still there. However, the 2 new surfaces that were created at the point of the break are able to make collisions with $O_2$ molecules. As a consequence the reaction will occur MORE QUICKLY / AT A FASTER RATE.



*This diagram shows that in a given amount of time there are **14 collisions** in total. **7 of them are successful.***

***% successful collisions = 7/14 x 100***
**= 50 %**

*Breaking the Mg into 2 pieces has created 2 new surfaces that before the break were not exposed and able to make contact with the $O_2$ molecules. Now there are a greater number of collisions occurring between the Mg atoms and the $O_2$ molecules. Before the surface area was increased there were 12 collisions in total in a given amount of time, 6 of them were successful. When the surface area was increased there was a total of 14 collisions in a given amount of time, 7 of them were successful. So the frequency of successful collisions increased from 6 to 7 resulting in an increase in the rate of the reaction. **The % of successful collisions however, is still the same at 50%.***

The more pieces the original piece of solid Mg is broken into, the greater the surface area exposed to the oxygen. Every time a piece of Mg is broken into 2 pieces, 2 new surfaces are created. It is not surprising that in industry solid reactants are often ground into a fine powder to maximise surface area.

So when the surface area of a solid increases, the rate of the reaction increases because the frequency of successful collisions between reactant particles has increased.

- *It is important to emphasise that it is the increase in the frequency of SUCCESSFUL COLLISIONS that has caused the increase in the rate of the reaction. The overall frequency of collisions has also increased but it is only the increase in frequency of the successful collisions that caused the increase in the rate of the reaction.*

*The percentage of successful collisions before and after the increase in surface area DID NOT CHANGE. With this example it remained at 50 %. When the frequency of collisions increases, the proportion of successful collisions compared to the total number of collisions remains the same. So before the increase in surface area of the Mg, there were 12 collisions between reactant molecules in total and 6 of them were successful. When the surface area of the Mg was increased, there were 14 collisions in total and 7 of them were successful. The rate of the reaction increased because now* *in a given amount of time there were 7 successful collisions instead of only 6. The fraction of successful collisions however, did not change.*

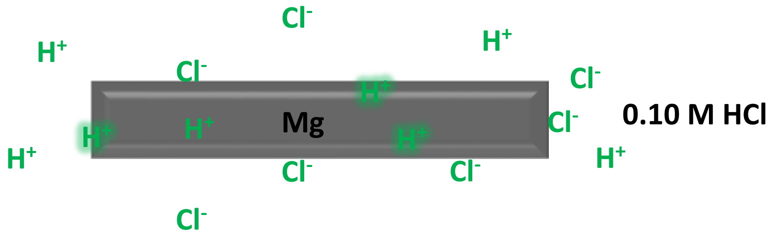
- *Only an increase in **TEMPERATURE** and adding a **CATALYST** will increase the fraction of successful collisions. This will be explored later in this chapter.*
- *The surface area of a liquid reactant can be increased by spraying it during the reaction. When a liquid is sprayed it forms tiny droplets which increase its surface area exposed to the other reactant. It has a similar effect to breaking a solid up into many smaller sized particles.*
- *Successful collisions are often referred to as "FRUITFUL COLLISIONS".*

## Increasing the concentration of reactants that are in solution

To explore how increasing the concentration of a solution causes an increase in the rate of a reaction, the reaction between solid Mg and hydrochloric acid (HCl) will be used as an example. Let's start off by looking at a piece of Mg metal reacting with 0.10 M HCl as can be seen in the equation below.

$Mg\ (s) + \underline{2HCl\ (aq)} \rightarrow MgCl_2\ (aq) + H_2\ (g)$
**0.10 M**

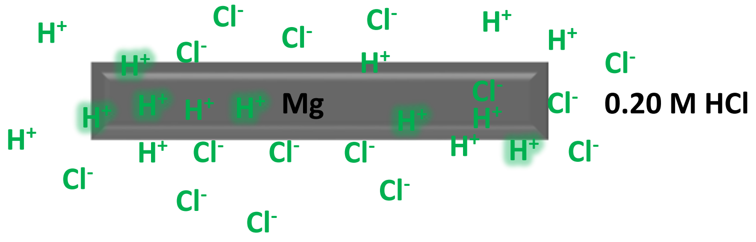
The reactant particles from the HCl are **$H^+$** and **$Cl^-$** ions. The diagram below shows 4 $H^+$ and 4 $Cl^-$ ions making collisions with the surface of the Mg. Only 3 $H^+$ ions are making fruitful collisions with the Mg atoms. These ions making successful collisions are shown with a green glow.



*This diagram shows that in a given amount of time there are **8 collisions** in total. **3 of them are successful.***

**% successful collisions = 3/8 x 100**
**= 38 %**

This time the Mg will not be broken up into smaller pieces. Instead the CONCENTRATION of the HCl reacting with the Mg will be INCREASED from 0.10 M to 0.20 M. When the concentration of a solution is increased, the number of particles in a given volume of solution will increase. So when the concentration of the HCl is doubled from 0.10 M to 0.20 M, the number of $H^+$ and $Cl^-$ ions in solution and hence the number of ions making collisions with the Mg will double as can be seen in the diagram below



*This diagram shows that in a given amount of time there are* **16 collisions in total. 6 of them are successful**.

**% successful collisions = 6/16 x 100**
**= 38 %**

More importantly, the number of successful collisions occurring will also increase resulting in an increase in the rate of the reaction.

So when the concentration of a reactant in solution increases, the frequency of successful collisions between the reactant particles increases resulting in an INCREASE in the rate of reaction.

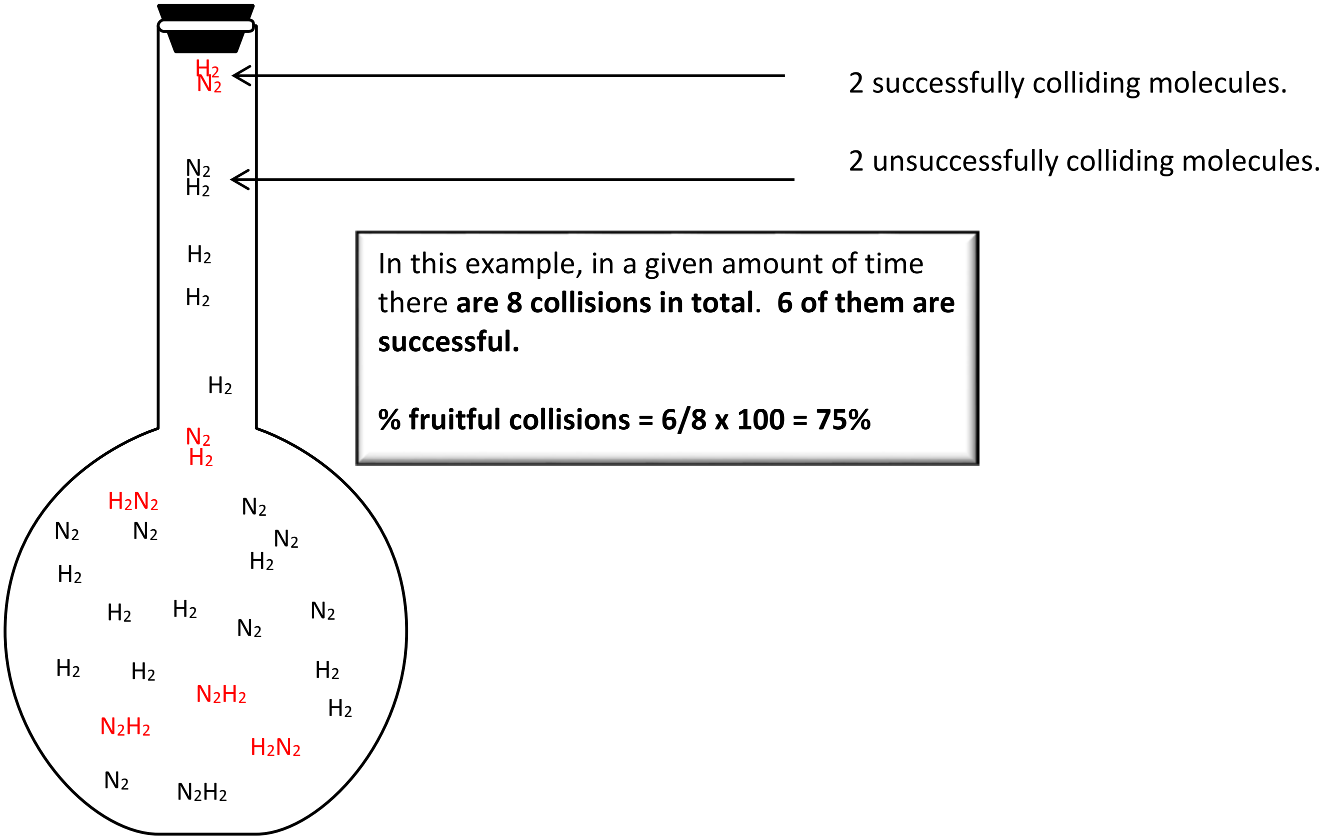
## Increasing the concentration / pressure of a gas

The concentration of a gas is similar to the concentration of an aqueous solution. A 0.10 M HCl solution contains 0.10 mol of HCl for every 1.0 L of solution. A vessel holding $NH_3$ gas with a 0.10 M concentration contains 0.10 mol of $NH_3$ gas for every 1.0 L of space.

As is the case with a reaction involving an aqueous solution, the rate of a reaction involving gaseous reactants will increase if the concentration of the gases increases. The reaction between $N_2$ and $H_2$ to produce $NH_3$ will be used as an example using 1.0 M $N_2$ and 1.0 M $H_2$. The molecules in red are showing successful collisions that are resulting in a chemical reaction.

$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$
1.0 M  1.0 M

The $N_2$ and $H_2$ molecules are moving randomly around the space in the flask. Eventually reactant molecules will collide and react if the force of their collisions are strong enough to break bonds.



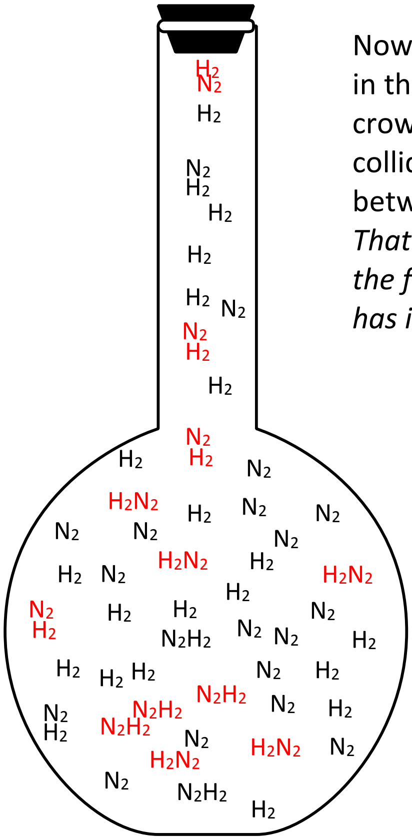
2 successfully colliding molecules.

2 unsuccessfully colliding molecules.

In this example, in a given amount of time there **are 8 collisions in total**. **6 of them are successful.**

**% fruitful collisions = 6/8 x 100 = 75%**

If the number of $N_2$ and $H_2$ molecules in the flask is doubled, the concentration of the gases will also double up to **2.0 M.**



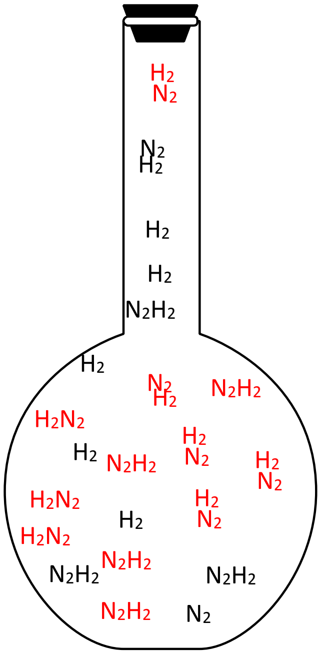
Now there are twice as many $N_2$ and $H_2$ molecules moving around but in the same amount of space as before. As the container is more crowded with molecules the likelihood of the reactant molecules colliding has increased. As a consequence the number of collisions between reactant molecules in a given amount of time has increased. *That is, the frequency of total collisions has increased and hence so has the frequency of successful collisions. Therefore the rate of the reaction has increased.*

In this example, in a given amount of time there **are 16 collisions in total**. **12 of them are fruitful.**

**% successful collisions = 12/16 x 100 = 75%**

- The rate of the reaction would also increase if the concentration of just one of the gases was increased. For example if the concentration of $N_2$ remained at 1.0 M but the concentration of $H_2$ was increased to 2.0 M.

Now the original mixture of 1.0 M $N_2$ and 1.0 M $H_2$ will be transferred into a flask with only half the volume. As a consequence the $N_2$ and $H_2$ will be twice as concentrated – **2.0 M.**

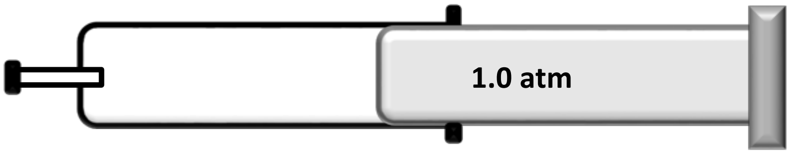


This flask has the same number of $N_2$ and $H_2$ molecules as the original flask. They are however, more crowded as they have less space to move around in. As a consequence there is a greater likelihood of $N_2$ and $H_2$ molecules colliding. Therefore the frequency of total collisions between molecules has increased as has the frequency of successful collisions. The reaction will now occur at a faster rate.

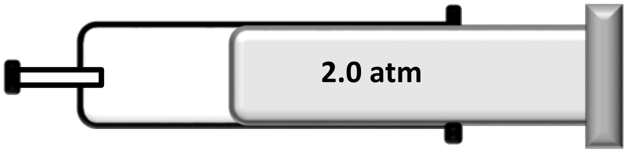
In this example, in a given amount of time there are **16 collisions in total. 12 of them are fruitful.**

**% successful collisions = 12/16 x 100 = 75%**

The concentration of gaseous reactants in a gas syringe can also be increased by reducing the volume by pushing in the plunger.



When the plunger of the syringe is pushed in, the volume is decreased resulting in a greater concentration of reactant gas particles.



*When the concentration of a gaseous mixture is increased either by adding more molecules or reducing the volume, the pressure of the* ***gases will also increase and by a proportionate amount*** *due to the greater number of collisions between the molecules and the walls of the container (refer to chapter 3). So all of the above discussion regarding the effect of concentration on the rate of gaseous reactions can be rewritten by substituting the word PRESSURE for CONCENTRATION.*

- *The effect of gas concentration / pressure does not only apply to reactions that involve gases only. The rate of the reaction between Mg and $O_2$ (shown on page 118) could be increased by increasing the concentration / pressure of the $O_2$ molecules. This would result in a greater frequency of collisions between the $O_2$ molecules and the piece of magnesium.*

## Increasing the temperature of a reaction.

The effect that increasing temperature has on the rate of a reaction is a bit more complicated than the effect of surface area and concentration that were previously discussed. These only increased the frequency of successful collisions. Increasing the temperature will increase both the

- frequency of total collisions and successful collisions and,
- %/fraction/proportion of successful collisions (**second** point made on page 117 at the start of the chapter.).

**At any given temperature, eg. 25$^0$C, particles have different kinetic energies.** That is, the particles are moving at different speeds. So at a given temperature the particles have **an average kinetic energy** but individual particles are moving at different speeds. This is why not all collisions between reactant particles result in a chemical reaction. The faster moving particles can make fruitful collisions that are strong enough to break bonds whereas the slower moving particles are just bouncing off each other as their collisions are not strong enough to break bonds.

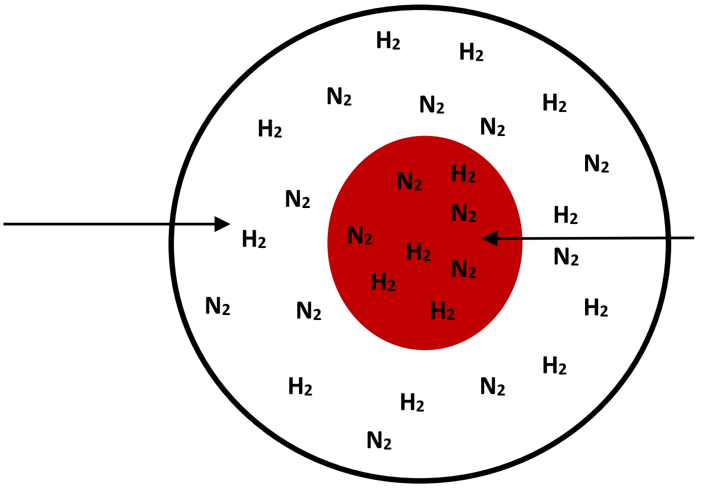
It is difficult to show molecules moving faster at higher temperatures using diagrams such as those that were used for examining the effect of surface area and concentration on the rate of a reaction. Instead, diagrams using circles to represent reactant particles with different kinetic energies will be used.

Let's look at a chemical reaction that is occurring at 100 $^0$C. We will use the reaction that produces ammonia gas as an example.

$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g)$

At 100 $^0$C, not all of the $N_2$ and $H_2$ molecules have the same kinetic energy. Some molecules are moving faster than others. As a consequence not all collisions between $N_2$ and $H_2$ molecules are strong enough to break bonds and cause a reaction. This situation is illustrated in the diagram on the next page. The big circle with the black border represents all of the $N_2$ and $H_2$ molecules that are colliding in a given amount of time. That is, everything inside this circle represents 100 % of the molecules that are colliding regardless of whether or not they are reacting. *The frequency of total collisions can be seen as 100 collisions per unit amount of time.* The smaller inner circle that is shaded red only represents the $N_2$ and $H_2$ molecules that have sufficient kinetic energy to react. This is 35 % of all of the $N_2$ and $H_2$ molecules that are colliding . The $N_2$ and $H_2$ molecules outside the red circle are slower moving molecules that are not colliding with sufficient force to react. They represent 65 % of the total molecules present. So at any given time during this reaction only 35 % of the molecules present are reacting.

100 $^0$C



***65 % of molecules are not reacting.***

***35 % of the molecules are reacting.***

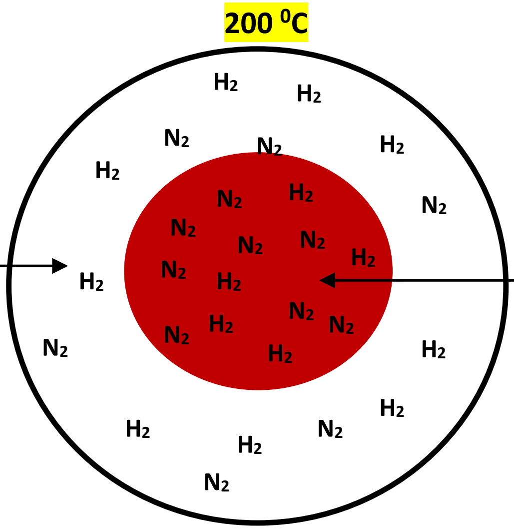
***35 successful collisions / 100 total collisions***

- Note that the kinetic energy of the molecules is able to change during the course of the reaction. The collisions between molecules causes kinetic energy to be transferred from one molecule to another. Slower moving molecules can also gain more energy from the heat source. So the slower moving $N_2$ and $H_2$ molecules in this example can gain kinetic energy and be part of the 35 % of molecules that are able to react. It is also possible for faster moving molecules to lose energy and slow down. If slower moving molecules didn't gain the kinetic energy required for a reaction, reactions would never reach completion. In this example that would leave 65 % of the $N_2$ and $H_2$ molecules left unreacted.

**If the temperature of this reaction is increased to 200 $^0$C**, the kinetic energy of all molecules present will increase. As a result of this, 2 major things are going to happen that will increase the rate of the reaction.

The first thing is that the frequency of total collisions will increase. This includes the 35 % of molecules in the red circle that already have sufficient energy to react, will collide more frequently due to their increased kinetic energy. That is, at this higher temperature the molecules are moving more quickly and are more likely to collide with each other. So in a given amount of time these molecules are making more collisions and are therefore reacting more quickly.

Now we need to look at the molecules outside of the red circle. These are the 65 % of molecules that did not have sufficient kinetic energy to react at the lower temperature of 100 $^0$C. These molecules will also gain kinetic energy at the higher temperature of 200 $^0$C. Now that these molecules are moving faster, some of them will be able to make collisions that are hard enough to break their bonds and cause a chemical reaction. That is, some of these molecules will be able to make fruitful collisions and react. As a consequence of this, ***the % of molecules with sufficient kinetic energy to react has just got larger.*** At 100 $^0$C, 35 % of the molecules were reacting, but now at the higher temperature of 200 $^0$C there might 55 % of the molecules present making collisions that are resulting in chemical reactions. That is, the original 35 % plus an extra 20 % of $N_2$ and $H_2$ molecules will be making fruitful collisions. This will cause the rate of the reaction to increase because now in a given amount of time, there are 55 % of the $N_2$ and $H_2$ molecules reacting as opposed to only 35 % at the lower temperature. So the diagram with the circles will now look something like this.



***45 % of molecules are not reacting.***

***55 % of the molecules are reacting.***

***110 successful collisions / 200 total collisions***

The red circle showing the molecules with sufficient energy to react is larger at the higher temperature of 200 $^{0}$C when compared to 100 $^{0}$C.

So when the temperature of a reaction is increased, the RATE OF REACTION INCREASES because the

- FREQUENCY of successful collisions increases and the
- % / FRACTION / PROPORTION of successful collisions increases.

❖ It is important to realise that the increase in **the proportion of successful collisions** at a higher temperature has a GREATER IMPACT on the increase in the rate of the reaction than the increase in frequency of successful collisions at a higher temperature.

The first 2 factors examined for increasing the rate of a reaction, increasing surface area and increasing concentration, only increase the FRQUENCY OF SUCCESSFUL COLLISIONS, not the proportion of successful collisions. Increasing surface area and concentration did not change the kinetic energy of the particles, therefore it did not change the proportion of the collisions that were successful. These factors increased the total number of collisions occurring in a given amount of time and the number of successful collisions increased by a proportionate amount. For example, on page 120 when the concentration of HCl reacting with Mg increased from 0.10 M to 0.20 M, the

frequency of collisions changed from ***8 total / 3 successful*** to ***16 total / 6 successful.*** In both cases the proportion of successful collisions was still 38%.

## Adding a catalyst to a reaction

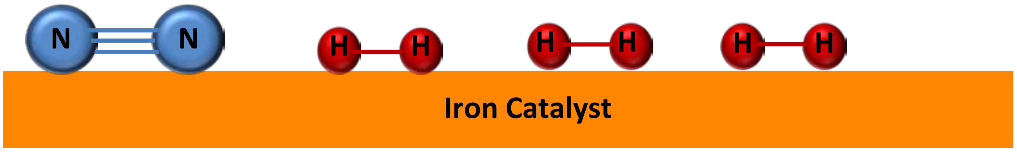
As was discussed earlier, not all reactant particles at a given temperature have the same kinetic energy. Some have sufficient kinetic energy to react and other particles do not. In other words some of the reactant particles are moving at a sufficiently fast speed so that the collisions are hard enough to break the bonds. Other reactant particles are moving at slower speeds and their collisions are much weaker resulting in the particles just bouncing off each other. These weak collisions do not result in a reaction.

If a catalyst is added to a chemical reaction, the reactant particles will interact with the catalyst particles. As a result of this interaction the bonds holding the atoms together in the reactant particles will be either **weakened** or totally **broken.**

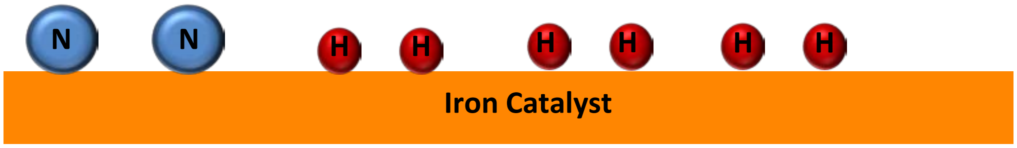
Let's see how a solid iron catalyst helps to increase the rate of reaction between nitrogen gas and hydrogen gas to produce ammonia:

$N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g)$

The $N_2$ and $H_2$ molecules adsorb (stick) onto the surface of the iron catalyst.

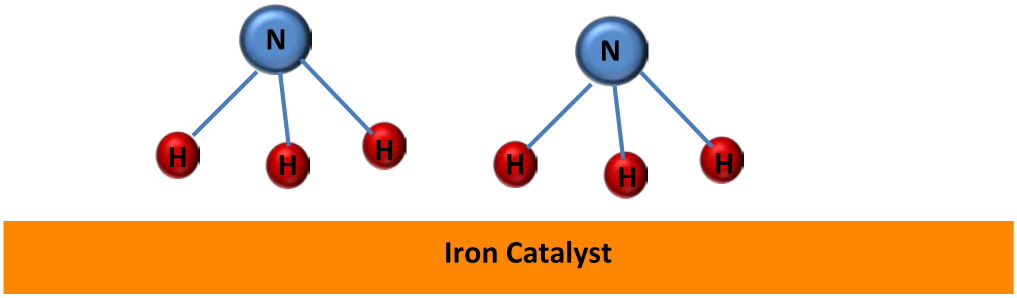


This interaction between the molecules and the catalyst will either weaken or break the bonds in the $N_2$ and $H_2$ molecules.

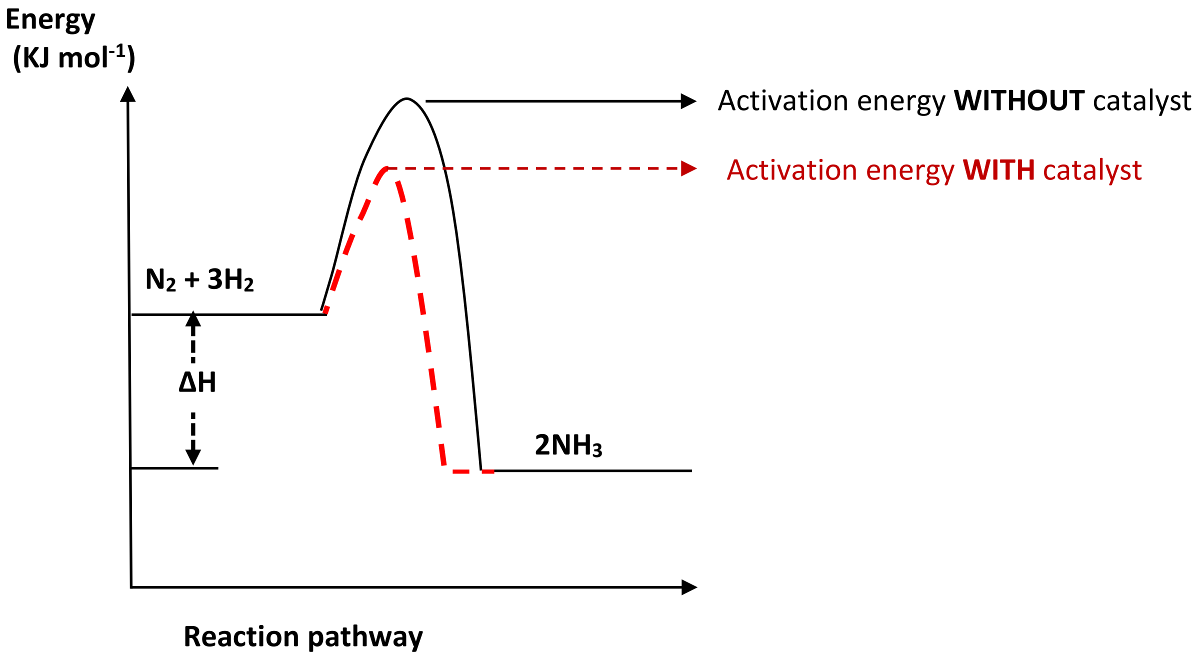


As the bonds holding the atoms together in the $N_2$ and $H_2$ molecules have been weakened, weaker collisions that previously did not result in a chemical reaction will now be hard enough to break the weakened bonds in the reactants. The separated N and H atoms can now come together to form new bonds. The product, $NH_3$, can leave the surface of the catalyst which is now free to interact with other $N_2$ and $H_2$ molecules.

- In this example the iron is a **heterogenous catalyst** as it is in a different state of matter to the reactants. The reactants are gases and the iron catalyst is a solid. A **homogenous** catalyst is one that is in the same state as the reactants.



By breaking or weakening the bonds in the reactants, the catalyst has **lowered the activation energy barrier for the reaction.** This means that the reactant molecules can absorb less heat energy in order to have successful collisions that cause a chemical reaction. The energy profile diagram below shows the activation energy for this reaction with and without a catalyst.

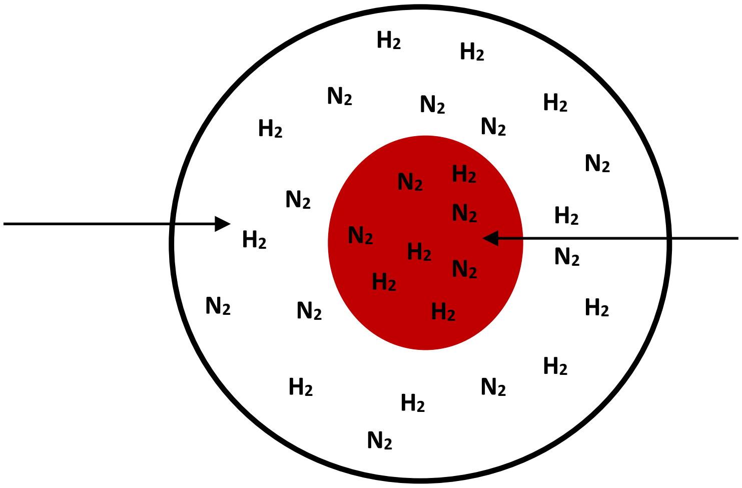


- The catalyst did not change the enthalpy of the reactants or products so the **ΔH of the reaction is not affected by the catalyst.**

Since the activation energy for the reaction was lowered by the catalyst, the reaction mixture will contain a higher number or proportion of reactant particles whose collisions are hard enough to break their bonds and cause a reaction. As a result the **rate of reaction will be faster.**

The effect that a catalyst has on the rate of a reaction can be illustrated using circles similar to those used to show the effect of temperature on the rate of a reaction.

**100 $^0$C**



***65 % of molecules are not reacting.***

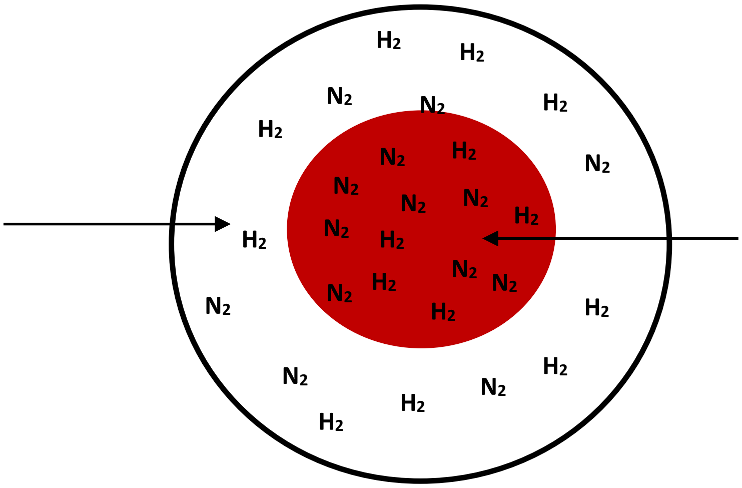
***35 % of the molecules are reacting.***

***35 successful collisions / 100 total collisions***

As has been discussed before, not all molecules at a given temperature have the same kinetic energy. At 100 $^0$C, only 35 % (red circle) of the $N_2$ and $H_2$ molecules present have sufficient kinetic energy for successful collisions that will cause a reaction. The remaining 65 % (outside the red circle) have lower kinetic energy that will not produce successful collisions.

If the temperature is kept at 100 $^0$C but a catalyst is added to the reaction mixture, the bonds in all reactants will be weakened. The weakening of the bonds in the 35 % of the molecules with sufficient energy to react is of very little consequence to the reaction rate as they were already reacting any way. The weakening of the bonds in the 65 % of molecules with insufficient energy to react is of a much greater consequence. The weakening of the bonds in these molecules means that some of them will undergo collisions that are strong enough to break bonds and cause a reaction. These molecules still have the same kinetic energy and are colliding with the same force as before the catalyst was added, but since their bonds have been weakened these collisions are now strong enough to break bonds and cause a reaction.

**100 $^0$C / CATALYST**



***45 % of molecules are not reacting.***

***55 % of the molecules are reacting.***

***55 successful collisions / 100 total collisions***

*A catalyst does not increase the kinetic energy of reactant particles. Only heat (increasing the temperature) can do that. As a consequence the total number of collisions between reactant particles is not increased by a catalyst.*

So some of the $N_2$ and $H_2$ molecules that were part of the 65 % of reactants that were not reacting will join the reacting molecules in the red circle. As a consequence the % of particles with the energy to react at any given time has just got larger resulting in an INCREASE IN THE RATE OF THE REACTION. So the % of reactants with sufficient energy to react has increased from 35 % to 55%.

The statements below show different ways of stating how a catalyst can increase the rate of a reaction:

- A catalyst increases the rate of a reaction by lowering the activation energy which allows for a greater proportion of molecules to make successful collisions that cause a reaction.

- A catalyst increases the rate of a reaction by weakening the bonds in the reactants which allows for a greater proportion of collisions that are strong enough to break bonds and cause a reaction.

- A catalyst increases the rate of a reaction by lowering the activation energy required for a chemical reaction to occur. As a consequence there will be a greater fraction of reactant particles at any moment that will be colliding with sufficient energy to produce a reaction.

- A catalyst increases the rate of reaction by providing an alternative pathway with a lower activation energy. As a consequence there is a greater number of reactant particles that possess the energy required for a reaction. The term "reaction pathway" refers to the pathway represented by an energy profile diagram when it is viewed from left to right. When the catalyst is present the pathway has a lower hill or activation energy. There will be a greater number of particles that can take this pathway as it requires less energy. This results in a faster rate of reaction. This concept of "reaction pathway" is a more abstract way of looking at how a catalysts work and many students find this unclear.

Some other important information regarding the functioning of catalysts is shown below.

- A catalyst can be either solid, liquid or gas.

- Catalysts do not take part in the reactions they catalyse so they are unchanged by the reactions they catalyse. As a consequence they can be used many times to catalyse a reaction.

- A small amount of catalyst can catalyse a large number of reactant particles.

- A solid catalyst will be more efficient (catalyse a greater number of reactant particles) as its surface area increases. This allows for a greater amount of catalyst surface to make bonds with reactant molecules.

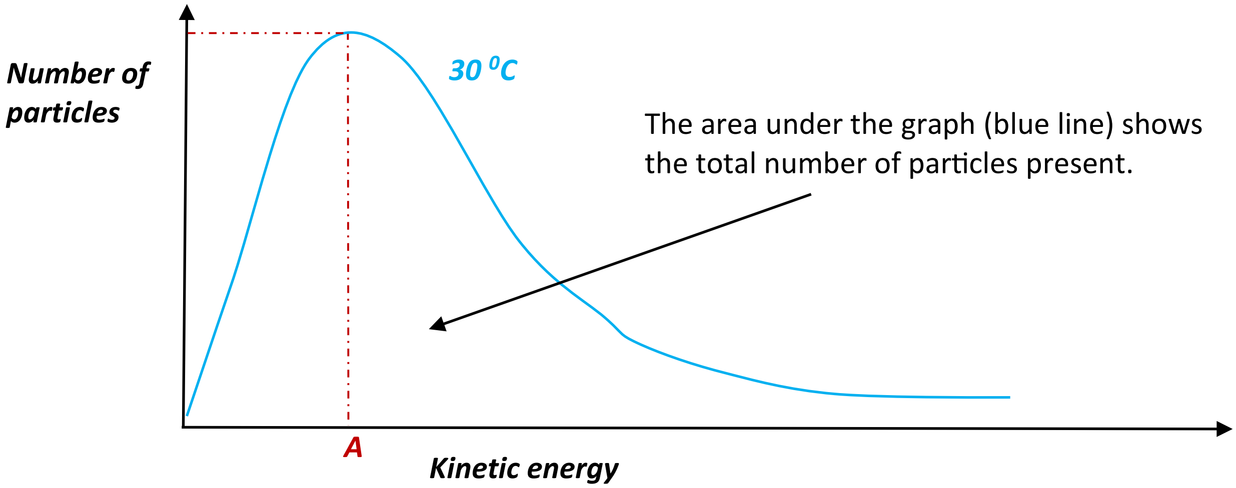
- **Enzymes and solid catalysts** can make reactant particles align themselves in ways that are favourable for a reaction to occur. That is, they can force the reactants to collide at angles that are more likely to cause a reaction. **Liquid and gaseous catalysts are unable to do this.** Enzymes will be covered in Unit 4 Chemistry Tutor.

- Inorganic catalysts can often catalyse many different types of reactions whereas organic catalysts such as enzymes are much more specific and will usually catalyse only one type of reaction.

- As a catalyst does not increase the kinetic energy or the amount of reactant particles present, it does NOT INCREASE THE FREQUENCY OF TOTAL COLLISIONS between reactant particles. Since a catalyst increases the proportion of successful collisions, it stands to the reason that the number of successful collisions in a given amount of time must also increase. Therefore a catalyst <u>INCREASES THE FREQUENCY OF SUCCESSFUL COLLISIONS.</u>

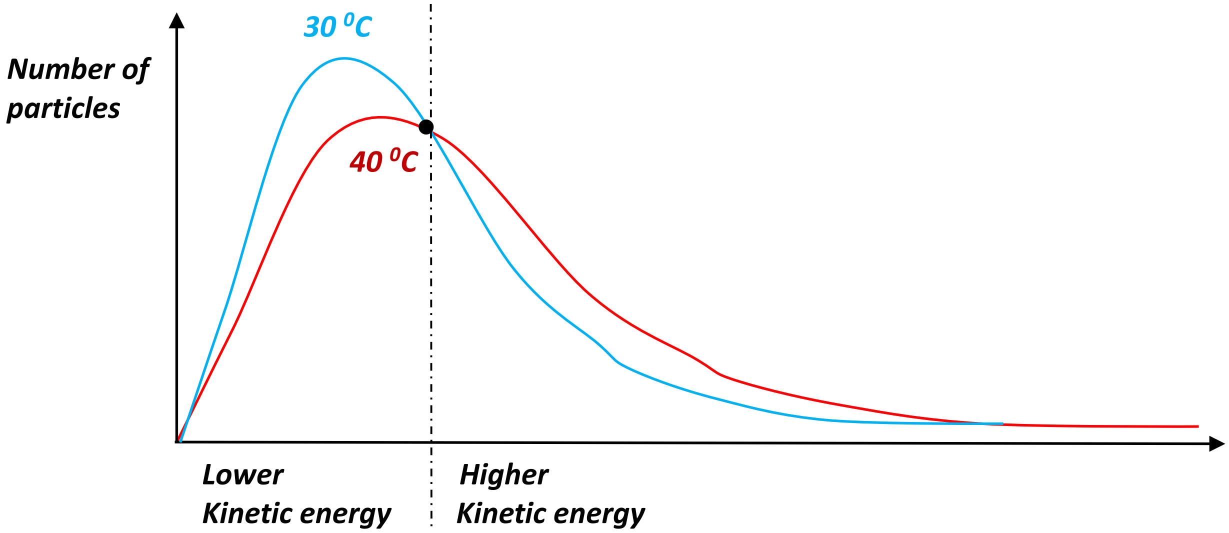
# Maxwell – Boltzmann Distributions

As has been mentioned several times in this chapter, the particles of a substance have a range of different kinetic energies at the same temperature. This can be illustrated in graphs known as **Maxwell – Boltzmann distributions** which show the distribution or variation of the kinetic energies of particles at a particular temperature. The graph below shows the distribution of the kinetic energies of particles at 30 $^0$C.



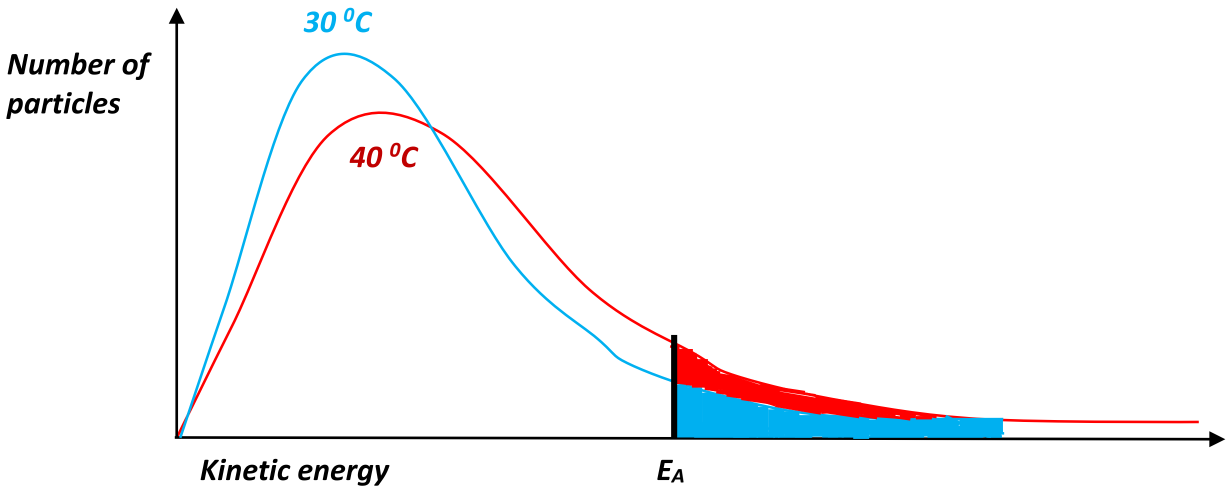
When reading this graph from left to right, it can be seen that as the kinetic energy of the particles increases so does the number of particles possessing that kinetic energy until the highest point (peak) on the graph is reached. The highest point on the blue line shows that at 30 $^0$C, there are more particles that have a kinetic energy equal to "A" than any other kinetic energy. As the kinetic energy of the particles gets greater than A, the number of particles possessing that kinetic energy decreases.

Often there are 2 graphs drawn on the same set of axes so that the distribution of the kinetic energy of particles at different temperatures can be compared. The graph below shows the distribution of the kinetic energies of particles at 30 $^0$C and 40 $^0$C.



The red graph shows the distribution of the kinetic energy of the particles at 40 $^0$C. Think of the red line as showing what has happened to the particles after they have had their temperature increase from 30 $^0$C to 40 $^0$C. A good reference point for comparing these 2 graphs is where they intersect which is shown with a black dot. At this point kinetic energy is relatively low. On the left hand side of this point of intersection (showing low kinetic energy), the blue line is always above the red line. This shows that at the lower temperature of 30 $^0$C, there are a greater number of particles with low kinetic energy than there are at a temperature of 40 $^0$C. On the right hand side of the point of intersection (high kinetic energy) the situation is the other way around. That is, the red line is now above the blue line. This shows that at the higher temperature of 40 $^0$C, there are a greater number of particles with high kinetic energy than there are at 30 $^0$C. So when the temperature increased from 30 $^0$C to 40 $^0$C, the slower moving particles gained energy and became faster moving particles. This is why the blue line (30 $^0$C) was above the red (40 $^0$C) at the lower kinetic energies and the red line above the blue line at the higher kinetic energies.

The above graph can be redrawn showing the activation energy on the horizontal axis. Now the particles represented by these graphs are REACTANT PARTICLES.



At 30 $^0$C, the shaded area under the graph (shown in blue) represents the number of reactant particles that have kinetic energy equal to or greater than the activation energy. So this blue shaded area shows the proportion of reactants at 30 $^0$C that are able to react at any instant during the reaction. Remember that the total area under the blue line represents all of the particles present at 30 $^0$C and the shaded part represents the number that are able to react.

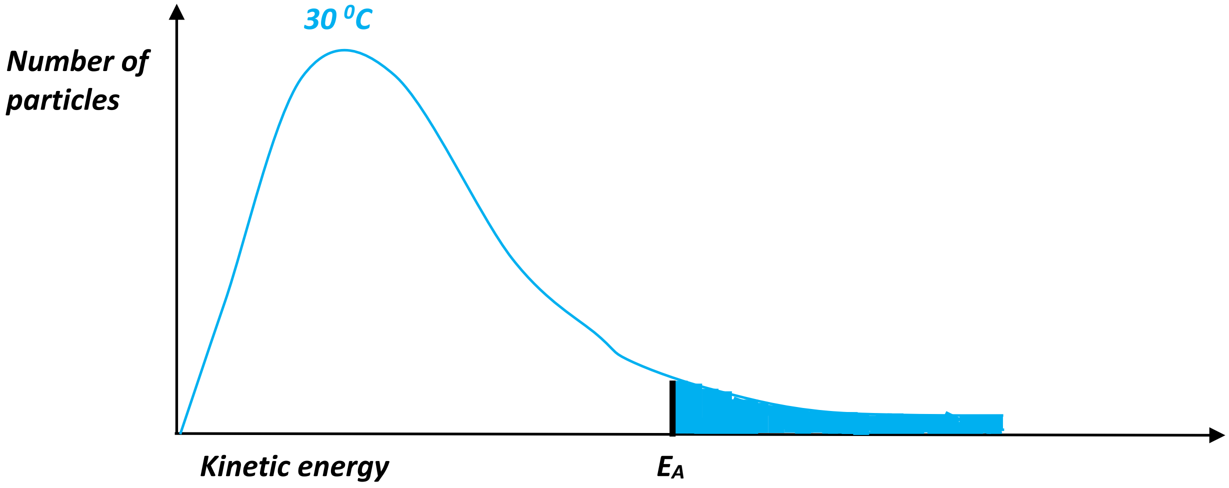
At 40 $^0$C the number of particles that possess kinetic energy that is either equal to or greater than the activation energy is represented by both **the red and blue shaded areas.** Since the red line is above the blue line at and beyond the $E_A$ on the horizontal axis, the area under this part of the line must also include the area under the blue line.

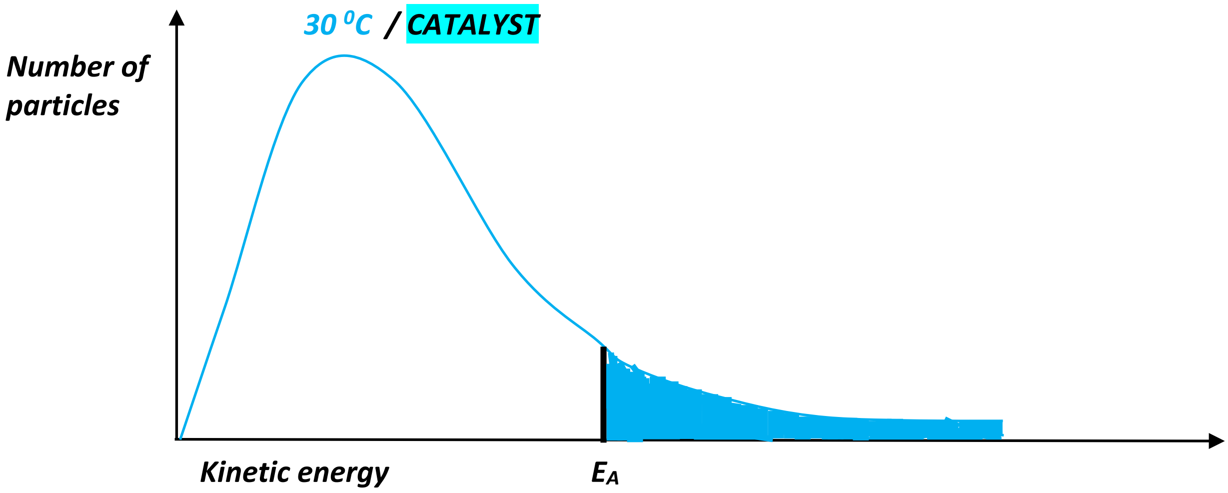
These 2 graphs clearly show that there is a greater proportion of reactant particles that are able to make successful collisions at 40 $^0$C than there are at 30 $^0$C.

- *The total area under the graph at 40 $^0$C is exactly the same as the area under the graph at*

*30 $^0$C. This has to be the case because increasing the temperature just makes the particles present gain kinetic energy and move faster. It does not add or take away particles.*

Maxwell – Boltzmann distributions can also be used to show how **catalysts** increase the proportion of reactant particles with sufficient energy to react. Since catalysts do not increase or decrease the kinetic energy of particles, the distribution of particles with different kinetic energies at a given temperature is identical whether a catalyst is present or not as can be seen in the graphs below.





The second graph shows that the temperature is still at 30 $^0$C but a catalyst has been added to the reactant particles. The catalyst has weakened the bonds in the reactants resulting in a lower activation energy for the reaction. As the activation energy is lower, the area under the graph corresponding to particles with kinetic energies that are either equal to or greater than the activation energy is greater than that for the first graph where no catalyst is present. Therefore the fraction of particles with sufficient energy to react is greater when a catalyst is present.

## Summary of reaction rates

- An increase in surface area and an increase in concentration will increase the frequency of total collisions and hence successful collisions between reactant particles. As a consequence the rate of reaction will increase.

- An increase in temperature will increase the frequency of total collisions and hence fruitful collisions between reactant particles. The proportion of successful collisions will also increase. These 2 factors will increase the rate of reaction. The second factor has a greater impact on the increase in the rate of reaction than the first factor.

- A catalyst will weaken the bonds in reactants resulting in a lowering of the activation energy required for the reaction. As a consequence the proportion of successful collisions will increase.

- A catalyst does not increase the kinetic energy of reactant particles so it does not cause an increase in the frequency of total collisions. It does however, increase the frequency of successful collisions. This is because increasing the proportion of successful collisions in a given amount of time results in a greater number of successful collisions in a given amount of time.

- The increase in the rate of a reaction is not necessarily proportional to the increase in the surface area, concentration, temperature or amount of catalyst added. For example, if the temperature of a reaction mixture doubles from 100 $^0$C to 200 $^0$C its rate may not double.

# CHAPTER 8 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
Which of the following actions will not increase the number of times in a 1 second time interval that reactant molecules will collide with each other?

- **A.** Increasing temperature and adding a catalyst.
- **B.** Adding a catalyst and increasing concentration.
- **C.** Increasing surface area.
- **D.** Adding **a** catalyst to gaseous mixture.

**Question 2**
When a mixture containing gaseous reactants is transferred to a container of smaller volume,

- **A.** the number of particles present increases.
- **B.** the total number of collisions remains the same but the frequency of successful collisions increases.
- **C.** the number of all collisions increases.
- **D.** the energy of the particles increases.

**Question 3**
When zinc granules are placed in 1.0 M $H_2SO_4$ solution, which of the following is not likely to increase the rate of the reaction?

- **A.** Adding a catalyst.
- **B.** Capturing the gaseous product in a gas syringe at very high pressure.
- **C.** Increasing the temperature of the $H_2SO_4$.
- **D.** Grinding the zinc granules into smaller sized particles.

**Question 4**
Sulfur trioxide can be produced by the oxidation of $SO_2$. The equation for this reaction is shown below.

$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)$

If the temperature of the reaction mixture is increased from 300 $^0$C to 500 $^0$C, 2 major things will happen:

1. The number of collisions between particles each second increases.
2. The fraction of collisions with kinetic energy above the activation energy increases.

Of these 2 factors,

- **A.** 2 is the only one that will increase the rate of the reaction.
- **B.** 1 and 2 will increase the rate of reaction to an equal extent.
- **C.** Both factors will cause an increase in the rate of the reaction but factor 1 has a greater impact on the increase in the reaction rate than factor 2.
- **D.** Both factors will cause an increase in the rate of the reaction but factor 1 has less of an impact on the increase in the reaction rate than factor 2.

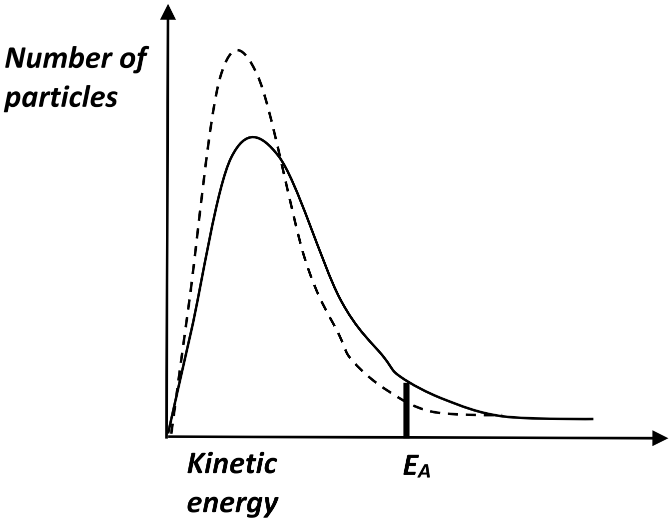
**Question 5**

The statement explaining the action of a catalyst that is incorrect is

**A.** Catalysts do not change the kinetic energy of particles.
**B.** Catalysts increase the proportion of fruitful collisions.
**C.** Catalysts can make reactant particles collide at angles that are more favourable for a chemical reaction.
**D.** Catalysts increase the number of collisions per unit time.

*Refer to the information below when answering questions 6 and 7.*

Each line on this graph shows the distribution of reactant particles with different kinetic energies at a particular temperature



**Question 6**

If the temperature of the particles shown by the broken line is 100 $^0$C, then the temperature of the particles shown by the solid line is

**A.** 50 $^0$C
**B.** 150 $^0$C.
**C.** 100 $^0$C
**D.** could be 100 $^0$C or 50 $^0$C.

**Question 7**

If a catalyst is added to the reaction mixture shown by the solid line,

**A.** the area under this line would increase.
**B.** the number of particles with higher kinetic energy would increase.
**C.** the number of particles with sufficient kinetic energy to cause a reaction will increase.
**D.** the shape of the line would start to resemble the shape of the broken line.

## Short Answers

**Question 1**
Use collision theory to explain the following:

**a.** Wood chips will burn more quickly than a log of wood of the same mass.

**b.** The decomposition of hydrogen peroxide,

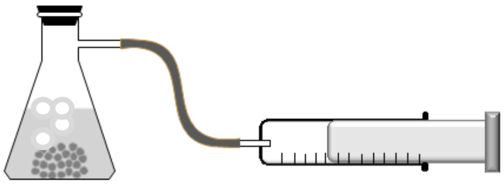
$2H_2O_2 \rightarrow 2H_2O + O_2$

will only occur in the presence of an $MnO_2$ catalyst at room temperature.

**c.** The souring of milk is much slower inside a fridge.

**Question 2**
The apparatus shown below is used to measure the rate of the reaction between marble chips ($CaCO_3$) and 20.0 mL of 0.20 M HCl. The equation for this reaction is shown below.

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$



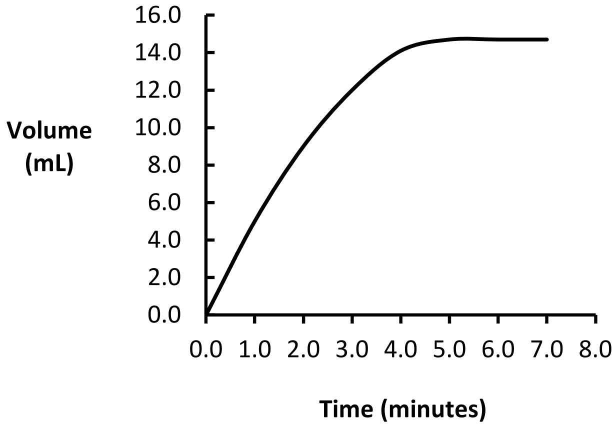
The $CO_2$ gas produced by the reaction is collected in a gas syringe at SLC conditions over a 5 minute period. The volume of $CO_2$ gas produced each minute during this time period is shown in the table below.

| Time (minutes) | Volume $CO_2$ (mL) |
|---|---|
| 0.0 | 0.0 |
| 1.0 | 5.0 |
| 2.0 | 9.0 |
| 3.0 | 12.0 |
| 4.0 | 14.1 |
| 5.0 | 14.1 |

**a.** Calculate the mass of $CaCO_3$ originally added to the flask. Assume that marble chips are pure $CaCO_3$ and that the HCl was in excess.

**b.** How did the rate of the reaction change during the 5 minute period of this reaction. Use collision theory to explain why the rate of the reaction changed in this way.

**c.** The graph of the time versus volume of $CO_2$ for this reaction is shown below.



The concentration of the HCl has been increased to 0.40 M. Draw a rough sketch of the graph using the axes above to show how the volume of $CO_2$ will change over time at this higher concentration.

**d.** Would the change in the rate of the reaction during the 5 minute period be the same if 40.0 mL 0.20 M HCl was used instead of 20.0 mL of 0.20 M HCl? You must support your answer with calculations.

**e.** Briefly describe another procedure that could be used to measure the rate of this reaction over a 5 minute period.

**f.** The activation energy of this reaction is less than the activation energy for the reverse reaction. Explain how this information can be used to justify that the temperature of this reaction mixture will increase during the 5 minute period.

**g.** A year 12 chemistry student looking over the results of this experiment stated that the volumes of $CO_2$ gas obtained at 4.0 minutes and 5.0 minutes were precise as they were both 14.1 mL. Do you agree with this student? Discuss. *You may need to refer to appendix 4.*

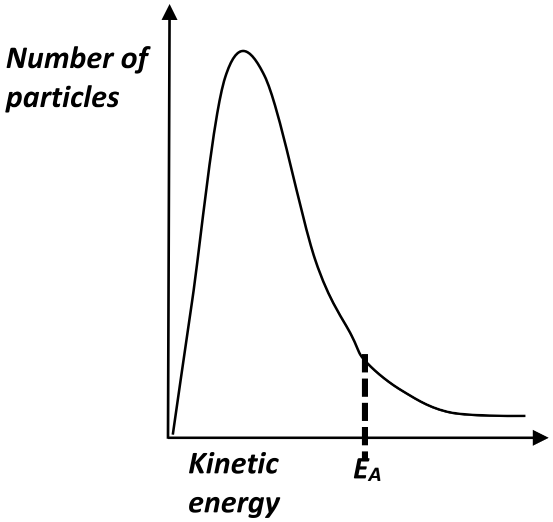
**h.** Give the dependent and independent variables for this experiment.

**i.** What is meant by the term, **valid results.** Give 3 variables that would need to be controlled in order to ensure the validity of the results if the procedure was performed multiple times.

**j.** Before this experiment was performed it was hypothesised that the volume of $CO_2$ gas produced over time would increase due to the increase in frequency of collisions between $CaCO_3$ and HCl particles. Comment on the accuracy of this hypothesis by referring to **collision theory.**

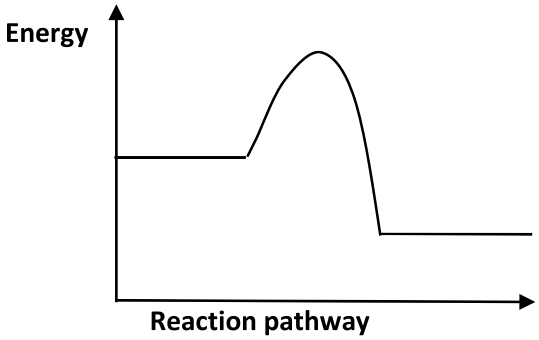
**Question 3.**

The distribution of the kinetic energy of particles of a reaction mixture at 120 $^0$C is shown below.



**a.** Make changes to this graph that would be consistent with the addition of a catalyst to the reaction mixture. Use the graph and the changes you made to explain the effect that the catalyst will have on the rate of the reaction.

**b.** The energy profile diagram for this reaction in the ABSENCE of a catalyst is shown below.



Make the necessary changes to this diagram to show the effect of a catalyst on the energy profile of the reaction.

# Chapter 9 – Equilibrium

So far in VCE chemistry all of the chemical reactions encountered have moved in the one direction. That is, from reactants to products. With the reactions that we have dealt with, if the moles of reactants are present in the ratio given by the balanced equation, all of the reactants are converted into products. If one of the reactants is in excess, all of the limiting reactant will be used up and some of the reactant that was in excess will remain unreacted. These reactions are said to go to **completion.**

It is possible however, for reactions to move in 2 directions. That is, they will start off converting reactants into products but once the products start to form, the products react with themselves to reform the reactants. That is, the reaction starts to go backwards. They simultaneously go from reactants to products and products to reactants. The rules of limiting and excess reactants do not apply to these reactions. These reactions are referred to as **EQUILIBRIUM REACTIONS.**

In order to understand equilibrium reactions it is useful to start off by investigating the reactions that we are most familiar with – those that go to completion.

- *It can be argued that a reaction involving an excess reactant does not reach completion because some of the excess reactant will be left behind. However, the reaction is complete in the sense that the moles of reactants used up are in accordance with the ratio given by the balanced equation. The term, incomplete reaction will be made clearer when equilibrium reactions are discussed.*

## Reactions that go to completion

2.0 moles of hydrochloric acid and 1.0 mole of $Na_2CO_3$ are placed in a 1.0 litre container. The container is filled up to the mark with distilled water. As a result the HCl is at a concentration of 2.0 M and the $Na_2CO_3$ is at a concentration of 1.0 M. The HCl and the $Na_2CO_3$ react with each other according to the following equation.

$$\begin{array}{lll} \underline{Na_2CO_3(aq)} & + \ \underline{2HCl(aq)} & \rightarrow \ 2NaCl(aq) + H_2O(l) + CO_2(g) \\ 1.0\text{ M} & \quad 2.0\text{ M} & \end{array}$$

According to the ratio given by the balanced equation, the moles of HCl present must be exactly double the moles of $Na_2CO_3$ present in order for a complete reaction to occur where all the reactants are used up. Therefore the 1.0 mole of $Na_2CO_3$ will completely react with the 2.0 moles of HCl. No reactants will be left unreacted. Only products will be present after the reaction is finished. The table on the next page shows this reaction occurring over a 5 second time frame.

$Na_2CO_3\,(aq) + 2HCl\,(aq) \rightarrow 2NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$

**Concentration of reactants (M)** **Concentration of products (M)**

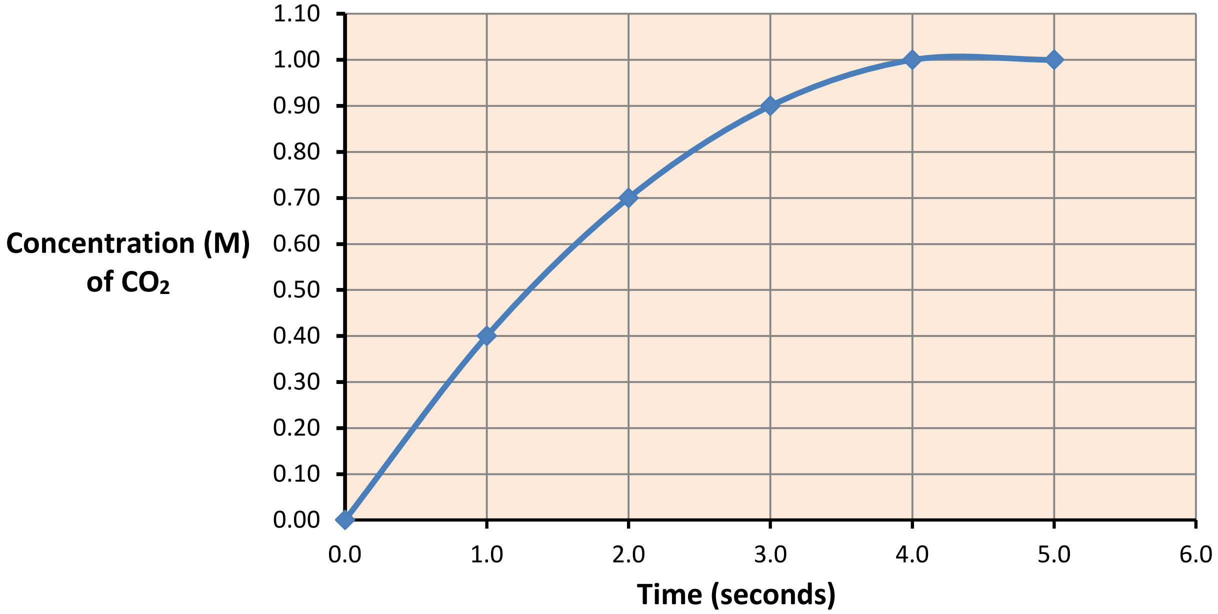
| Time (seconds) | $Na_2CO_3$ | HCl | NaCl | $H_2O$ | $CO_2$ |
|---|---|---|---|---|---|
| **0s** | 1.0M | 2.0M | 0M | 56M | 0M |
| **1s** | 0.60M (0.4 mol used) | 1.2M (0.8 mol used) | 0.80M | 56M | 0.40M |
| **2s** | 0.30M (0.7 mol used) | 0.60M (1.4 mol used) | 1.4M | 56M | 0.70M |
| **3s** | 0.10M (0.9 mol used) | 0.20M (1.8 mol used) | 1.8M | 56M | 0.9M |
| **4s** | 0M (1.0 mol used) | 0M (2.0 mol used) | 2.0M | 56M | 1.0M |
| **5s** | 0M (1.0 mol used) | 0M (2.0 mol used) | 2.0M | 56M | 1.0M |

- *As all the reactants and products of this reaction are in 1.0 L of water, the moles and concentration of each substance are the same value. For example, the 2.0 mol of HCl placed in the 1.0 L of water is equivalent to a concentration of 2.0 M*

  At time 0s, the concentration of $Na_2CO_3$ is 1.0 M and the concentration of HCl is 2.0 M. The concentration of the products, NaCl and $CO_2$ are both 0 M as the reaction has not started yet. Interestingly the concentration of the $H_2O$ is a massive 56M even though none of it has been made yet. We need to be aware that the reaction is occurring in water as all of the reactants are in aqueous solution. When water is a solvent, its concentration in all aqueous solutions is ***56 M.***

  At time 1 s, some of the reactants have been used up. Of the 1.0 mol of $Na_2CO_3$ that we started with, 0.40 mol has reacted leaving 0.6 mol that is unreacted (1.0 – 0.4 = 0.60 mol). This unreacted 0.60 mol of $Na_2CO_3$ is dissolved in 1.0 L of water so its concentration is 0.60 M. If 0.40 mol of $Na_2CO_3$ has reacted, then according to the ratio of the balanced equation, 0.4 x 2 = 0.80 mol of HCl must react with it. So of the 2.0 mol of HCl present at the start of the reaction, 0.80 mol has reacted leaving 1.2 mol unreacted (2.0 – 0.8 = 1.2 mol). This 1.2 mol is dissolved in 1.0 L of water so its concentration is 1.2 M. If 0.40 mol of $Na_2CO_3$ reacts, then according to the mole ratio 0.80 mol of NaCl and 0.40 mol of $CO_2$ must be produced.

This trend continues until the 4 second mark of the reaction where the remaining moles of reactants have been used up. Now the concentration of the reactants, $Na_2CO_3$ and HCl are both 0 M and the concentration of the products: NaCl is 2.0 M and the concentration of $CO_2$ is 1.0 M, representing a complete reaction. The graph below shows how the concentration of $CO_2$ is changed during the 5 second time interval of the reaction.



This graph (and table) clearly show that *the rate of $CO_2$ production slows down as the reaction approaches completion.* At the end of the first second 0.4 mol of $CO_2$ was produced. At the end of the following second the moles of $CO_2$ only increased by an extra 0.30 mol (0.40 to 0.70). At the end of the third second the moles of $CO_2$ only increased by an extra 0.20 mol (0.70 to 0.90). At the end of the fourth second the moles of $CO_2$ increased by 0.10 mol (0.90 to 1.00). Collision theory can be used to explain why the rate of this reaction slowed down as it approached completion.

- At the start of the reaction the concentration of reactants was at its highest because they hadn't reacted yet. So the frequency of successful collisions and hence rate of reaction, was at its highest at the start of the reaction.

- As the reaction continues the number of reactant particles decreases as they are converted into products. So with each passing second, there are less reactant particles remaining resulting in a decrease in the frequency of successful collisions and hence a decrease in the rate of reaction.

This is the case with all chemical reactions. As a chemical reaction proceeds, the number of reactant particles decreases as they are converted into products, leaving less reactant molecules available to collide with each passing second. So the rate of a reaction is always at its fastest when the reactants are first mixed together but it slows down as more and more reactants are converted into products.

# Reactions that don't go to completion

Now we will draw up a table similar to the one on page 141, for the reaction between nitrogen and hydrogen to produce ammonia.

1.0 mol of $N_2$ and 3.0 mol of $H_2$ gas are mixed together in a 1.0 litre vessel. As a consequence the concentration of $H_2$ is 1.0 M and the concentration of $H_2$ is 3.0 M. The equation for the reaction is

$\underline{N_2\,(g)} + \underline{3H_2\,(g)} \rightarrow 2NH_3\,(g)$
**1.0 M      3.0 M**

According to the ratio in the equation, the 1.0 mol of $N_2$ should completely react with the 3.0 mol of $H_2$ to produce 2.0 mol of $NH_3$. So like the reaction between $Na_2CO_3$ and HCl, this one should also go to completion. The table below shows the progress of this reaction over a 5 second time period.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

| | Concentration of reactants (M) | | Concentration of products (M) |
|---|---|---|---|
| **Time (seconds)** | **$N_2$** | **$H_2$** | **$NH_3$** |
| **0s** | 1.0M | 3.0M | 0M |
| **1s** | 0.85M (0.15 mole used) | 2.55M (0.45 mole used) | 0.30M |
| **2s** | 0.75M (0.25 mole used) | 2.25M (0.75 mole used) | 0.50M |
| **3s** | 0.70M (0.30 mole used) | 2.1M (0.9 mole used) | 0.60M |
| **4s** | 0.70M (0.30 mole used) | 2.1M (0.90 mole used) | 0.60M |
| **5s** | 0.70M (0.30 mole used) | 2.1M (0.90 mole used) | 0.60M |

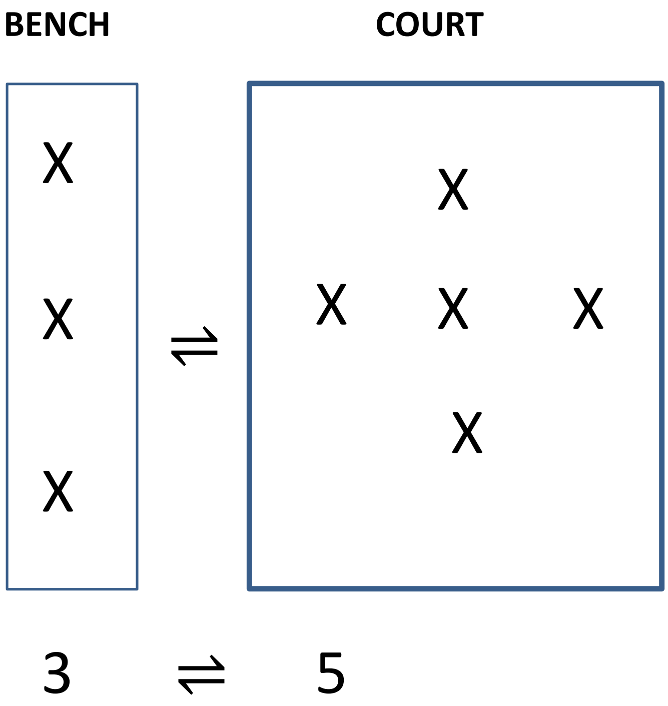
When reading this table, it is important to realise that the moles shown in red are the moles of the reactants that have been used up. When these moles are subtracted from the initial moles (0s), they give the moles and hence concentration of the reactant remaining. Eg. at 3s, 0.30 mol of $N_2$ has been used. The moles of $N_2$ left unreacted is 1.0 – 0.30 = 0.70 M

Initially at 0 seconds, there are 1.0 mol of $N_2$ and 3.0 mol of $H_2$ and no moles of $NH_3$ as the reaction has not started yet.

After 1 second, 0.15 mol of the 1.0 mol of $N_2$ has reacted leaving 0.85 mol of $N_2$ unreacted. The mol of $H_2$ required to react with this is 0.15 x 3 = 0.45 mol (using the mole ratio). The mol of $N_2$ remaining is 3.0 – 0.45 = 2.55 mol. The mol of $NH_3$ produced is 3 x 0.15 = 0.45 mol (using the mole ratio)

Up until the 3 second mark, the reactants continue to get used up and the products continue to increase as is expected. After this time however, a strange thing seems to happen. The reactants stop decreasing in concentration and the products stop increasing in concentration. The concentration of the unreacted $N_2$ remains at 0.70 M, the concentration of the $H_2$ remains at 2.1 M and the concentration of the $NH_3$ remains at 0.60 M. The reactants were supplied in the correct ratio for a complete reaction so it is expected that they should all get used up and the reaction reach completion. It is as if the reaction has just suddenly stopped. The reaction has not stopped. It has reached a state of EQUILIBRIUM. To understand what this means it might be a good idea to forget chemistry for a moment and look at a simpler example showing an equilibrium state.

In a game of basketball a team has 8 players. 5 of them are on the court playing and the other 3 are on the bench. During the course of the game which lasts about an hour, the number of players on the court will always be equal to 5 and the number of players on the bench will always be equal to 3. This can be described as an EQUILIBRIUM SYSTEM because at any given time during the game, the number of players on the bench is always EQUAL to 3 and the number of players on the court is always EQUAL to 5. It never deviates from those values. This system is illustrated below.



X = 1 PLAYER

Being in equilibrium does not mean that the number of players on the court and the bench has to equal the same value. It means that they will be equal to a constant value that doesn't change over time, i.e. 3 on the bench and 5 on the court in this example.

This system is known as a DYNAMIC EQUILIBRIUM because it involves movement. During the game it is very unlikely that the same 5 players will always be on the court and the same 3 players will always be on the bench. It is likely that the coach will replace players on the court with those on the bench.

If 1 player from the court goes to the bench, 1 player from the bench will go onto the court.
If 2 players from the court go to the bench, 2 players from the bench will go onto the court.
If 3 players from the court go to the bench, 3 players from the bench will go onto the court.

<u>This shows that the rate of movement from the bench onto the court is always equal to the rate of movement from the court onto the bench.</u> In this way the number of players on the court will always equal 5 and the number of players on the bench will always equal 3.

This system can be represented using 2 way arrows ($\rightleftharpoons$) to represent the movement that is **occurring in 2 directions and at the same rate.**

$$3 \quad \rightleftharpoons \quad 5$$

**Bench** **Court**

A similar situation applies to the reaction between $N_2$ and $H_2$. After 3 seconds, this reaction reached a state of **DYNAMIC EQUILIBRIUM.** When the 3 second mark in this reaction was reached, every time 1 $N_2$ and 3 $H_2$ molecules reacted to produce 2 $NH_3$ molecules, at the same time, 2 $NH_3$ molecules reacted with each other to produce 1 $N_2$ and 3 $H_2$ molecules. That is, 2 $NH_3$ molecules have reacted with each other and REPLACED the 1 $N_2$ and 3 $H_2$ molecules that had previously reacted. So the backwards reaction continuously replaces the reactants and the forwards reaction continuously replaces the products. When the $N_2$ and $H_2$ molecules react they are like the players on the bench moving onto the court. The conversion of the $NH_3$ back into $N_2$ and $H_2$ is like the players on the court replacing the players on the bench. *<u>Since the forward and backward reactions are occurring simultaneously and at the same rate, the concentration of the reactants and products will remain at constant values.</u>*

As long as this reaction between $N_2$ and $H_2$ remains in equilibrium, the concentration of $N_2$ will always equal 0.70 M, the concentration of $H_2$ will always equal 2.1 M and the concentration of $NH_3$ will always equal 0.60 M.

- Reactions that reach a state of equilibrium are often referred to as a SYSTEM.
- Reactions in a state of equilibrium will maintain a constant temperature.
- If an equilibrium system is in the gaseous state, the constant values of concentration in the reactants and products results in a constant pressure.

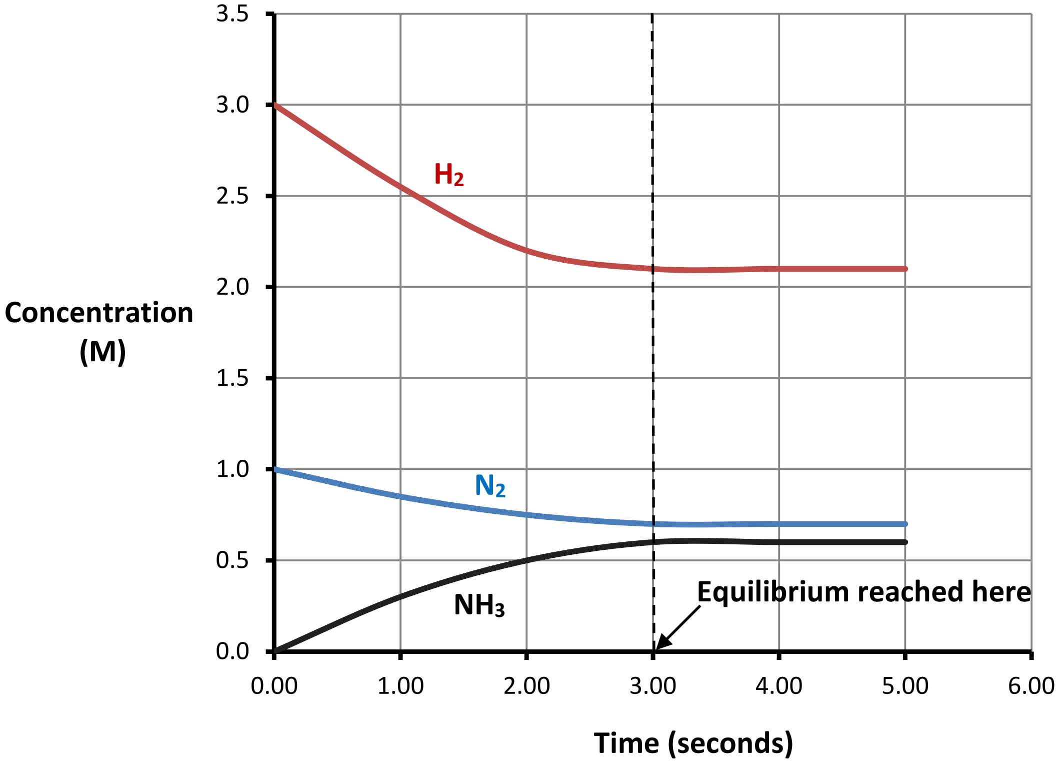
It is important to realise that the reverse reaction is occurring well before a reaction reaches equilibrium. When the $N_2$ and $H_2$ were initially mixed together at 0s, only the forward reaction was able to occur as there were no $NH_3$ molecules present yet. Once the forward reaction starts to make $NH_3$, the $NH_3$ molecules are able to collide with each other and reform the $N_2$ and $H_2$

molecules. However, at this early stage the concentration of the $NH_3$ is quite low so the frequency of successful collisions between $NH_3$ molecules is also low resulting in the rate of the reverse reaction being much slower than the rate of the forward reaction. This results in an overall forward reaction so the concentration of the reactants decreases and the concentration of the products increases. As the reaction continues the rate of the forward reaction gets slower as the concentration of the reactants decreases (↓ frequency of successful collisions) and the rate of the forward reaction gets faster (↑ frequency of successful collisions) as the concentration of the products increases. Eventually the rate of the reverse reaction becomes equal to the rate of the forward reaction and the system reaches equilibrium.

The reaction showing the formation of ammonia must now be written using the 2 way equilibrium arrows.

**$N_2\,(g) + 3H_2\,(g) \rightleftharpoons NH_3\,(g)$**

The graph below shows the changes in concentration of the reactants and products over time as the reaction approaches equilibrium.



- This graph shows that the reaction rate at the start was at its highest. This is evident by the fact that the lines showing the decrease in $N_2$ and $H_2$ concentration and increase in $NH_3$ concentration are at their steepest at the start of the reaction. The lines start to level off as time goes by.

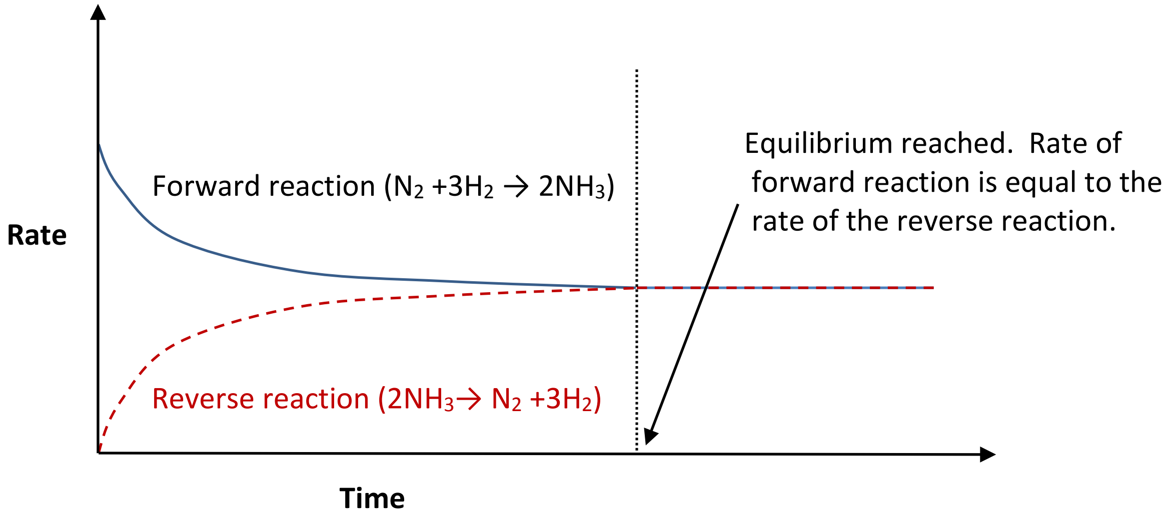
- When the reaction reaches equilibrium (at 3 seconds) the lines representing the concentration of $H_2$, $N_2$ and $NH_3$ all level off and become horizontal. This shows that at equilibrium the concentration of the reactants and products remain at a constant value.

- When the reaction is at equilibrium the fact that the concentrations of the reactants and products doesn't change gives the impression that the reaction has stopped. Remember that at equilibrium the rate of the forward and backward reaction are occurring at the same rate which causes the concentrations of the reactants and products to remain at a constant value.

- If you look closely at this graph you will notice that the concentration of the $H_2$ is decreasing at 3 times the rate of the decrease in concentration of the $N_2$. This is due to the MOLE RATIO in the equation. According to the ratio, if 1.0 mol of $N_2$ reacts then 3.0 mol (3 times more) of $H_2$ will react. So at any given time during this reaction, the decrease in moles of the $H_2$ will be 3 times the decrease in moles of the $N_2$.

- A close look at the graph also shows that the increase in concentration of the $NH_3$ is slightly greater than the decrease in concentration of the $N_2$ but slightly lower than the decrease in concentration of the $H_2$. Once again this is due to the mole ratio in the balanced equation. According to the ratio, if 1.0 mol of $NH_3$ is produced, 0.50 mol (1.0 x ½ ) of $N_2$ will react and 1.50 mol (1 x 3/2 ) of $H_2$ will react.

A **time** versus **rate** graph can be used to show that a reaction is in equilibrium. The graph below shows how the rate of the forward and reverse reaction changes as the reaction between $N_2$ and $H_2$ reaches equilibrium.



- This graph shows that initially (right at the start of the reaction), the rate of the forward reaction is quite high as the reactants have just been added and they are at their highest concentration. The rate of the reverse reaction is zero as no products have been made yet so the reverse reaction cannot happen.

- After the reaction has started, the forward reaction gradually decreases in rate as $N_2$ and $H_2$ molecules are converted into $NH_3$. This reduces the concentration of the reactants, $N_2$ and $H_2$, resulting in a lower frequency of successful collisions and hence slower reaction rate.

- After the reaction has started, the rate of the reverse reaction gradually starts to increase. This is because the forward reaction is occurring at a much faster rate which causes the concentration of $NH_3$ to increase. As a consequence the frequency of successful collisions between $NH_3$ molecules increases causing an increase in the rate of the reverse reaction.

- As time goes on the decrease in the rate of the forward reaction slows down. The increase in the rate of the forward reaction also slows down. Eventually both rates become EQUAL and the system reaches EQUILIBRIUM.

- So when 2 reactants are mixed together, the rate of the forward reaction will always be greater than the rate of the reverse reaction as the reaction approaches equilibrium. The reaction is said to approach equilibrium via the forward reaction.

So in summary, an **equilibrium** reaction is one where,

- The forward and reverse reactions are occurring simultaneously and the rate of the reverse reaction is equal to the rate of the forward reaction.

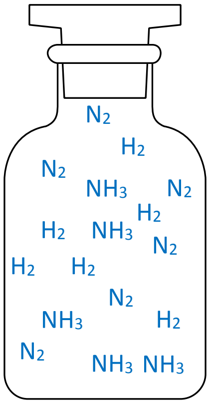
- The concentration of the reactants and products will always remain at a constant value due to the fact that the rate of the reverse and forward reactions are equal. *This does not mean that the concentration of all reactants and products are equal to the same value. As was seen with the example showing the formation of* $NH_3$*, the equilibrium concentration of* $N_2$ *was 0.70 M,* $H_2$ *was 2.1 M and* $NH_3$ *was 0.60 M. The term "constant value" means that the equilibrium concentration of the reactants and products will remain at values that do not change over time, these values however, are likely to be different from each other.*

- Other conditions and properties such as temperature, pressure, colour, pH etc. will remain at constant levels when a system is at equilibrium.

# Why do some reactions reach equilibrium?

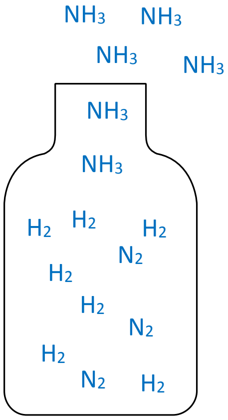
Not all reactions reach equilibrium. A reaction will only reach a state of equilibrium if it is in a **CLOSED SYSTEM.** That is, the reaction is occurring in a vessel that is closed where the reactants and products are contained and unable to escape each other. In such an environment the products stay in contact with each other and are able to collide and react to reform the reactants. The equilibrium reaction described above showing the formation of ammonia ($NH_3$) could occur in a gas jar that has been closed with a stopper. The $NH_3$ molecules are able to make contact with each other and react to reform the $N_2$ and $H_2$ reactants. The $N_2$ and $H_2$ are also able to react to reform the $NH_3$ and the system will reach a state of equilibrium.

**Closed system.** Reactants and products are trapped in a confined space and are forced to make contact with each other.



If the stopper is removed from this gas jar, an **OPEN SYSTEM** is created and it is possible for molecules to escape. If there was a way to only allow the $NH_3$ molecules to escape, this reaction would reach completion. This is because the $N_2$ and $H_2$ molecules would continue to react to produce $NH_3$ but as the $NH_3$ molecules are escaping the bottle they are unable to react with each other to reform the $N_2$ and $H_2$.

**Open system.** $NH_3$ products are allowed to escape and are unable to reform the reactants. This reaction can only move forward and will reach completion. The equation must be written using a one way arrow.



$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$

The reaction between $Na_2CO_3$ and HCl described on page 141 was in an open system. The 1.0 L container was open allowing the $CO_2$ produced to bubble out of the solution and escape. As a consequence it was not possible for a backwards reaction to occur as all products, NaCl, $H_2O$ and $CO_2$ need to remain in contact in order to reform the reactants. If the container was sealed in some way a closed system would be made and the $CO_2$ produced could be trapped and forced back into the solution and allowed to react with the NaCl and $H_2O$. Under these circumstances an equilibrium system could be made. Many reactions occurring in solution have the potential to reach equilibrium as the water is a bit like a container and acts a closed system forcing the reactants and products to remain in contact with each other. If a reaction in aqueous solution produces a gas however, it is likely that the gas will escape and the reaction will go to completion.

## The Equilibrium Constant (K or Kc)

**The equilibrium constant (K),** is a fraction that has the molar concentration of the products as the numerator and the molar concentration of the reactants as the denominator when a reaction is in a state of the equilibrium.

$$K = \frac{[PRODUCTS]}{[REACTANTS]} \qquad [\,] = \text{molar concentration (M)}$$

Let's calculate the equilibrium constant for the reaction between $N_2$ and $H_2$:

**$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$**

First of all we must derive the **equilibrium expression.** This involves placing the formula of the products in square brackets and raising them to the power of their coefficients in the equation. If there are 2 or more products in the equation they must be multiplied together. The same is done to the reactants but they are placed on the denominator of the fraction. Here is the expression for the reaction between $N_2$ and $H_2$:

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} \quad M^{-2}$$

The equilibrium expression for this reaction is given units, $M^{-2}$. The units are derived by placing "M" into the square brackets and simplifying the expression using the first and second index laws. That is, when multiplying numbers with the same base the indices are added together and when dividing numbers with the same base the indices are subtracted.

$$\frac{M^2}{M \times M^3}$$

$$= \frac{M^2}{M^4}$$

$$= M^{2-4}$$

$$= M^{-2}$$

Now we can work out the actual numerical value of the equilibrium constant. To do this we must substitute the molar equilibrium concentrations of the reactants and products into the equilibrium expression. From page 143 the equilibrium concentrations for the reaction between $N_2$ and $H_2$ were

$[NH_3]$ = 0.60 M
$[N_2]$ = 0.70 M
$[H_2]$ = 2.1 M

$$K = \frac{0.60^2}{0.70 \text{ x } 2.1^3} = 0.0555 = 0.056 \text{ M}^{-2}$$

- The units ($M^{-2}$ in this example) must be included when giving the equilibrium constant.

## What does the equilibrium constant tell us?

The reason why the equilibrium constant is calculated for an equilibrium reaction is because it gives an indication of the EXTENT OF THE REACTION. The meaning of the term, extent of the reaction, can be looked at in a number of different ways.

- The extent of a reaction refers to how many of the reactants were converted into products when a reaction reached equilibrium.

- The extent of a reaction refers to how far the forward reaction moved when equilibrium was reached.

- The extent of the reaction refers to what proportion of reactants were converted into products when equilibrium was reached.

- The extent of the reaction refers to the proportion of products present compared to reactants present in a mixture when a reaction is in a state of equilibrium.

The reaction between $N_2$ and $H_2$ occurred to a relatively low extent. When equilibrium was reached, 0.70 M of the original 1.0 M of $N_2$ remained and 2.1 M of the original 3.0 M of $H_2$ remained. So less than half of the reactants were converted into products when the reaction reached equilibrium. Under different conditions of temperature, the extent of this reaction could be higher or lower . For example if the extent of the reaction was very high, almost all of the $N_2$ and $H_2$ would have been converted into products when equilibrium was reached. If the extent of reaction was very low , only a very small number of reactants would have been converted into products when equilibrium was reached.

The value of the equilibrium constant (K) shows if the extent of the reaction is HIGH or LOW. As the equilibrium constant is a fraction with products in the numerator and reactants in the denominator,

- **A low K** shows a reaction that has occurred to a **small extent**.
- **A high K** shows a reaction that has occurred to a **large extent**.

Let's use the reaction between $N_2$ and $H_2$ to show how the equilibrium constant can be used to show the extent of a reaction. If the reaction between $N_2$ and $H_2$ occurred to a **LOW EXTENT** the equilibrium concentrations of the reactants and products might be,

$[N_2] = 0.985$ M
$[H_2] = 2.955$ M
$[NH_3] = 0.030$ M

- *These equilibrium concentrations are based on equilibrium being reached after 0.015 mol of $N_2$ reacted and 0.045 mol of $H_2$ reacted.*

So only a very small amount of reactants were converted into products when equilibrium was reached. Of the original 1.0 M of $N_2$, 0.985 M still remains (almost all of it). Of the original 3.0 M $H_2$, 2.955 M still remains. As hardly any of the $N_2$ and $H_2$ reacted when equilibrium was reached, the concentration of the product, $NH_3$, at equilibrium must be very low – 0.03 M.

$$K = \frac{0.030^2}{0.985 \times \ 2.955^3} = 0.000035411 = 3.5 \times 10^{-5}\ M^{-2}$$ (LOW K = LOW EXTENT OF REACTION)

As you would expect the calculation of K is very low as the concentration of the products at the top of the fraction are very low and the concentration of reactants on the bottom of the fraction are very high in comparison.

If the reaction between $N_2$ and $H_2$ occurred to a **LARGE EXTENT** the equilibrium concentrations of the reactants and products might be,

$[N_2] = 0.0050$ M
$[H_2] = 0.015$ M
$[NH_3] = 1.99$ M

- *These equilibrium concentrations are based on equilibrium being reached after 0.995 mol of $N_2$ reacted and 2.985 mol of $H_2$ reacted.*

$$K = \frac{1.99^2}{0.0050 \times \ 0.015^3} = 234{,}672{,}592.6 = 2.3 \times 10^{8}\ M^{-2}$$ (HIGH K = HIGH EXTENT OF REACTION)

As you would expect the calculation of K is very high as the concentration of the products at the top of the fraction are very high and the concentration of reactants on the bottom of the fraction are very low. This reaction almost went to completion when equilibrium was reached.

When equilibrium constants are given, it is common to see the temperature of the system recorded as well. This is because the equilibrium constant of a reaction will change when the temperature is changed. This will be explored later in this chapter.

❖ The equilibrium constant gives NO INDICATION of the RATE of a reaction. A system with a high K value or a low K value could be reacting quickly or slowly.

## Worked Example 1

A sealed 3.0 L flask contains an equilibrium mixture consisting of 0.142 mol of $SO_3$, 0.630 mol of $SO_2$ and 0.331 mol of $O_2$ at a temperature of 980 $^0$C. Calculate the equilibrium constant for this system if the equation for the reaction is

$2SO_2\ (g)\ +\ O_2\ (g)\ \rightleftharpoons\ 2SO_3\ (g)$

## Worked Example 1 Solutions

First of all write out the expression for this reaction.

$$K = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]} \quad M^{-1}$$

Then calculate the equilibrium concentration for the reactants and products using the formula

$$C = \frac{n}{V}$$

$$[SO_3] = \frac{0.142}{3.0} = 0.04733\ M$$

$$[SO_2] = \frac{0.630}{3.0} = 0.210\ M$$

$$[O_2] = \frac{0.331}{3.0} = 0.11033\ M$$

Now substitute the equilibrium concentrations into the equilibrium expression.

$$K = \frac{0.04733^2}{0.210^2 \text{ x } 0.11033} = 0.46041 = 0.46\ M^{-1}$$

## Worked Example 2

Sulfur dioxide gas and oxygen gas can react according to the equation,

$2SO_2\ (g)\ +\ O_2\ (g)\ \rightleftharpoons\ 2SO_3\ (g)$

An empty 2.00 L bottle is filled with 1.50 mol of $SO_2$ and 2.00 mol of $O_2$. The mixture is allowed to reach equilibrium and analysis shows that the moles of $SO_2$ remaining in the mixture is 0.846 mol. Calculate the equilibrium constant for this reaction.

## Worked Example 2 Solutions

At first impression this question seems exactly like the previous example. If you read this question carefully however, you will notice a significant difference. In worked example 1 the moles of $SO_2$, $O_2$ and $SO_3$ were all clearly at equilibrium. With this example, the 1.50 mol of $SO_2$ and 2.00 mol of $O_2$ are not at equilibrium. They are the initial moles that have just been placed in the bottle. They have not had a chance to react so there is no possible way that they are equilibrium moles. We are told later that the equilibrium moles of the $SO_2$ is equal to 0.846 mol. In order to calculate the equilibrium constant we need to calculate the **equilibrium moles of $O_2$ and $SO_2$.** The best way to do this is to use a table like the one below.

| | $2SO_2$ + | $O_2$ $\rightleftharpoons$ | $2SO_3$ |
|---|---|---|---|
| n (initial) | 1.50 mol | 2.00 | 0 |
| n (reacted/produced) (↓) (↑ ) | 1.50 – 0.846 = 0.654 ↓ | 0.654 x ½ = 0.327 ↓ | 0.654 ↑ |
| n (equilibrium) | 0.846 mol | 2.00 – 0.327 = 1.673 mol | 0 + 0.654 = 0.654 mol |
| [equilibrium] C = $\frac{n}{V}$ | $\frac{0.846}{2.00}$ = 0.423 M | $\frac{1.673}{2.00}$ = 0.8365 M | $\frac{0.654}{2.00}$ = 0.327 M |

The first part of the table, n (initial), just shows the moles that were present right at the start before the reaction began. The question only mentioned that 1.50 mol of $SO_2$ and 2.00 mol of $O_2$ were placed in the bottle. Therefore the initial moles of $SO_3$ must be zero as it is a product and the reaction has not started yet.

The second part of the table, n (reacted/produced) should be ignored for now. Instead, we should go to the third row showing the moles at equilibrium.

We are told that the moles of $SO_2$ at equilibrium are 0.846 mol. As the initial moles of $SO_2$ was equal to 1.50 mol and the moles left at equilibrium are equal to 0.846 mol, it can be concluded that the moles of $SO_2$ that reacted when equilibrium was reached was , 1.50 – 0.846 = 0.654 mol. **So of the 1.50 mol of $SO_2$ present at the start of the reaction, 0.846 mol has reacted leaving an unreacted amount of 0.654 mol that is present at equilibrium.**

So in the n (reacted/produced) part of the table, we show that 0.654 mol of the $SO_2$ reacted by placing a down arrow (0.654 ↓) beside it to show that this number of moles was taken away from the initial amount.

If 0.654 mol of $SO_2$ reacted then according to the ratio of the equation, the mol of $O_2$ that reacted = ½ x 0.654 = 0.327 mol. This 0.327 mol must also be shown with a downward arrow as this amount is taken away from the initial moles of $O_2$. **So of the 2.00 mol of $O_2$ present at the start of the reaction, 0.327 mol of it reacted. The unreacted mol of $O_2$ present at equilibrium is therefore equal to 2.00 – 0.327 = 1.673 mol.**

- ❖ When using this table the mole ratio can only be applied to the moles that are either reacted or produced. NEVER apply stoichiometry to the MOLES PRESENT AT EQUILIBRIUM. As is shown in the table these values depend on the initial moles of reactants and products which have no pattern or relationship with the coefficients in the balanced equation.

The initial moles of the $SO_3$ present was zero. If 0.654 mol of $SO_2$ and 0.327 mol of $O_2$ reacted, then according to the ratio the moles of $SO_3$ produced must be equal to 0.654 mol which is shown with an upwards arrow as this amount is made and added to the initial moles of $SO_3$. The calculation of the moles of $SO_3$ produced can be based on the reacted moles of $SO_2$ or $O_2$:

n ($SO_3$) produced = n ($SO_2$) reacted
= 0.654 mol

OR

n ($SO_3$) produced = n ($O_2$) reacted x 2
= 0.327 x 2 = 0.654 mol

We have completed the hardest part of the task. Now the calculation of the equilibrium constant is the same as the previous example. The moles at equilibrium are divided by the volume of the bottle to calculate the molar concentration of the reactants and products which are finally substituted into the equilibrium expression to calculate the equilibrium constant for the reaction.

$$K = \frac{0.327^2}{0.423^2 \times 0.8365} = 0.7144 = 0.714\ M^{-1}$$

## Concentration Fraction / Reaction Quotient (Q)

The concentration fraction is calculated in exactly the same way as the equilibrium constant, however, it is the fraction [products/[reactants] when the system is not at equilibrium. The table on page 143 showed that when the reaction was at equilibrium, the $N_2$ concentration was 0.70 M, the $H_2$ concentration was 2.1 M and the $NH_3$ concentration was 0.60 M. This table also shows that at the 2 second mark before the reaction was at equilibrium, the $N_2$ concentration was 0.75 M, the $H_2$ concentration was 2.25 M and the $NH_3$ concentration was 0.50 M. As these concentrations are not at equilibrium, if they are substituted into the equilibrium expression they will give the concentration fraction or quotient, not the equilibrium constant (K):

$$Q = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} \quad M^{-2}$$

$$Q = \frac{0.50^2}{0.75 \text{ x } \ 2.25^3} = 0.029264 = 0.029 \ M^{-2}$$

### How is the concentration fraction used?

The concentration fraction has 2 uses.

1. It can show whether or not a reaction is at equilibrium.
2. If a reaction is not at equilibrium it can show whether the reaction will need to move in the forward or backwards direction to attain equilibrium.

Worked example 3 will show how the concentration fraction is used.

### Worked Example 3

At 705 K the K value for the reaction, $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$, is equal to 48.7. Analysis of a reaction mixture of $H_2$, $N_2$ and HI at 705 $^0$C yields the following results.

$[H_2]$ = 1.25 M
$[I_2]$ = 0.765 M
[HI] = 0.15 M

Is this mixture at equilibrium? If not, will the reaction attain equilibrium by the forward or reverse reaction?

## Worked Example 3 Solutions

First of all calculate Q.

$$Q = \frac{[HI]^2}{[H_2] \times [I_2]}$$

$$Q = \frac{0.15^{2}}{1.25 \times 0.765} = 0.023529 = 0.024$$

In this example there are no units for Q because when "M" is substituted into the expression they cancel out.

$$\frac{M^2}{M \times M} = \frac{M^2}{M^2} = M^{2-2} = M^0 = 1$$

The value of Q (0.024) is less than the value of K (48.7) so the reaction is not at equilibrium. In order to get to equilibrium, the concentration fraction of 0.024 needs to change to the larger value of 48.7. In order to do this, the [products] at the top of the fraction must get larger and the [reactants] at the bottom of the fraction must get smaller. Therefore this reaction needs to move in the FORWARD direction to get to equilibrium. As the reaction moves in the forward direction, reactants are converted into products so the concentration of the products in the numerator get larger and the concentration of the reactants in the denominator get smaller, resulting in a higher Q.

- *It is likely that in this example, the reactants had just been mixed together and the reaction had not had sufficient time to get to equilibrium. So for the reaction to get to equilibrium it just needs to keep on moving in the forward direction.*

## Worked Example 4

At 705 K the K value for the reaction, $H_2$ (g) + $I_2$ (g) $\rightleftharpoons$ 2HI (g), is equal to 48.7. Analysis of a reaction mixture of $H_2$, $N_2$ and HI at 705 $^0$C yields the following results.

$[H_2] = 0.0255$ M
$[I_2] = 0.1175$ M
$[HI] = 1.59$ M

Is this mixture at equilibrium? If not, will the reaction attain equilibrium by the forward or reverse reaction?

## Worked Example 4 Solutions

First of all calculate Q.

$$Q = \frac{[HI]^2}{[H_2] \times [I_2]}$$

$$Q = \frac{1.59^{2}}{0.0255 \times 0.1175} = 843.75 = 844$$

Q (844) is larger than K (48.7) so the system is not at equilibrium. In order to get to equilibrium, the concentration fraction of 844 needs to change to the smaller value of 48.7. In order to do this, the [products] at the top of the fraction must get smaller and the [reactants] at the bottom of the fraction must get larger. Therefore this reaction needs to move in the BACKWARDS direction to get to equilibrium. As the reaction moves in the backwards direction, products are converted into reactants, causing the concentration of the products in the numerator to get smaller and the concentration of the reactants in the denominator to get larger, resulting in a lower Q.

- As Q was larger than K, the situation in this example must be different to the situation in worked example 3. If the system starts with only reactants as was the case with worked example 3, then the reaction has to move forward until the fraction of products over reactants equals the K value. So Q will have to start at zero and the reaction will only be able to move in the forward direction, causing Q to get larger and larger until it equals the K value of 48.7. It is impossible for the reaction to keep moving forward causing the fraction to get greater than K. A reaction will always try to re-establish the K value, it will never move past it provided the temperature does not change. So in this example it is likely that initial amounts of $H_2$, $I_2$ and the product HI were present causing the concentration fraction, products/reactants, to be higher than the K value.

## MANIPULATING EQUATIONS AND THE EQUILIBRIUM CONSTANT (K)

**If an equation is reversed (written backwards) K will be the reciprocal (inverse) of the original K value.**

This is because the equation will be the reverse of the original equation. This will tip the original K fraction upside down as what used to be the reactants are now the products and vice versa. So if the original K was 0.296 $M^{-2}$, the reciprocal will be $\frac{1}{0.296}$ = 3.3784 = 3.38 $M^2$

The units will also change because the fraction is tipped upside down:

Reciprocal of $M^2 = \frac{1}{M^2} = M^{-2}$

Let's explore this in more detail by looking at the following equilibrium mixture.

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$[N_2] = 2.00M$
$[H_2] = 3.00M$
$[NH_3] = 4.00M$

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} \quad M^{-2}$$

$$K = \frac{4.00^2}{2.00 \times 3.00^3} = 0.296296 = 0.296\ M^{-2}$$

If the equation is reversed:

$2NH_3\,(g) \rightleftharpoons N_2\,(g) + 3H_2\,(g)$

$$K = \frac{[N_2] \times [H_2]^3}{[NH_3]^2}\ M^2$$

$$K = \frac{2.00 \times 3.00^3}{4.00^2} = 3.375 = 3.38\ M^2$$

Calculation of the units:

$$\frac{M \times M^3}{M^2} = \frac{M^4}{M^2} = M^{4-2} = M^2$$

The K value for the reverse reaction (3.38 $M^2$) is the reciprocal of the original K value (0.296$M^{-2}$).

**If the coefficients in a balanced equation are doubled, the new K will be the square of the original K.**

If the coefficients in the equation are doubled, then the molar concentrations of the reactants and products will be raised to values that are double what they were before. **Mathematically this will cause the new K to be the square of the original K.** Consider the following equilibrium mixture as an example.

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$[N_2] = 2.00M$
$[H_2] = 3.00M$
$[NH_3] = 4.00M$

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}\ M^{-2}$$

$$K = \frac{4.00^2}{2.00 \times 3.00^3} = 0.296296 = 0.296\ M^{-2}$$

If the coefficients in the equation are doubled:

$2N_2\,(g) + 6H_2\,(g) \rightleftharpoons 4NH_3\,(g)$

The new K expression will be

$$K = \frac{[NH_3]^4}{[N_2]^2 \times [H_2]^6}\ M^{-4}$$

$$K = \frac{4.00^4}{2.00^2 \times 3.00^6} = 0.08779 = 0.0878\ M^{-4}$$

Calculation of the units:

$$\frac{M^4}{M^2 \times M^6} = \frac{M^4}{M^8} = M^{4-8} = M^{-4}$$

The original units, $M^{-2}$ are squared, $(M^{-2})^2 = M^{-2\times2} = M^{-4}$

The new K, 0.0878 $M^{-4}$, is the square of the K value for the original equation, 0.296 $M^{-2}$.
$0.296^2 = 0.0878$

If the coefficients in a balanced equation are tripled (×3), the new K will be the cube (raised to the power of 3) of the original K. If the coefficients in a balanced equation are quadrupled (×4), K will be the original K value raised to the power of 4 etc…………

**If the coefficients in a balanced equation are halved, K will be the square root of the original K value.**

Halving the coefficients means that the concentration of the reactants and products in the equilibrium expression will be raised to values that are half those of the original expression. **Mathematically this will cause the new K to be the square root of the original K.** Consider the following equilibrium mixture as an example.

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$[N_2] = 2.00M$
$[H_2] = 3.00M$
$[NH_3] = 4.00M$

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} \quad M^{-2}$$

$$K = \frac{4.00^2}{2.00 \times 3.00^3} = 0.296296 = 0.296\ M^{-2}$$

If the coefficients in the equation are halved:

$½\,N_2\,(g) + 1½\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

$$K = \frac{[NH_3]}{[N_2]^{0.5} \times [H_2]^{1.5}} \quad M^{-1}$$

$$K = \frac{4.00}{2.00^{0.5} \times 3.00^{1.5}} = 0.54433 = 0.544\ M^{-1}$$

Calculation of the units:

$$\frac{M}{M^{0.5} \times M^{1.5}} = \frac{M}{M^2} = M^{1-2} = M^{-1}$$

The new K, 0.544 $M^{-1}$, is the square root of the original K, 0.296 $M^{-2}$

$\sqrt{0.296} = 0.544$

## Worked Example 5

Consider the equation below.

$A + B \rightleftharpoons 2C \quad K = 2.4$

What will be the value of K for the equation shown below?

$C \rightleftharpoons \frac{1}{2}A + \frac{1}{2}B$

## Worked Example 5 Solutions

The new equation has been derived by **reversing** the original equation and **halving** the coefficients. Therefore the K of the new equation will be the **reciprocal** and the **square root** of the original K.

$K = \frac{1}{\sqrt{2.4}} = 0.645497 = 0.65$

- *Be careful not to confuse the rules for determining the K value when equations are manipulated with the rules used for determining ΔH. For example when the coefficients of an equation are doubled, the new K will be the square of the original K but the new ΔH will be DOUBLE the value of the original ΔH. Refer to page 75 of chapter 6.*

# Le Chatelier's Principle

When a reaction reaches a state of equilibrium, it is in a condition where the reaction is most stable and it will naturally have a tendency to go back to that state if external changes are made to the system. To understand how an equilibrium system responds to these changes we need to know about Le Chatelier's principle.

**Le Chatelier's principle** states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of this change**.**

Le Chatelier's principle shows how an equilibrium system will respond to the following changes.

- Adding extra reactant or product.
- Removing reactant or product.
- Increasing or decreasing the pressure of a gaseous system.
- Diluting an aqueous system.
- Increasing or decreasing the temperature.

## Adding extra reactant

The best way to understand the above definition of Le Chatelier's principle is to go straight into an example.

To show the effect of changing an equilibrium system by adding extra reactant, the reaction showing the formation of $NH_3$ from $N_2$ and $H_2$ will be examined.

$\mathbf{N_2\ (g)\ +\ 3H_2\ (g)\ \rightleftharpoons\ 2NH_3\ (g)}$

When this reaction is at equilibrium, the concentration of the reactants and products remain at a constant value at a particular temperature (as is shown in the table on page 143). As a consequence the *equilibrium constant, [products]/[reactants], will also remain at a constant value.*

**If some extra $N_2$ is added to the system**, the concentration of $N_2$ and hence the fraction, [products]/[reactants], will be different to what it was before the $N_2$ was added. That is*, the system is no longer at equilibrium and it will make changes to return to equilibrium.*

The system will oppose the change of adding extra $N_2$, that is, it will remove it from the system. The only way the system can oppose a change that has been made to it is to momentarily increase the rate of either the forward reaction or the reverse reaction. Since the system needs to remove $N_2$, the rate of the FORWARD REACTION will increase. This will result in the $N_2$ reacting at a rate that is faster than the rate at which the reverse reaction can replace it. This will cause the concentration of the $N_2$ in the system to decrease. However, as the definition of Le Chatelier's principle states, the system will only *partially oppose the effect of the change.* That is, only some, not all of the extra $N_2$ added to the system will be removed. The rate of the forward reaction will only be faster than the rate of the reverse reaction until enough $N_2$ has been removed from the system to allow **the fraction, [products/reactants] (equilibrium constant) to return to what it was before the change was made**. That is, the system will return to equilibrium and the rate of the forward and reverse reaction will be equal again.

Here is a shortened explanation of how the system opposes the addition of extra $N_2$.

- When $N_2$ is added to the system, a NET FORWARD REACTION will occur to partially oppose the effect of the change.

The term, NET FORWARD REACTION, is very appropriate because it means that both the forward and reverse reactions are still occurring but the rate of the forward reaction is faster in order to remove some of the extra $N_2$.

Here are some other statements that can be used to describe how the system opposes the addition of extra $N_2$.

- When extra $N_2$ is added, the system partially opposes the change by FAVOURING THE FORWARD REACTION.
- When extra $N_2$ is added, the system partially opposes the change by SHIFTING THE POSITION OF EQUILIBRIUM TO THE RIGHT.
- When extra $N_2$ is added, the system partially opposes the change by FAVOURING THE FORMATION OF PRODUCTS OVER THE REACTANTS.

The equilibrium constant for the system described on page 143 was

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} = 0.056\ M^{-2}.$$

So when extra $N_2$ is added and the system returns to equilibrium via a net forward reaction, the concentrations of the $N_2$, $H_2$ and $NH_3$ will be different to what they were before the change was made to the system. However, when they are substituted back into the expression, **the K value will still be equal to 0.056 $M^{-2}$.** Some students find this to be counterintuitive. You need to realise that mathematically, there are an infinite number of combinations of $[N_2]$, $[H_2]$ and[ $NH_3$] that can be plugged into the expression to give a fraction equal to 0.056 $M^{-2}$

If more of the other reactant, $H_2$ was added, the system would respond in an identical way to the addition of extra $N_2$. That is, there would be a net forward reaction as this will reduce the concentration of $H_2$ in the system.

## Adding extra product

The reaction

**$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$**

will be used to show how a system responds to the **addition of extra product.**

If extra $NH_3$ is added to this system, the system will partially oppose this change by a NET BACK REACTION. That is, the rate of the back reaction will be faster than the rate of the forward reaction as this will use up more $NH_3$ than can be produced by the forward reaction. The back reaction will only partially oppose the change. That is not all of the extra $NH_3$ will be removed from the system. Only enough $NH_3$ is removed to allow the fraction [products/reactants] to return back to the original equilibrium constant. That is, the **equilibrium constant is not changed.**

Here are some other statements that can be used to describe how the system opposes the addition of extra $NH_3$.

- When extra $NH_3$ is added, the system partially opposes the change by FAVOURING THE BACK/REVERSE REACTION.
- When extra $NH_3$ is added, the system partially opposes the change by SHIFTING THE POSITION OF EQUILIBRIUM TO THE LEFT.
- When extra $NH_3$ is added, the system partially opposes the change by FAVOURING THE FORMATION OF REACTANTS OVER THE PRODUCTS.

## Removing Reactant

The reaction

**$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$**

will be used to show how a system responds to the **removal of reactant.**

If some $H_2$ is removed from the system, a NET BACK REACTION will occur as this will increase the concentration of $H_2$ in the system. As always it is just a partial change and only some of the $H_2$ that was removed will be replaced. The net back reaction will occur until the fraction of [products/[reactants] returns to the original equilibrium constant. The rate of the forward and reverse reaction will be equal again.

If some $N_2$ was removed the system would respond in exactly the same way.

## Removing Product

The reaction

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

will be used to show how a system responds to the **removal of product.**

If some of the product, $NH_3$, is removed, the system will partially oppose the change by favouring the FORWARD REACTION as this will make more $NH_3$. The forward reaction will only be favoured until the fraction [products/[reactants] returns to the original equilibrium constant.

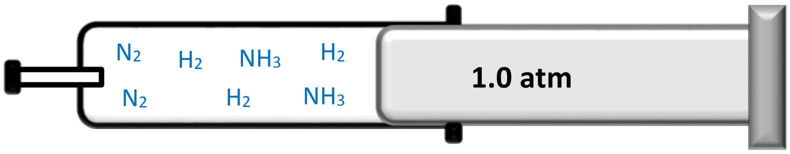
## Increasing the pressure of a gaseous system

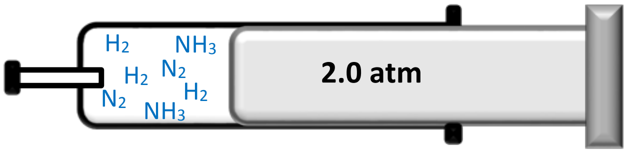
The reaction

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

will be used to show how a gaseous system responds to an **increase in pressure**.

The pressure of a gaseous equilibrium system can be increased by reducing its volume. This can be done by either placing the mixture into a smaller container or reducing the volume using a gas syringe as is shown below.





When the plunger of the gas syringe is pushed in the overall pressure of the system increases as the reduction in volume causes an increase in the frequency of collisions between the molecules and the walls of the container.

The equilibrium system will oppose this change by decreasing the pressure. To understand how the system responds we need to look at the coefficients in the equation.

**$N_2$ (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)**
4 gas particles 2 gas particles

On the reactant side of the equation there are 1 $N_2$ and 3 $H_2$ gas molecules. 1 + 3 = 4 gas molecules (particles) in total. On the product side of the equation there are 2 $NH_3$ molecules. That is there are 2 gas particles.

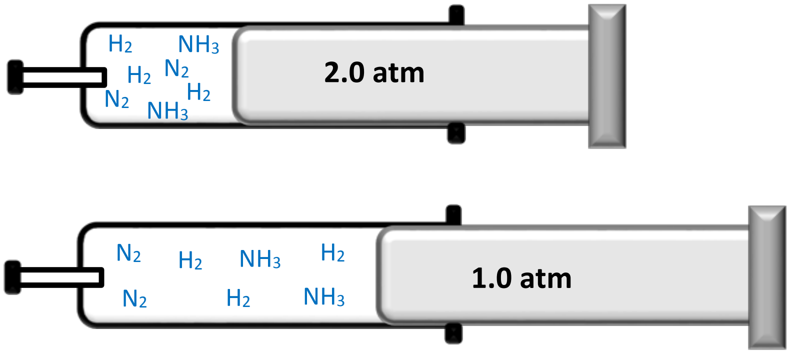
In order to oppose the increase in pressure of the system, the FORWARD REACTION will be favoured as this will REDUCE THE NUMBER OF GAS MOLECULES in the system and lower the pressure. Every time the forward reaction occurs, **4 gas molecules react (and are removed) to produce only 2 gas molecules.** This results in a decrease in the number of molecules in the system and hence a lowering of the pressure. The increase in pressure is only partially opposed by the favouring of the forward reaction. The forward reaction will only be favoured until the concentration of the $N_2$, $H_2$ and $NH_3$ allow the fraction [products/reactants] to return to the original equilibrium constant.

## Reducing the pressure of a gaseous system

The reaction

**$N_2$ (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)**

will be used to show how a gaseous system responds to a **decrease in pressure**. The pressure of a gaseous equilibrium system can be decreased by either placing the mixture into a larger container or increasing the volume using a gas syringe as is shown below.



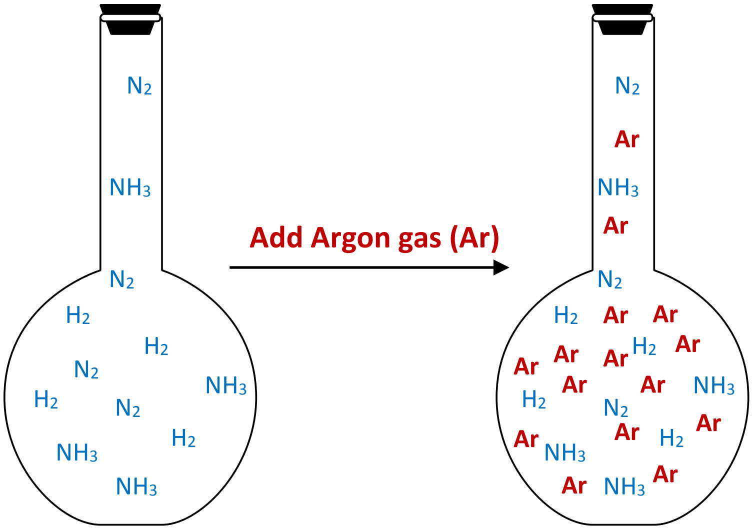
When the plunger of the gas syringe is pulled out the overall pressure of the system decreases as the increase in volume causes a decrease in the frequency of collisions between the molecules and the walls of the container.

The system will respond by favouring the BACK REACTION. Every time the back reaction occurs, 2 $NH_3$ molecules turn into 1 $N_2$ and $3H_2$ molecules. That is the back reaction turns 2 molecules into 4 which increases the number of gas molecules in the container causing a partial increase in the pressure of the system. The back reaction will only be favoured until the concentration of the $N_2$, $H_2$ and $NH_3$ allow the fraction [products/reactants] to return to the original equilibrium constant.

## Increasing the pressure by adding an INERT GAS

Another way of increasing the pressure of a gaseous equilibrium system is to keep the volume of the container the same but add molecules of an **inert gas**. An inert gas is one that is not part of the equilibrium system and does not react with any of the reactants or products in the system. For example, Argon gas could be added to the equilibrium system:

**$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$**



If argon gas is added to an equilibrium mixture containing $N_2$, $H_2$ and $NH_3$, the overall pressure of the system is increased as the Ar atoms have increased the number of particles in the container resulting in an increase in the frequency of collisions between the gas particles and the walls of the container.

Despite the fact that the pressure has been increased, the system **will not respond** by favouring either the forward or the reverse reaction. This is because the Ar atoms have increased the overall pressure in the container but they have **not increased the partial pressure** of the $N_2$, $H_2$ and $NH_3$. The term partial pressure refers to the pressure that each gas is individually exerting in the system. Before the argon was added, the total pressure in the flask was the sum of the partial pressure of the $N_2$, $H_2$ and $NH_3$. The presence of the Ar atoms in the flask does not change the number of collisions that the $N_2$, $H_2$ and $NH_3$ molecules are making with the walls of the container so the system does not respond. When the pressure is increased by reducing the volume however, each gas in the system is in a smaller volume (more concentrated) resulting in a greater number of collisions with the walls of the container and hence an increased partial pressure. As the partial pressure of each gas in the system has increased, the system responds by favouring the forward reaction.

- If the pressure of a gaseous system is increased by reducing the volume, the system will respond by favouring the reaction which produces **the lower number of gas particles.**

- If the pressure of a gaseous system is decreased by increasing the volume, the system will respond by favouring the reaction which produces the **greater number of gas particles.**

- *Pressure only applies to EQUILIBRIUM SYSTEMS INVOLVING GASES.*

## Diluting an aqueous system

An aqueous system refers to an equilibrium system where the reactants and products are dissolved in water. It usually involves a reaction where the reactants and products are ions. An example of such a system is shown below.

$\mathbf{Fe^{3+}(aq) + 3SCN^{-}(aq) \rightleftharpoons Fe(SCN)_3^{2+}(aq)}$

4 particles (ions) 1 particle (ion)

If this system is diluted with water, the concentration of each ion and the overall concentration of the ions in the system will DECREASE. As a consequence the system will respond by favouring the REVERSE REACTION as this will turn 1 ion into 4 ions as can be seen in the above equation. As a result the number of ions in the solution will increase causing an overall increase in the concentration of the ions in the system. The back reaction is favoured only until the original equilibrium constant for the reaction is re-established. After the system returns to equilibrium the concentration of the ions will be less than before the change was made. As always the system only partially opposes the change.

## Increasing the temperature

To understand how Le Chatelier's principle applies to changes in temperature, we need to know whether a reaction is **exothermic (ΔH =-)** or **endothermic (ΔH =+)**.

The reaction

$\mathbf{N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -90.0\ KJ\ mol^{-1}}$

will be used to show how an **exothermic reaction** will respond when the temperature is increased. In order to make this easier to follow we need to revisit a few things regarding exothermic and endothermic reactions from chapter 6:

- Exothermic reactions have **ΔH =-** and endothermic reactions have **ΔH =+**.

- Exothermic reactions release heat into the surrounding environment. As a consequence they cause the temperature of the surrounding environment to INCREASE.

- Endothermic reactions absorb heat from the surrounding environment. As a consequence they cause the temperature of the surrounding environment to DECREASE.

- When an equilibrium reaction is written out showing the ΔH (thermochemical equation), the ΔH is given for the forward reaction only. So for the above equation, the forward reaction is exothermic as it has a ΔH of -90.0 KJ mol$^{-1}$. If the forward reaction is exothermic, then the reverse reaction must be **endothermic**. So for the above reaction, the reverse reaction,

  $2NH_3\ (g) \rightarrow N_2\ (g) + 3H_2\ (g)$ **ΔH =+**

  is endothermic. This however is NEVER SHOWN in the equation. Only the ΔH of the forward reaction is shown.

The equilibrium reaction showing the formation of ammonia can be looked at in the following way:

**ΔH = +90.0 KJ mol$^{-1}$** **$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$** **ΔH = -90.0 KJ mol$^{-1}$**

**COOLS DOWN SYSTEM** **HEATS UP SYSTEM**

**(↓ TEMPERATURE)** **(↑ TEMPERATURE)**

This shows that the *forward reaction is exothermic*. If the forward reaction is favoured it will **release heat and heat up the system/surrounding environment (increase the temperature).**

The *reverse reaction is endothermic*. If the reverse reaction is favoured it will **absorb heat from the surroundings and cool down the system /surrounding environment (decrease the temperature).**

- ❖ To make this easier you need to think of the system and the surrounding environment as the SAME THING.

- *In the exam DO NOT write out an equation showing the ΔH of the reverse reaction as is shown above. This has only been done to make the application of Le Chatelier's principle to changes in temperature easier to understand.*

So if the temperature of this reaction when at equilibrium is increased by an external factor such as a hot water bath, flame from a Bunsen burner etc., the reaction will respond to partially oppose the change. That is, it will respond in a way that will lower the temperature of the surroundings/system. As this reaction is exothermic (forward reaction), the REVERSE REACTION will be favoured as it is ENDOTHERMIC and will cool down the system by ABSORBING HEAT from the surroundings causing a LOWERING IN THE TEMPERATURE.

When the system returns to equilibrium the value of the **EQUILIBRIUM CONSTANT WILL BE DIFFERENT TO THE ORIGINAL VALUE.**

- ❖ Of all the external changes that can be made to an equilibrium system, **TEMPERATURE** is the only one that will **change the value of K**.

With this example, the increase in temperature caused the reaction to shift towards the left which causes a decrease in the concentration of the products ($NH_3$) and an increase in the concentration of the reactants ($N_2$ and $H_2$). **So the new equilibrium constant (K) will be lower** than the original value as the numerator in the fraction is now lower and the denominator is greater.

LOWER [PRODUCTS]

↙

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3} = \textbf{LOWER K}$$

↖

GREATER [REACTANTS]

Now let's try this out on an endothermic reaction. That is, an equilibrium system where the forward reaction is endothermic.

**$C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)$ $\Delta H = +139$ KJ $mol^{-1}$**

**$\Delta H = -139$ KJ $mol^{-1}$** **$C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)$** **$\Delta H = +139$ KJ $mol^{-1}$**

**HEATS UP SYSTEM** **COOLS DOWN SYSTEM**

**(↑ TEMPERATURE)** **(↓ TEMPERATURE)**

So if the temperature of this reaction when at equilibrium is increased by an external factor such as a hot water bath, flame from a Bunsen burner etc., the reaction will respond to partially oppose the change. That is, it will respond in a way that will lower the temperature of the surroundings/system. As this reaction is ENDOTHERMIC (forward reaction), the FORWARD REACTION will be favoured as it will cool down the system by ABSORBING HEAT from the surroundings causing a LOWERING IN THE TEMPERATURE.

The increase in temperature caused the reaction to shift towards the right which causes an increase in the concentration of the products ($NH_3$) and a decrease in the concentration of the reactants ($N_2$ and $H_2$). **So the new equilibrium constant (K) will be greater** than the original value as the numerator in the fraction is now larger and the denominator is smaller.

HIGHER [PRODUCTS]

↙

$$K = \frac{[C_2H_4] \times [H_2]}{[C_2H_6]} = \textbf{HIGHER K}$$

↖

LOWER [REACTANTS]

## Decreasing the temperature

To start with let's look at decreasing the temperature of an exothermic reaction.

**$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ $\Delta H = -90.0$ KJ $mol^{-1}$**

**$\Delta H = +90.0$ KJ $mol^{-1}$** **$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$** **$\Delta H = -90.0$ KJ $mol^{-1}$**
**COOLS DOWN SYSTEM** **HEATS UP SYSTEM**
**(↓ TEMPERATURE)** **(↑ TEMPERATURE)**

So if the temperature of this reaction when at equilibrium is decreased by an external factor such as an ice water bath, the reaction will respond to partially oppose the change. That is, it will respond in a way that will increase the temperature of the surroundings/system. As this reaction is EXOTHERMIC (forward reaction), the FORWARD REACTION will be favoured as it will HEAT UP the system by RELEASING HEAT into the surroundings causing an INCREASE IN TEMPERATURE.

The decrease in temperature caused the reaction to shift towards the right which causes an increase in the concentration of the products ($NH_3$) and a decrease in the concentration of the reactants ($N_2$ and $H_2$). **So the new equilibrium constant (K) will be greater** than the original value as the numerator in the fraction is now larger and the denominator is smaller.

$$K = \frac{\overset{\text{HIGHER [PRODUCTS]}}{\overset{\swarrow}{[NH_3]^2}}}{\underset{\text{LOWER [REACTANTS]}}{\underset{\nwarrow}{[N_2] \times [H_2]^3}}} = \textbf{HIGHER K}$$

Now let us look at decreasing the temperature of an endothermic reaction.

**$C_2H_6 (g) \rightleftharpoons C_2H_4 (g) + H_2 (g)$ $\Delta H = +139$ KJ $mol^{-1}$**

**$\Delta H = -139$ KJ $mol^{-1}$** **$C_2H_6 (g) \rightleftharpoons C_2H_4 (g) + H_2 (g)$** **$\Delta H = +139$ KJ $mol^{-1}$**
**HEATS UP SYSTEM** **COOLS DOWN SYSTEM**
**(↑ TEMPERATURE)** **(↓ TEMPERATURE)**

So if the temperature of this reaction when at equilibrium is decreased by an external factor such as an ice water bath the reaction will respond to partially oppose the change. That is, it will respond in a way that will increase the temperature of the surroundings/system. As this reaction is ENDOTHERMIC (forward reaction), the REVERSE REACTION will be favoured as it will HEAT UP the system by RELEASING HEAT into the surroundings causing an INCREASE IN TEMPERATURE.

The decrease in temperature caused the reaction to shift towards the left which causes a decrease in the concentration of the products ($NH_3$) and an increase in the concentration of the reactants ($N_2$ and $H_2$). **So the new equilibrium constant (K) will be lower** than the original value as the numerator in the fraction is now lower and the denominator is greater.

LOWER [PRODUCTS]

$$K = \frac{[C_2H_4] \times [H_2]}{[C_2H_6]} = \textbf{LOWER K}$$

HIGHER [REACTANTS]

- In general, any change in temperature that causes a **net forward reaction** will **increase the value of K.**

- In general, any change in temperature that causes a **net back reaction** will **decrease the value of K.**

Applying Le Chatelier's principle to changes in temperature can be challenging for some students. Here is another way to approach it. Since exothermic reactions produce heat, the heat can appear on the right hand side of the equation as if it was a product. For example,

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g) \quad \Delta H = -90.0 \text{ KJ mol}^{-1}$$

Can be rewritten as

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g) + 90.0 \text{ KJ of HEAT}$$

If the temperature of this reaction is increased, it can be interpreted as adding an extra product, heat. As a consequence a net back reaction will occur as some of the heat will be used up by the back reaction.

For an endothermic reaction the heat can appear on the reactant side of the equation as these reactions absorb heat. So the equation

$$C_2H_6 (g) \rightleftharpoons C_2H_4 (g) + H_2 (g) \ \Delta H = +139 \text{ KJ mol}^{-1}$$

can be rewritten as

$$C_2H_6 (g) + 139 \text{ KJ of HEAT} \rightleftharpoons C_2H_4 (g) + H_2 (g)$$

If the temperature of this system is decreased, this can be interpreted as removing some of the reactant, heat. A net back reaction will occur as this will oppose the change by producing more heat.

### Adding a catalyst

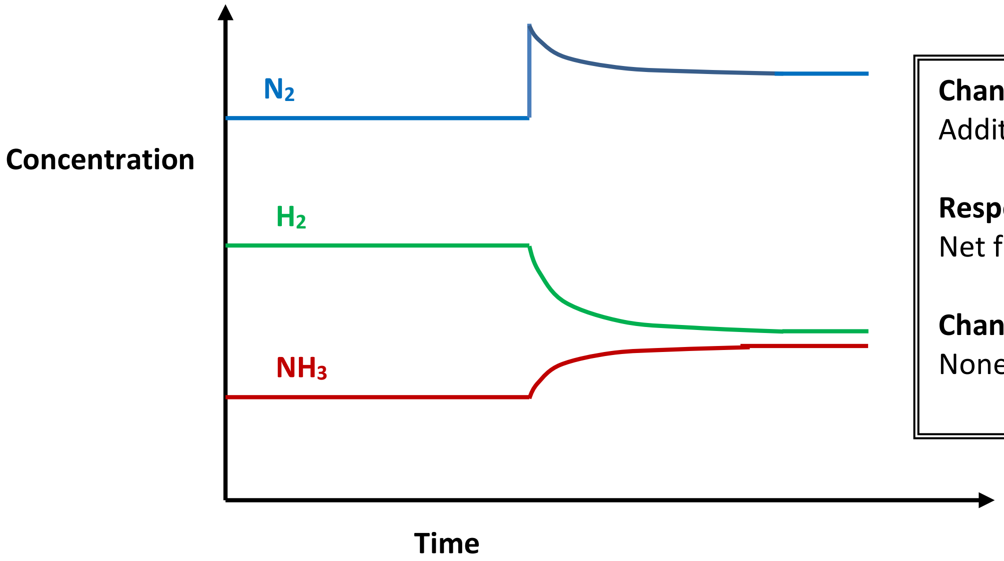
If a catalyst is added to an equilibrium system, the rate of both the forward and reverse reactions will be increased and to the same extent. As a consequence the reaction will stay in equilibrium and there will be no shift in the direction of the reaction.

## Concentration versus time graphs

All of the applications of Le Chatelier's principle that were just covered can be illustrated using **concentration versus time graphs.** Examining these graphs is an excellent way of enhancing our understanding of Le Chatelier's principle as they help to distinguish between the **external change** that is made to a system and the **response** that the system makes in partially opposing the change.

We will now examine a concentration versus time graph for each of the applications of Le Chatelier's principle that were just covered.

### Adding extra $N_2$ to the system: $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$



**Change made to system:**
Addition of $N_2$

**Response of system:**
Net forward reaction

**Change to K:**
None

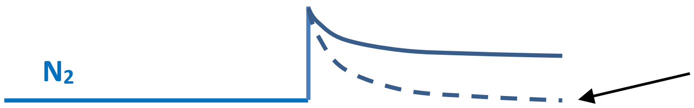
The concentrations of the $N_2$, $H_2$ and $NH_3$ are constant for some time as is indicated by the perfectly horizontal lines. This shows that the system is at equilibrium during this time as the concentrations of all reactants and products are constant. It appears as though there is a pattern between the initial concentrations of the $N_2$, $H_2$ and $NH_3$ and their positions in the equation. This is not the case. The initial concentration of the $NH_3$ could easily have been the highest of all 3. The initial concentrations of the reactants and products can be absolutely anything. It just depends on the quantities that are added at the beginning of the reaction. After some time there is an obvious change in the direction of all 3 horizontal lines. The concentration of the $N_2$ has instantly spiked up. **This shows that some extra $N_2$** was just added to the system. At the time the $N_2$ was added there was no similar dramatic change to the concentration of the $H_2$ and $NH_3$ as neither of these was added or removed from the system. What we see however, is a gradual increase in the concentration of the $NH_3$, a gradual decrease in the concentration of the $H_2$ and a gradual decrease in the concentration of the $N_2$ after the initial spike in its concentration. These gradual changes are showing that Le Chatelier's principle has just "kicked in." That is, the reaction has responded to the change that was made to the system.

Since the change made to the system was the addition of extra $N_2$, the system responds by favouring the forward reaction as this uses up some of the $N_2$ that was just added. The net forward reaction is evident in the graph by the gradual decrease in the concentration of $N_2$ and $H_2$ as they are reacting with each other and the gradual increase in the concentration of the $NH_3$ as it is being produced.

If you look closely at the graph you will notice that the decrease in concentration of the $H_2$ is happening at 3 times the rate (3 times steeper) of the decrease of the $N_2$. This is due to the coefficients in the equation. For every 1 .0 mol of $N_2$ that reacts, 3.0 mol of $H_2$ reacts. The increase in the concentration of the $NH_3$ is happening at a rate that is just above the rate at which the $N_2$ is reacting and just below the rate at which the $H_2$ is reacting. This is to be expected as the balanced equation shows that for every 2.0 mol of $NH_3$ that is produced, 1.0 mol of $N_2$ reacts and 3.0 mol of $H_2$ reacts.

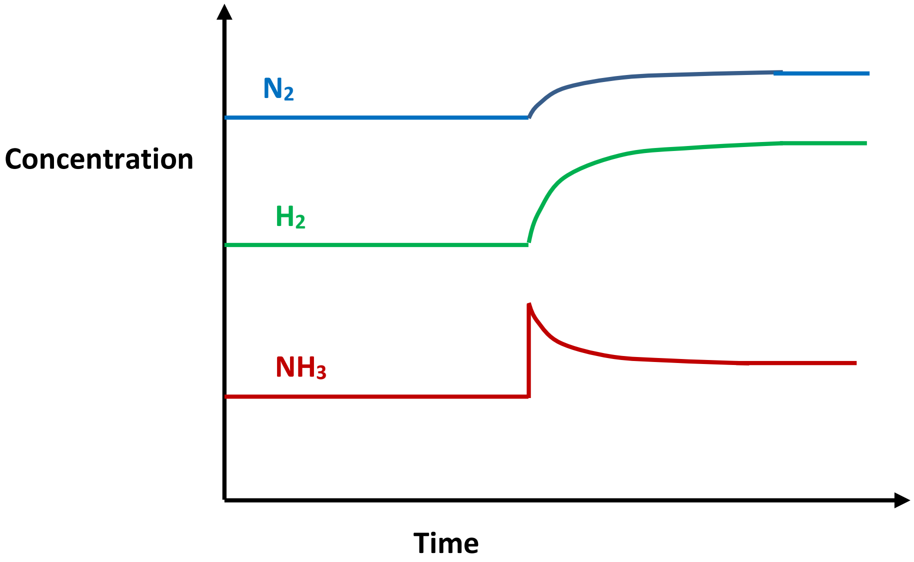
Eventually the concentration of all 3 gases becomes constant again at exactly the same time on the horizontal axis. This shows that the reaction has gone back to equilibrium. The graph clearly shows that at the new equilibrium, the concentrations of the $N_2$, $H_2$ and $NH_3$ are different values when compared to the original equilibrium. The calculated value of K however, is the same as when the original equilibrium concentrations are used (before the addition of extra $N_2$). Recall that only changes in temperature will change the equilibrium constant.

- *It is very important when drawing this graph to not allow the concentration of the $N_2$ to return back to the concentration it had before the extra $N_2$ was added. Remember that Le Chatelier's principle states that the system will PARTIALLY OPPOSE, not fully oppose the change that was made to it.*



***This is incorrect as the line is level with the [$N_2$] at the original equilibrium.***

## Adding extra $NH_3$ to the system: $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$



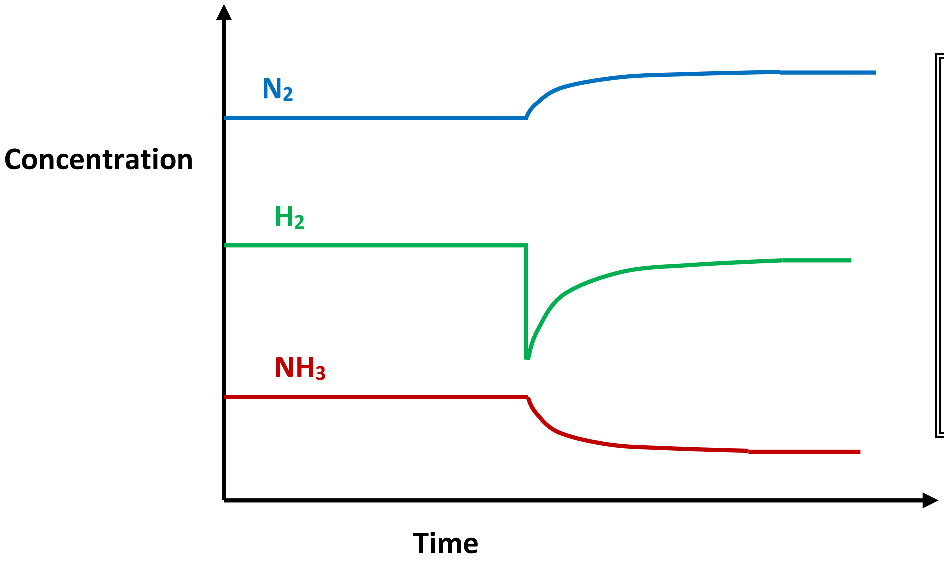
**Change made to system:**
Addition of $NH_3$

**Response of system:**
Net back reaction

**Change to K:**
None

If extra $NH_3$ is added to the system, the concentration the $NH_3$ will spike up as can be seen in the above graph. When Le Chatelier's principle kicks in, the reaction shifts towards the reactants in order to oppose the change. This is evident in the graph as the concentration of the $NH_3$ gradually decreases and the concentration of the 2 reactants $N_2$ and $H_2$ gradually increase. Eventually all 3 lines level off and become horizontal showing that the concentrations of the reactants and products have become constant when equilibrium is re-established. As was the case with the previous example, the rate in change of the concentrations of $N_2$, $H_2$ and $NH_3$ are consistent with the mole ratio given in the balanced equation.

## Removing $H_2$ from the system: $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$



**Change made to system:**
Removal of $H_2$

**Response of system:**
Net back reaction

**Change to K:**
None

The steep and instantaneous drop in the concentration of $H_2$ shows that some $N_2$ was removed from the system. The system opposes this change by shifting to the left as this will make more $H_2$.

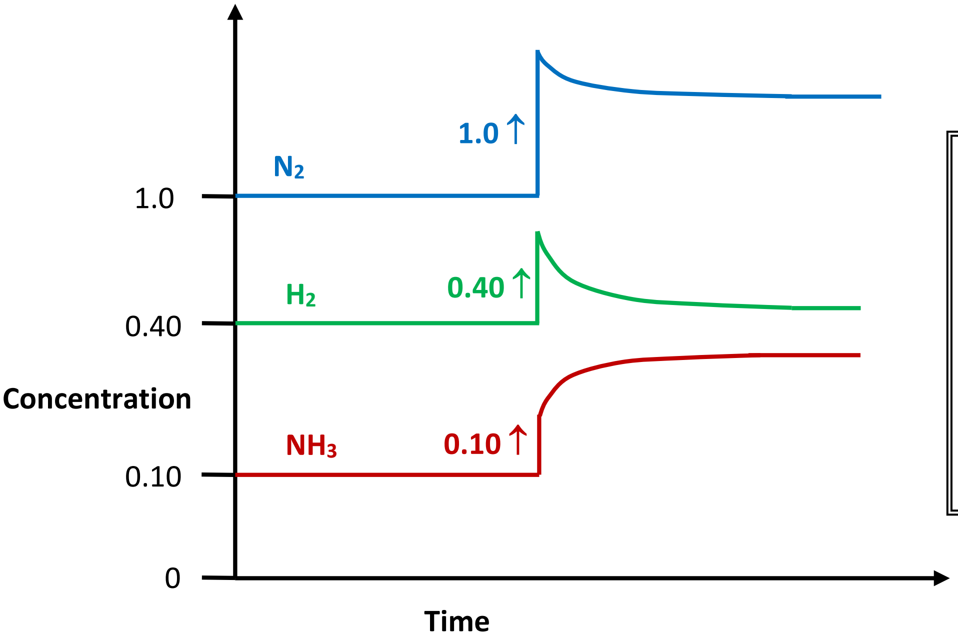
The net back reaction is evident by the increase in concentration of the 2 reactants $N_2$ and $H_2$ and the decrease in concentration of the product, $NH_3$.

When viewing a concentration versus time graph showing the addition or removal of a reactant or product:

- The addition of a reactant or product is shown by a steep and instantaneous increase in the concentration of the reactant or product that has been added.
- The removal of reactant or product is shown by a steep and instantaneous drop in the concentration of the reactant or product that has been removed.
- When Le Chatelier's principle kicks in, the concentrations of the reactants and products change gradually.

## Increasing the pressure by reducing the volume of the system:

**$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$**



**Change made to system:**
↑ pressure by ↓ volume.

**Response of system:**
Net forward reaction

**Change to K:**
None

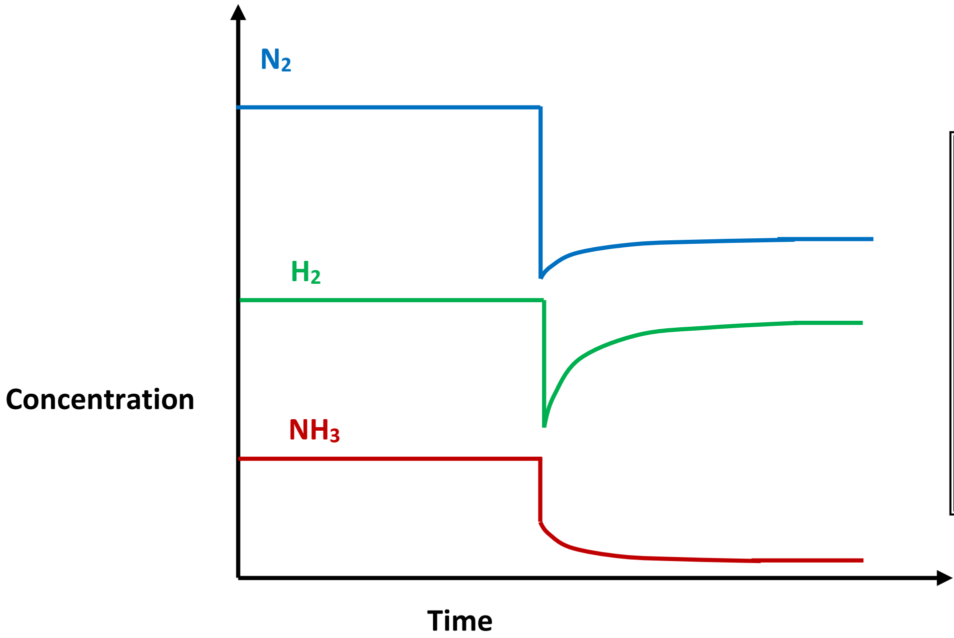
If the volume of a gaseous equilibrium system is reduced, not only does the pressure of each gas increase but the concentration of each gas will increase as well. On the graph each reactant and product shows an instantaneous and steep increase in concentration when the volume is reduced. It is important to realise however, that the increase in concentration of each gas varies. The increase in concentration of each gas is related to its initial concentration at equilibrium before the volume is reduced.

To help show how this works the equilibrium concentrations of each gas are shown on the vertical axis. The concentrations are not to scale. Let's assume that this system is reacting inside a gas syringe and the volume is exactly halved. This would cause the concentration of each gas to double.

If the concentration of the $N_2$ doubles it will go from 1.0 M up to 2.0 M. That is, its concentration will increase by 1.0 on the vertical axis. The initial equilibrium concentration of the $H_2$ is only 0.40 M so it will increase to 0.80 M. That is only an increase of 0.40 on the vertical axis. Finally the $NH_3$ has the lowest initial concentration of 0.10 M. So when its concentration doubles it will show the lowest increase. It will change from 0.10 M to 0.20 M which is only an increase of 0.10 on the vertical axis. *So when the volume of a gaseous equilibrium system is decreased, the higher the equilibrium concentration of the gas the greater its increase in concentration.*

For this reaction the increase in pressure has resulted in a net forward reaction as this produces the lower number of gas particles resulting in a decrease in the pressure of the system. The net forward reaction is evident by the decrease in the concentration of the reactants, $N_2$ and $H_2$ and increase in the concentration of the product, $NH_3$.

## Decreasing the pressure by increasing the volume of the system:
## $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$



**Change made to system:**
↓ pressure by ↑ volume

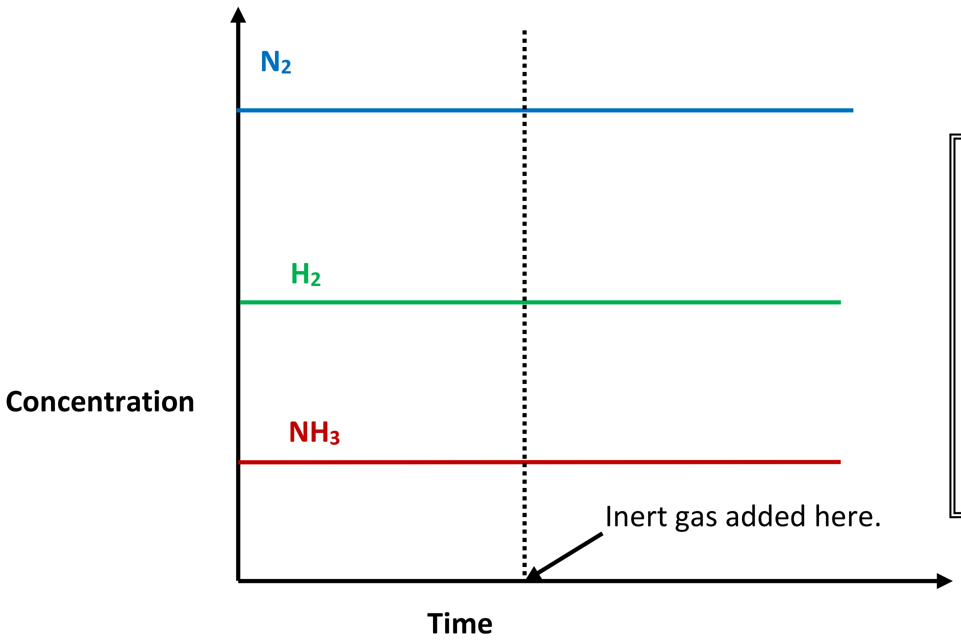
**Response of system:**
Net back reaction

**Change to K:**
None

If the volume of this gaseous equilibrium system is increased, the pressure and concentration of each gas will decrease. On the graph each reactant and product shows an instantaneous and steep drop in concentration when the volume is increased. In accordance with the previous example, the higher the equilibrium concentration of the reactant or product the greater the change in concentration when the volume is changed. So when the volume of this system is increased, the $N_2$ will show the greatest drop in concentration as it has the highest equilibrium concentration. The $H_2$ will show a lower drop in concentration and the $NH_3$ will show the lowest drop in concentration as it has the lowest equilibrium concentration of all three reactants.

The system will oppose the change by shifting in the reverse direction as this will produce more particles and increase the pressure. The net back reaction is shown in the graph by the increase in concentration of both of the reactants $N_2$ and $H_2$ and the decrease in the concentration of the $NH_3$ product.

### Increasing the pressure by adding an inert gas (eg. He) to the system:
### $N_2\,(g) + 3H_2 \rightleftharpoons 2NH_3\,(g)$



**Change made to system:**
↑ pressure by adding inert gas

**Response of system:**
None

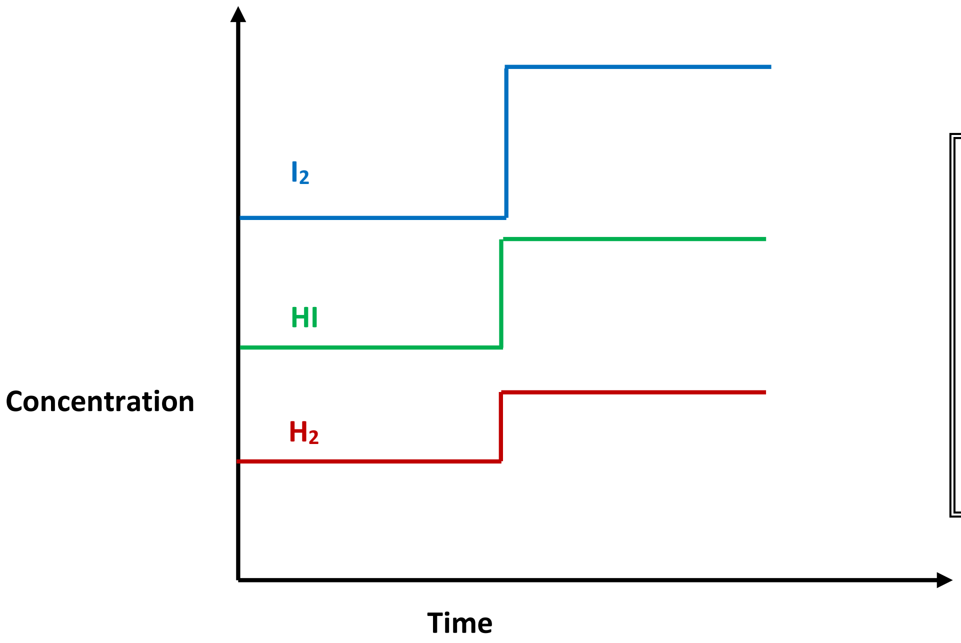
**Change to K:**
None

When an inert gas such as He is added to this system, the He atoms increase the number of collisions between gas particles and the walls of the container. As a consequence the overall pressure in the container has increased. The concentration and hence partial pressure of the $N_2$, $H_2$ and $NH_3$ is unaffected by the presence of the He atoms. Therefore the system does not favour either the forward or reverse reaction and the system just stays at equilibrium. The concentration of the $N_2$, $H_2$ and $NH_3$ remain constant before and after the inert gas is added.

## Increasing the pressure by reducing the volume of the system:

**$H_2$ (g) + $I_2$ (g) ⇌ 2HI (g)**

2 gas particles 2 gas particles



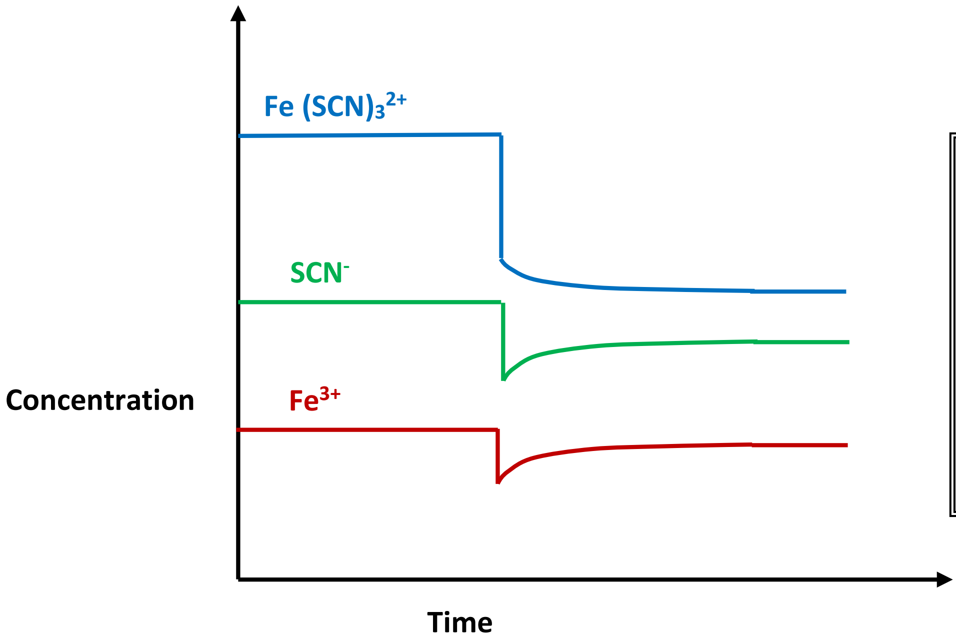
**Change made to system:**
↑ pressure by adding reducing volume

**Response of system:**
None

**Change to K:**
None

The reduction in volume has increased the pressure and caused the concentrations of the reactants and products to increase steeply and instantaneously. The reaction DOES NOT RESPOND by favouring either the forward or reverse reaction. This is because the forward reaction produces 2 molecules of gas and the reverse reaction also produces 2 molecules of gas. Since the pressure will not be changed by favouring either reaction , the system does not respond and maintains equilibrium with each gas at a higher concentration.

## Diluting the aqueous system: $Fe^{3+}(aq) + 3SCN^{-}(aq) \rightleftharpoons Fe(SCN)_3^{2+}(aq)$



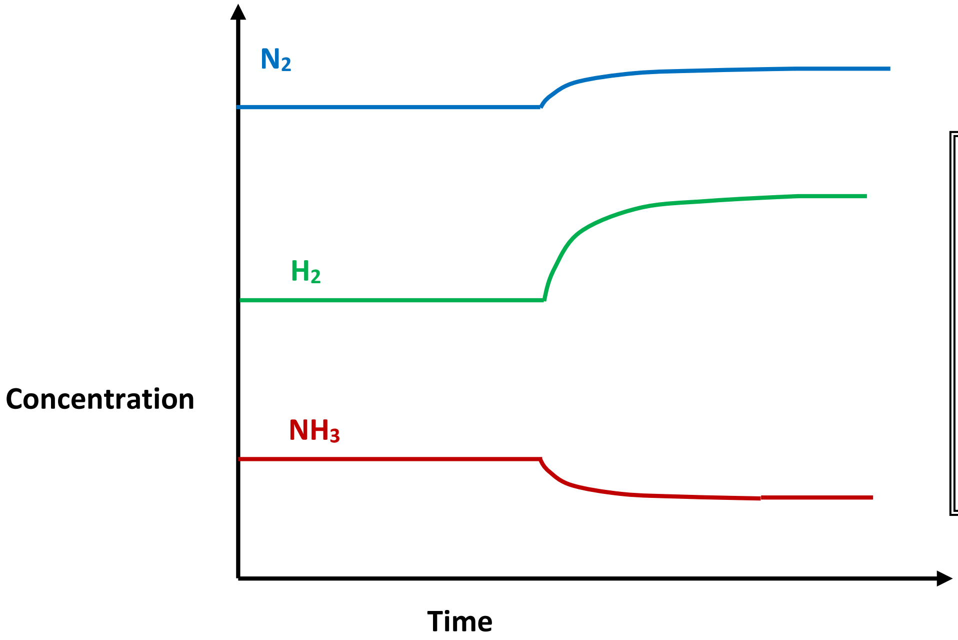
**Change made to system:**
Diluting system

**Response of system:**
Net back reaction

**Change to K:**
None

When this aqueous system is diluted the concentration of all reactants and products will drop steeply and instantaneously. The reaction will shift backwards as this will increase the number of ions in the solution as 1 $Fe(SCN)_3^{2+}$ ion breaks down into 1 $Fe^{3+}$ and 3 $SCN^{-}$ ion (4 ions in total) causing an overall increase in the concentration of ions in the system. The net back reaction can be seen in the graph by the increase in the concentration of the reactants $Fe^{3+}$ and $SCN^{-}$ and a decrease in the concentration of the product, $Fe(SCN)_3^{2+}$.

## Increasing the temperature of the system:
## $N_2\ (g)\ +\ 3H_2\ (g)\ \rightleftharpoons\ 2NH_3\ (g)\quad \Delta H = -90.0\ KJ\ mol^{-1}$



**Change made to system:**
Increase in temperature

**Response of system:**
Net back reaction

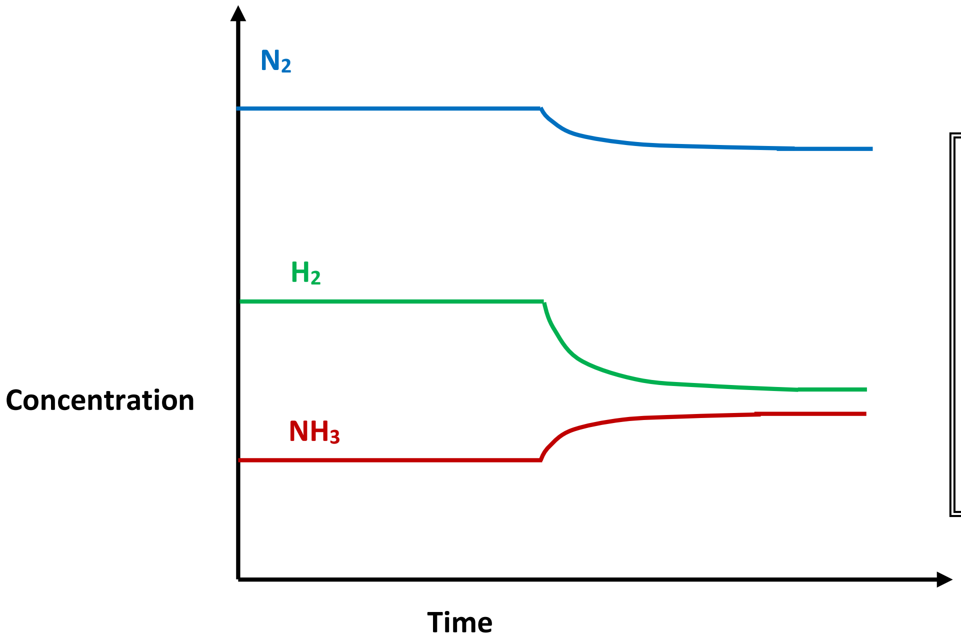
**Change to K:**
Decrease

***A change in temperature is the only change that will not cause an instantaneous change to the concentration of the reactants and products.*** That is, unlike the other changes, a change in temperature will not cause a steep increase or decrease in the concentration of any of the reactants or products. So when the temperature of this system is increased, everything just gets hotter and that will not change the concentration of anything in the system.

The only changes seen in the graph will be the gradual changes in concentration when Le Chatelier's principle kicks in. As this is an exothermic reaction, the reaction will oppose the increase in temperature by shifting backwards. The backwards reaction is endothermic and will reduce the temperature of the system by absorbing heat. The net back reaction can be seen in the graph by the increase in concentration of the 2 reactants, $N_2$ and $H_2$ and a decrease in the concentration of the $NH_3$ product. As the reaction shifted backwards, the value of K will decrease. *Recall that changing the temperature is the only factor that will change the value of the equilibrium constant.*

## Decreasing the temperature of the system:

**$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g) \quad \Delta H = -90.0 \text{ KJ mol}^{-1}$**



**Change made to system:**
Decrease in temperature

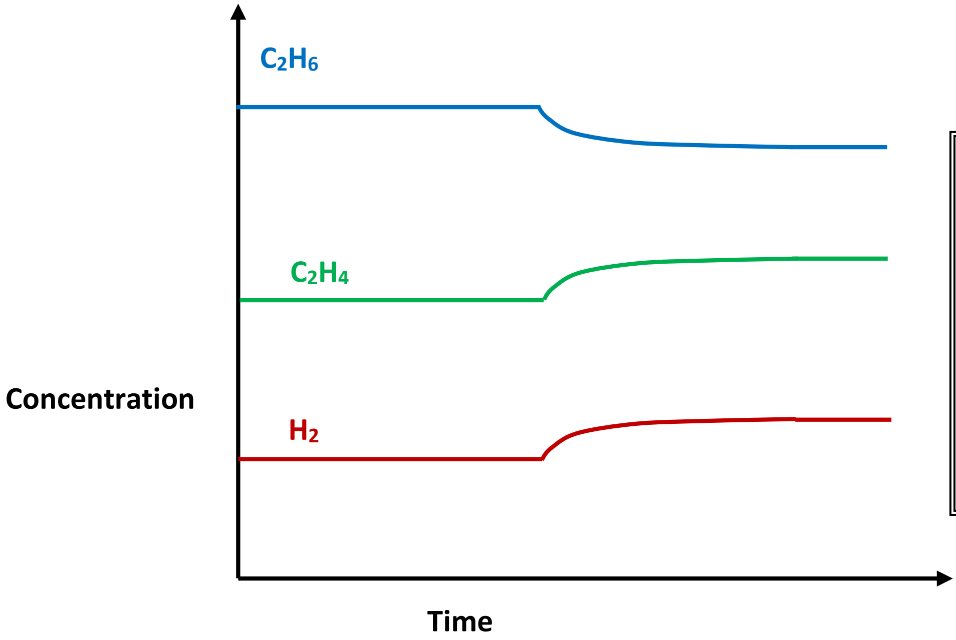
**Response of system:**
Net forward reaction

**Change to K:**
Increase

As this is an exothermic reaction, the reaction will oppose the decrease in temperature by shifting forwards. The forward reaction is exothermic and will increase the temperature of the system by releasing heat. The net forward reaction can be seen in the graph by the decrease in concentration of the 2 reactants, $N_2$ and $H_2$ and an increase in the concentration of the $NH_3$ product. As the reaction shifted forwards, the value of K will increase.

### Increasing the temperature of the system:

**$C_2H_6\ (g) \rightleftharpoons C_2H_4\ (g) + H_2\ (g) \quad \Delta H = +139\ KJ\ mol^{-1}$**



**Change made to system:**
Increase in temperature

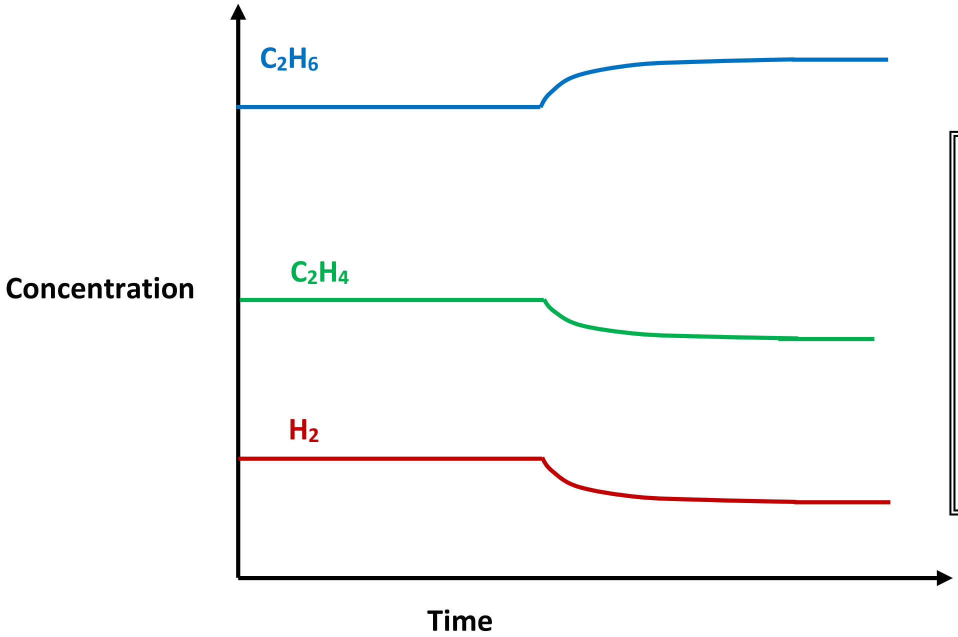
**Response of system:**
Net forward reaction

**Change to K:**
Increase

As this is an endothermic reaction, the reaction will oppose the increase in temperature by favouring the forward reaction. As the forward reaction is endothermic, it will reduce the temperature of the system by absorbing heat. The net forward reaction can be seen in the graph by the decrease in concentration of the reactant, $C_2H_6$ and an increase in the concentration of the products, $C_2H_4$ and $H_2$.

## Decreasing the temperature of the system:

**$C_2H_6$ (g) ⇌ $C_2H_4$ (g) + $H_2$ (g)  ΔH = + 139 KJ $mol^{-1}$**



**Change made to system:**
Decrease in temperature

**Response of system:**
Net back reaction

**Change to K:**
Decrease

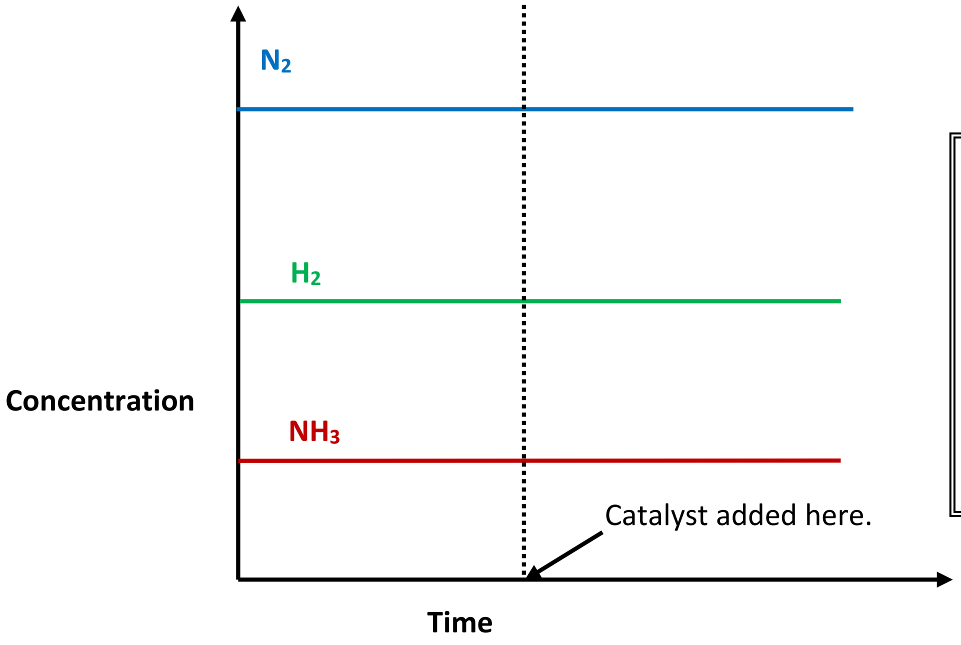
As this is an endothermic reaction, the reaction will oppose the decrease in temperature by favouring the back reaction. As the back reaction is exothermic, it will increase the temperature of the system by releasing heat. The net back reaction can be seen in the graph by the increase in concentration of the reactant, $C_2H_6$ and a decrease in the concentration of the products, $C_2H_4$ and $H_2$.

- When applying Le Chatelier's principle to changes in temperature, it is important to differentiate between **external changes in temperature caused by flames, hot water etc.** and changes in temperature caused by a reaction shifting in a particular direction. For example, if extra $N_2$ is added to the reaction,

  $N_2$ (g) + $3H_2$ (g) ⇌ $2NH_3$ (g)  ΔH = -90.0 KJ $mol^{-1}$

  a net forward reaction will occur as this will use up some of the extra $N_2$. As this is an exothermic reaction, the net forward reaction will also produce heat and cause an increase in the temperature of the system. Now the temptation is to conclude that the K value has changed since the temperature has changed. K WILL NOT CHANGE because the increase in temperature was caused by the heat produced by the reaction moving towards the products, not by an external change in temperature. <u>The external change made to the system was the addition of extra $N_2$ into the system so K will not change.</u>

## Adding a catalyst to the system:
## $N_2$ (g) + $3H_2$ $\rightleftharpoons$ $2NH_3$ (g)



**Change made to system:**
Adding a catalyst

**Response of system:**
None

**Change to K:**
None

When a catalyst is added to an equilibrium system it will increase the rate of both the forward and back reactions equally. As a consequence the reaction will just stay in equilibrium and there will be no shift in the direction of the reaction.

## Yield of a reaction

The term **yield** refers to the amount of product obtained during a chemical reaction. For equilibrium reactions, the yield of the reaction can be increased by causing the reaction to shift in the FORWARD DIRECTION. For example the yield of the reaction,

$N_2$ (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) $\Delta H = -90.0$ KJ $mol^{-1}$

can be increased by decreasing the temperature, increasing the pressure, adding more $N_2$ or $H_2$ and removing $NH_3$ from the system. All of these changes will be opposed by a net forward reaction, therefore they increase the amount of product and hence increase the YIELD of the reaction.

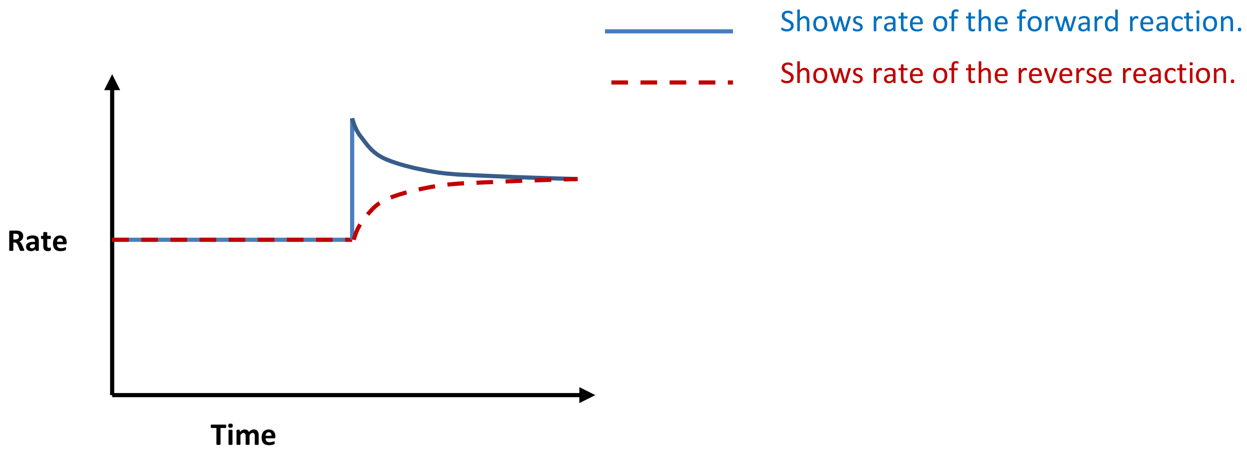
The proportion of products compared to the proportion of reactants in an equilibrium system is often referred to as the **% yield.**

# Rate versus time graphs

Le Chatelier’s principle cannot only be illustrated using concentration versus time graphs but also with **rate versus time graphs.** The following examples will show rate versus time graphs for when extra reactant /product is added to a system and when reactant / product is removed from a system.

## Adding extra reactant to an equilibrium system

**Eg. Adding extra $N_2$ or $H_2$ to the system: $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$**



This graph shows the rate of the forward reaction with a solid blue line and the rate of the reverse reaction with a broken red line. At equilibrium the rate of the forward and reverse reactions are equal as is shown by the overlapping of the 2 lines.

When extra reactant such as $N_2$ or $H_2$ (or both) is added to the system, the concentration of the reactants increases resulting in an increase in the frequency of successful collisions and hence an increase in the rate of the forward reaction. This is why the blue line shows a steep and instantaneous increase, to show the increase in the rate of the forward reaction when extra reactant is added.

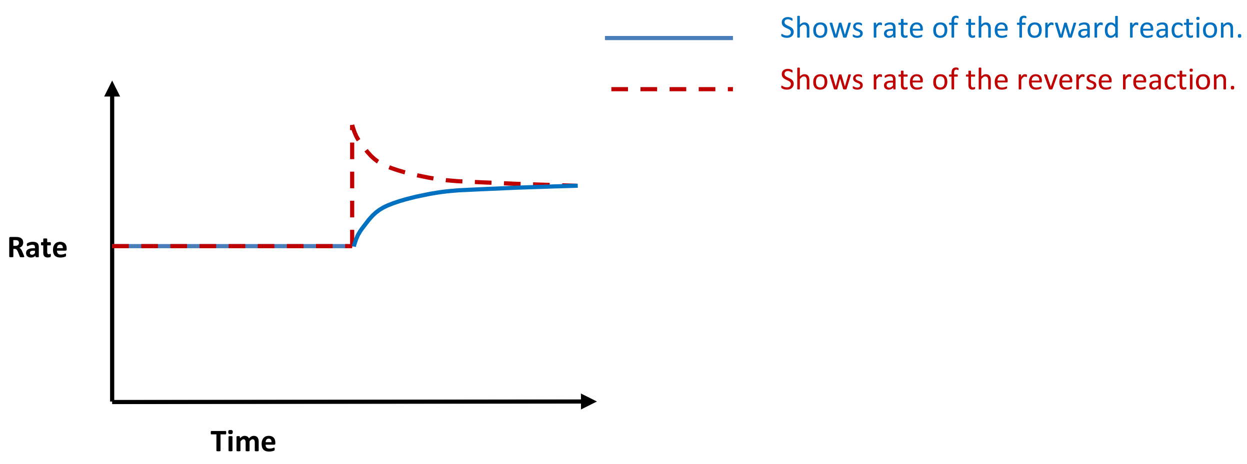
The red broken line showing the rate of the reverse reaction does not show an instantaneous increase or decrease. This is because the concentration of the products ($NH_3$) is not instantaneously (initially) affected by the addition of extra reactants.

As the rate of the forward reaction is faster than the rate of the reverse reaction, the overall reaction is moving towards the right (net forward reaction).

As can be seen in the graph, the rate of the forward reaction gradually decreases due to the decrease in frequency of successful collisions caused by the reduction in the number of reactant molecules as they are used up by the forward reaction. The rate of the reverse reaction gradually increases due to the increase in frequency of successful collisions as the concentration of products gradually increases as a result of the net forward reaction. Eventually the rate of the forward and reverse reactions are equal again when the system regains equilibrium. At the new equilibrium, the rate of both the forward and reverse reactions are faster than when they were at the original equilibrium. This is due to the fact that adding extra reactants has resulted in an overall increase in the number of reactant and product molecules when the system regains equilibrium

## Adding extra product to an equilibrium system

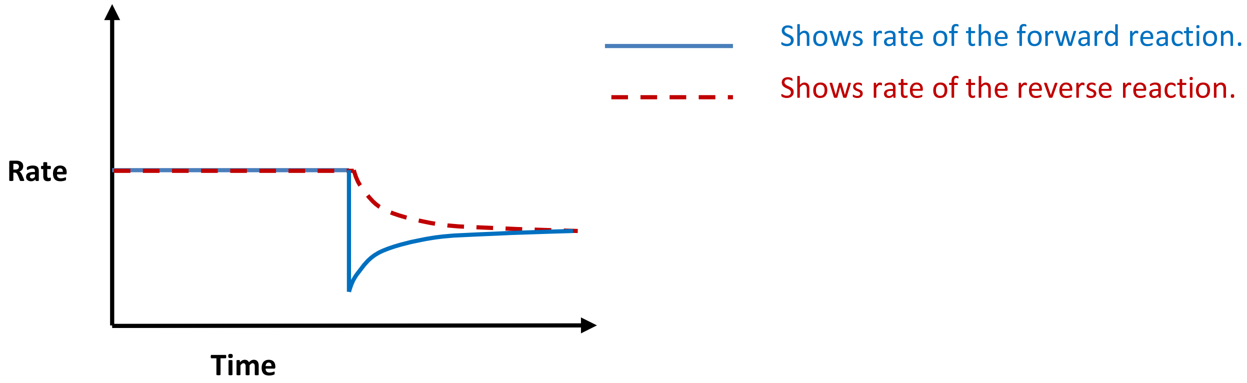
**Eg. Adding extra $NH_3$ to the system: $N_2$ (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)**



Adding extra product such as $NH_3$ to the above equilibrium system, will cause an instantaneous increase in the rate of the reverse reaction as the concentration and hence frequency of successful collisions of product molecules has increased. The rate of the forward reaction shows no initial change. The reaction will shift towards the reactants as the rate of the reverse reaction is faster than the rate of the forward reaction. The rate of the reverse reaction decreases due to the reduction in the number of product molecules as they react with each other. The rate of the forward reaction increases as the concentration of the reactants increases due to the net back reaction. Eventually the system regains equilibrium and the rate of the forward and reverse reaction become equal again.

## Removing reactant from an equilibrium system

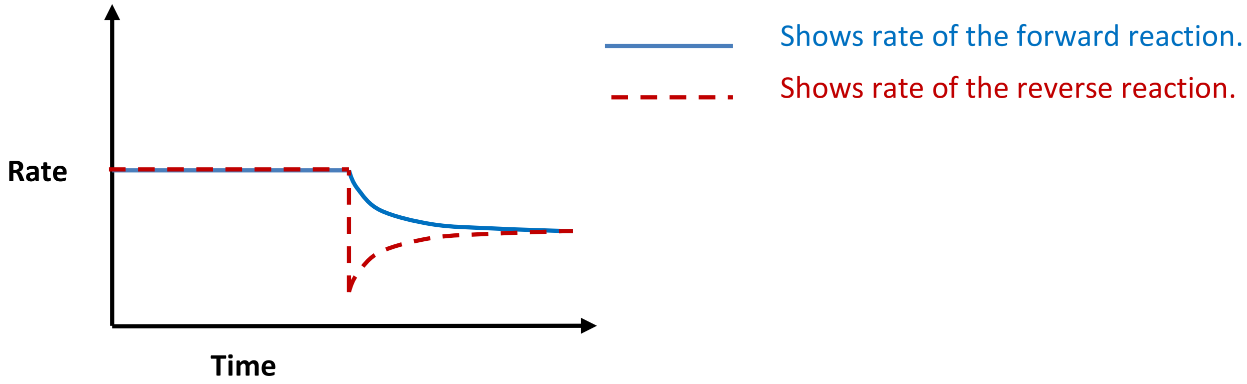
**Eg. Removing $N_2$ or $H_2$ to the system: $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$**



If either of the reactants, $N_2$ or $H_2$ are removed from the system, the rate of the forward reaction will decrease as the concentration of reactants is lower resulting in a decrease in the frequency of successful collisions. The rate of the reverse reaction will initially be unaffected. Since the rate of the forward reaction has decreased and the rate of the reverse reaction is unchanged, the reaction will shift backwards as the rate of the reverse reaction is now quicker than the rate of the forward reaction. The net back reaction will cause the number of reactant particles to gradually increase in concentration resulting in an increase in the rate of the forward reaction. The rate of the back reaction gradually decreases as the net back reaction lowers the concentration of products which in turn slows down the rate of the back reaction. Eventually the rate of the forward and reverse reactions become equal again. The removal of reactant molecules has caused an overall decrease in the number of both reactant and product molecules when equilibrium is re-established. Therefore the rate of both the forward and reverse reactions are slower at the new equilibrium.

## Removing product from an equilibrium system

**Eg. Removing $NH_3$ from the system: $N_2$ (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)**

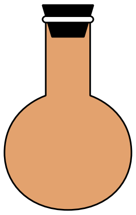


If some of the $NH_3$ product is removed from the system, the concentration of $NH_3$ will be lowered and the frequency of successful collisions between $NH_3$ molecules will decrease resulting in an instantaneous decrease in the rate of the reverse reaction. At this instant, the rate of the forward reaction will be unaffected and as a consequence there will be a net forward reaction as the rate of the forward reaction is now faster than the rate of the reverse reaction. As the net forward reaction uses up $N_2$ and $H_2$ molecules, the frequency of successful collisions between reactant molecules decreases resulting in a gradual decrease in the rate of the forward reaction. The net forward reaction increases the concentration of the $NH_3$ molecules. As a consequence the number of fruitful collisions between the product molecules increases causing a gradual increase in the rate of the reverse reaction. Once the system comes back to equilibrium the rate of both the reverse and forward reactions are lower as the removal of product molecules has resulted in an overall reduction in the number of molecules in the system.

# Using Le Chatelier's principle to determine if a reaction is exothermic or endothermic.

Le Chatelier's principle can be used to determine if a reaction is **exothermic or endothermic.** This is done by observing the changes occurring in a system when the temperature is either increased or decreased. Equilibrium systems that have different coloured reactants and products are most suited to this purpose. The equilibrium that exists between dinitrogen tetraoxide ($N_2O_4$) and nitrogen dioxide ($NO_2$) is a good example.

$\mathbf{N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)}$
Colourless Brown



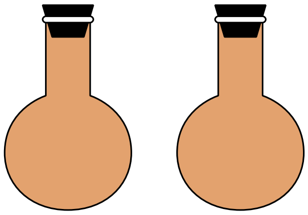
This flask contains an equilibrium mixture of colourless $N_2O_4$ and brown $NO_2$. Since the $N_2O_4$ is colourless it cannot be seen in the flask. Only the brown $NO_2$ is visible. Colourless means clear so the $N_2O_4$ molecules are invisible to our eye.

A simple experiment to determine if the reaction,

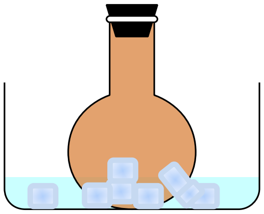
$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

is exothermic or endothermic is to observe the colour of the equilibrium mixture when the temperature is both increased and decreased. Consider the experiment shown below.

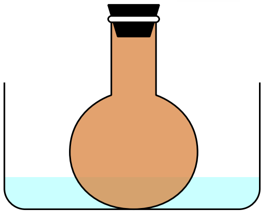
Fill 2 flasks with the equilibrium mixture of $N_2O_4$ and $NO_2$. It is important to ensure that both flasks contain the same amount of the mixture so that the intensity of the brown colour is the same in both flasks. The initial temperature of both flasks must also be the same.



Decrease the temperature of one flask by placing it in a container of ice cold water. Increase the temperature of the other flask by placing it in a container of boiling water.

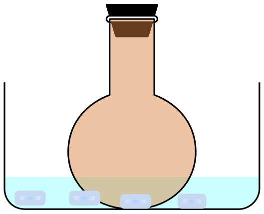


**ICE WATER**
**(LOW TEMPERATURE)**

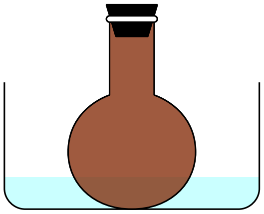


**BOILING WATER**
**(HIGH TEMPERATURE)**

After a few minutes, observe the colour of the gas mixture in each flask.



**ICE WATER**
**(LOW TEMPERATURE)**
Brown colour lighter



**BOILING WATER**
**(HIGH TEMPERATURE)**
**Brown colour darker**

The brown colour of the flask in the ice water has got LIGHTER/LESS INTENSE.

The brown colour of the flask in the boiling water has got DARKER/MORE INTENSE.

Now these observations can be used to determine whether this reaction is exothermic or endothermic. This can be explained from the observation of the color change in the ice water or the colour change in the boiling water.

When the flask was placed in boiling water, the brown colour became **more intense.** This shows that the reaction opposed the increase in temperature by favouring the FORWARD REACTION resulting in an increase in the concentration of the brown $NO_2$. Therefore the forward reaction must be decreasing the temperature by absorbing heat energy and is ENDOTHERMIC.

When the flask was placed in ice water, the brown colour became **less intense.** This shows that the reaction opposed the decrease in temperature by favouring the REVERSE REACTION resulting in a decrease in the concentration of the brown $NO_2$. Therefore the reverse reaction must be increasing the temperature by releasing heat energy into the system and is therefore exothermic. If the reverse reaction is exothermic then the forward reaction must be ENDOTHERMIC.

Here are a few points to consider when tackling questions involving using Le Chatelier's principle to classify reactions as either exothermic or endothermic.

- *The colour change will show whether the forward or reverse reaction has been favoured by the external change in temperature.*

- *Always remember that a reaction will oppose or undo a change that has been made to it. So if an equilibrium reaction has an external increase in temperature and the forward reaction is favoured, then it must be concluded that the forward reaction is decreasing the temperature and is therefore endothermic. If a reaction has an external decrease in temperature and the forward reaction is favoured, then it can be concluded that the forward reaction is increasing the temperature and is therefore exothermic.*

- *NEVER justify a shift in the direction of a reaction in terms of the concentration of a COLOURLESS reactant or product. For example, when the* $N_2O_4$ */* $NO_2$ *system was placed in ice water the brown colour became less intense showing that the back reaction was favoured. Avoid making statements such as, "when the reaction shifted backwards the concentration of the colourless* $N_2O_4$ *increased causing the brown colour of the mixture to become less intense / more colourless." As the* $N_2O_4$ *is colourless, the number of molecules present does not affect the colour of the mixture as they cannot be seen. A high concentration and a low concentration of* $N_2O_4$ *look the same – clear (colourless). In other words you can't see a thing!! There are no degrees of colourless so statements such as "more colourless" are incorrect. Only discuss the colour changes of a mixture in terms of the coloured species present in the mixture, in this case the brown* $NO_2$*. So a decrease in the brown colour of the mixture can only be due to a DECREASE IN THE CONCENTRATION OF BROWN* $NO_2$*, NOT an increase in the concentration of colourless* $N_2O_4$*.*

- *When asked to determine whether an equilibrium reaction is exothermic or endothermic, it is only for the* ***FORWARD REACTION.*** *In other words the heat of reaction (ΔH) is only given for the forward reaction.*

# Competing equilibria – carbon monoxide poisoning

When we breathe in, oxygen gas is absorbed by the blood surrounding our lungs which transports the oxygen to our cells. Haemogblobin, a large protein molecule in our blood is responsible for carrying the oxygen to our cells. Haemoglobin bonds to the oxygen molecules to produce oxyhaemoglobin. When oxyhaemoglobin is transported to our cells the oxygen is released and used by the cells to produce energy through the process of cellular respiration (this will be covered in chapter 12 of Unit 4 Chemistry Tutor). The binding of oxygen to haemoglobin is an equilibrium reaction:

**Oxygen + Haemoglobin ⇌ Oxyhaemoglobin**

A more detailed description of this reaction is

**$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$**

This equation shows that four $O_2$ molecules bind to one haemoglobin (Hb) molecule to produce one oxyhaemoglobin molecule ($Hb(O_2)_4$). The equilibrium constant for this reaction is quite large so when we breathe in a large number of the $O_2$ molecules taken in will react with Hb to produce $Hb(O_2)_4$. So the equilibrium concentration of $Hb(O_2)_4$ will be high.

Carbon monoxide gas (CO) is a toxic, colourless and odorless gas produced during the incomplete combustion of carbon containing compounds. Incomplete combustion was covered in chapter 6. Like $O_2$, CO is able to bind to haemoglobin and form an equilibrium mixture:

**$Hb + 4CO \rightleftharpoons Hb(CO)_4$   Kc = very large value**

The equilibrium constant for this reaction is much greater than the reaction between $O_2$ and Hb. This is because CO makes stronger bonds with Hb than what $O_2$ does. The consequence of this is that if a person is breathing in an environment that has a high concentration of CO, most of the Hb molecules in the blood surrounding the lungs will make bonds with CO instead of $O_2$. So the extent of the reaction between CO and Hb is greater than that between $O_2$ and Hb.

The problems associated with this are 2 fold. First of all the cells of the body are going to receive a large amount of the toxic CO gas. The second problem is that they will receive only a small amount of $O_2$. This is because only a small amount of Hb molecules are available to bond with $O_2$ as the CO molecules bonded with most of them. In terms of Le Chatelier's principle, the lowering of the concentration of Hb will drive the equilibrium reaction between Hb and $O_2$ backwards as this will increase the concentration of Hb. That is, $Hb(O_2)_4$ will decompose back into Hb and $O_2$ resulting in a decrease in the amount of $Hb(O_2)_4$ transported to the cells.

**Treatment of person suffering from carbon monoxide poisoning**

A person suffering from carbon monoxide poisoning may experience dizziness, sleepiness, breathing difficulties and confusion. If the amount of CO reaching the cells is high enough death may occur.

Treatment of a person suffering from carbon monoxide poisoning includes placing them in an oxygen rich environment. This may include giving them pure $O_2$ through a mask. This will increase the concentration of $O_2$ in the equilibrium reaction between Hb and $O_2$. According to Le Chatelier's principle, the system will oppose the increase in $O_2$ concentration by favouring the forward reaction as this will use up some of the $O_2$. Now the concentration of oxyhaemoglobin is increased resulting in the transport of more $O_2$ to the cells of the body. Now the amount of Hb available to react with CO will be lower. This reduction in the concentration of Hb will be opposed by the equilibrium reaction between Hb and CO shifting to the left causing $Hb(CO)_4$ in the lungs to be converted into CO which can be exhaled from the lungs.

Removing a person suffering carbon monoxide poisoning from the source of CO gas is very important. If the air the person is breathing in contains less CO, the concentration of the CO in the equilibrium reaction between Hb and CO will decrease. According to Le Chatelier's principle, the reduction in the concentration of CO will be opposed by a net back reaction as this will produce more CO gas. The CO gas produced by the back reaction can now be exhaled and removed from the lungs. This will free up a large number of Hb molecules that are now available to join up with $O_2$ again. The increase in concentration of Hb will be opposed by the reaction between Hb and $O_2$ shifting forward, resulting in a higher concentration of $Hb(O_2)_4$.

The reactions of $O_2$ and Hb and CO and Hb are referred to as **competing equilibria** because the CO and $O_2$ are competing for the same reactant, the Hb. The equilibrium reaction with the larger equilibrium constant will use up more of that reactant (in this case the Hb). This will decrease the extent of the reaction with the lower equilibrium constant.

# CHAPTER 9 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
This equilibrium expression,

$$K = \frac{[A] \times [B]^3}{[C]^2}$$

belongs to the equation

**A.** $A + 3B \rightleftharpoons 2C$
**B.** $2C \rightleftharpoons A + 3B$
**C.** $\frac{1}{2} A + 1\frac{1}{2} B \rightleftharpoons C$
**D.** A and C are both correct.

**Question 2**
Consider the equation,

$a\,Y \rightleftharpoons b\,X + c\,Z$

If the value of K is 125 M, the values of *a, b and c* are respectively

**A.** 1,2 and 3
**B.** 2, 1 and 1
**C.** 2, 1 and 2
**D.** 2, 2 and 2.

**Question 3**
2.0 mol of hydrogen iodide decomposes in a 1.0 L vessel according to the equation:

$2HI \rightleftharpoons H_2 + I_2$

What is the equilibrium constant for this reaction if 0.50 mol of $I_2$ is present at equilibrium?

**A.** 4
**B.** 0.25
**C.** 2.0
**D.** 0.17

*Questions 4, 5 and 6 refer to the following equilibrium reaction.*

$4HCl\ (g) + O_2\ (g) \rightleftharpoons 2H_2O\ (g) + 2Cl_2\ (g)$

$K = 1.98 \times 10^3$ at $105\ ^0C$

**Question 4**
The equilibrium expression for this reaction is

**A.** $\dfrac{[H_2O]^2 \times [Cl_2]^2}{[HCl]^4 \times [O_2]}$

**B.** $\dfrac{HCl]^4 \times [O_2]}{[H_2O]^2 \times [Cl_2]^2}$

**C.** $\dfrac{H_2O] \times [Cl_2]}{[HCl] \times [O_2]}$

**D.** $\dfrac{2[H_2O] \times 2[Cl_2]}{4[HCl] \times [O_2]}$

**Question 5**
A mixture of these gases at equilibrium is immersed into a container holding 100 mL of hot water. As a result the temperature of the mixture of gases increases from 20 $^0C$ to 90 $^0C$. When the system regains equilibrium at the new temperature, the number of molecules in the mixture has *decreased.* It can be concluded that

**A.** the reaction is exothermic.
**B.** the reduction in the number of molecules caused a net forward reaction to occur.
**C.** the reaction opposed the increase in temperature by shifting towards the reactants.
**D.** the reverse reaction produces heat.

**Question 6**
At 105 $^0$C, the equilibrium constant for the reaction,

$4H_2O\ (g) + 4Cl_2\ (g) \rightleftharpoons 8HCl\ (g) + 2O_2\ (g)$

is

**A.** 0.000505
**B.** $2.6 \times 10^{-7}$
**C.** $3.9 \times 10^{6}$
**D.** 0.00101

**Question 7**
An empty gas jar is filled with 2.0 mol of $H_2$ and 2.0 mol of $Cl_2$ gas. The 2 gases are allowed to form an equilibrium mixture according to the following equation.

$H_2\ (g) + Cl_2\ (g) \rightleftharpoons 2HCl\ (g)\ \ \Delta H < 0$

As the reaction approaches equilibrium

**A.** the moles of HCl produced will always be double the moles of $Cl_2$ remaining.
**B.** the pressure in the gas jar will be increased.
**C.** the moles of $Cl_2$ remaining will equal the moles of $H_2$ remaining.
**D.** the concentration fraction will always be greater than the K value for the reaction.

**Question 8**
When the temperature of the equilibrium system,

$2NO\ (g) + Cl_2\ (g) \rightleftharpoons 2NOCl\ (g)\ \ \Delta H = -39\ KJ\ mol^{-1}$

is increased,

**A.** the rate of the forward reaction increases.
**B.** the rate of the forward reaction decreases.
**C.** the proportion of reactants to products decreases.
**D.** the pressure decreases.

**Question 9**
Unsaturated hydrocarbon molecules are produced by a process known as *cracking.* This process involves the thermal decomposition of saturated molecules.
An example of a cracking reaction is shown below.

$C_5H_{12}\ (g) \rightleftharpoons C_5H_{10}\ (g) + H_2\ (g)\ \ \Delta H = +\ value$

The conditions that would not favour a high yield of $C_5H_{10}$ include

**A.** using a catalyst, low pressure and high temperature.
**B.** cooling the product mixture.
**C.** using a catalyst and low pressure.
**D.** increasing the volume of the reaction mixture.

**Question 10**
An equilibrium reaction is represented by the equation

$A\ (g) + 2B\ (g) \rightleftharpoons A_2B\ (g) \qquad K = 10^{-7}\ M^{-2}$

When 1.0 mol of A is allowed to react with 3.0 mol of B, the moles of $A_2B$ produced would be expected to be

**A.** 2.0 mol
**B.** 1.0 mol
**C.** Less than 1.0 mol
**D.** 4.0 mol

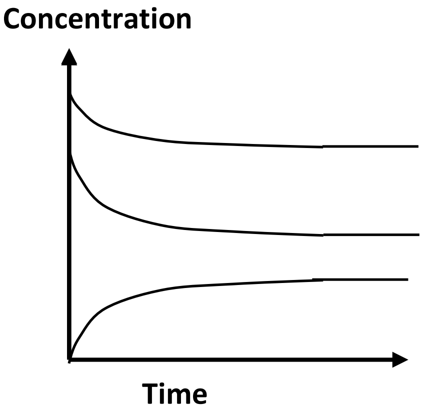
**Question 11**

The rate of an exothermic reaction will ALWAYS increase when

**A.** the temperature is decreased and a catalyst is employed.
**B.** When the pressure is increased and the temperature decreased.
**C.** the pressure is decreased and heat allowed to escape from the system.
**D.** the pressure is increased and the temperature increased.

**Question 12**

Consider the graph below which shows how the concentration of reactants and products change when a reaction approaches equilibrium.



The reaction represented by this graph is

**A.** $N_2 + 3H_2 \rightleftharpoons 2NH_3$
**B.** $S + O_2 \rightleftharpoons SO_2$
**C.** $H_2 + O_2 \rightleftharpoons 2H_2O$
**D.** $2HI \rightleftharpoons H_2 + I_2$

**Question 13**

In which one of the following equations would the position of equilibrium be affected by an increase in volume?

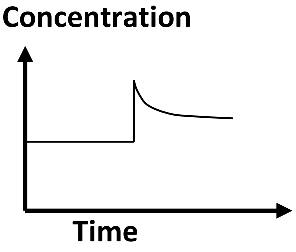
**A.** $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$
**B.** $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$
**C.** $N_2\ (g) + 2O_2\ (g) \rightleftharpoons N_2O_4\ (g)$
**D.** $KNO_3\ (aq) \rightleftharpoons K^+\ (aq) + NO_3^-(aq)$

**Question 14**

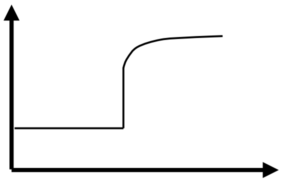
Which of the following graphs correctly shows the change in the concentration of $SO_2$ gas when the following equilibrium system is compressed at constant temperature? This reaction is represented by the following equation.

$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$

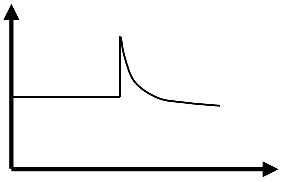
**A.**



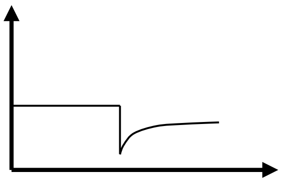
**B.**



**C.**



**D.**



## Short Answers

**Question 1**

Give the expression for the equilibrium constant for the following equations. You must include the units.

**a.** $H_2$ (g) + $Cl_2$ (g) $\rightleftharpoons$ $2HCl$ (g)
**b.** $4HCl$ (g) + $O_2$ (g) $\rightleftharpoons$ $2H_2O$ (g) + $2Cl_2$ (g)
**c.** $2NO_2$ (g) $\rightleftharpoons$ $N_2O_4$ (g)

**Question 2**

A gaseous equilibrium mixture consisting of 0.251 mol of CO, 0.5001 mol of $O_2$ and 2.5 mol of $CO_2$ is held in a 3.0 L sealed flask at 250 $^0$C.

**a.** Calculate the equilibrium constant if the equation for the reaction is

$2CO$ (g) + $O_2$ (g) $\rightleftharpoons$ $2CO_2$ (g)

**b.** Another mixture of these gases held at 100 $^0$C in a sealed 3.0 L flask has the following composition, 0.171 mol of CO, 0.4601 mol of $O_2$ and 2.58 mol of $CO_2$. Calculate the K value at this temperature.

**c.** Using your answers to **a** and **b,** determine if the reaction described by the equation,

$2CO$ (g) + $O_2$ $\rightleftharpoons$ $2CO_2$ (g)

is exothermic or endothermic.

**Question 3**

An equilibrium mixture is made by allowing 5.98 mol of CO to react with 2.73 mol of $H_2$ in a 2.0 L vessel. When equilibrium is reached the moles of $CH_3OH$ in the mixture are equal to 1.21 mol. Calculate the equilibrium constant for this reaction. The equation is shown below.

$CO$ (g) + $2H_2$ (g) $\rightleftharpoons$ $CH_3OH$ (g)

**Question 4**

Nitrogen dioxide can be produced by the following equation.

$2NO$ (g) + $O_2$ (g) $\rightleftharpoons$ $2NO_2$ (g)

**a.** A 1.0 L vessel is filled with 0.645 mol of NO, 2.18 mol of $O_2$ and 0.76 mol of $NO_2$. After some time analysis of the mixture revealed that the amount of the $O_2$ increased by 0.24 mol. Calculate the equilibrium constant for this reaction at 25 $^0$C**.**

**b.** Another equilibrium mixture consisting of the same gases was placed in a freezer. Analysis of this mixture at the lower temperature revealed that the moles of $NO_2$ present at equilibrium decreased by 0.25 mol. Is the formation of $NO_2$ described by the above equation an exothermic or endothermic process? Explain your answer.

**c.** Calculate the pressure in atmospheres, of the vessel described in part **a.** when equilibrium was established.

**Question 5**

The equilibrium constant for the reaction,

$2H_2O$ (g) + $2Cl_2$ (g) $\rightleftharpoons$ $4HCl$ (g) + $O_2$ (g)

at 380 K is $4.8 \times 10^{-4}$ M.

**a.** $5.0 \times 10^{-4}$ mol of $Cl_2$ is mixed with $H_2O$ in a 3.0 L flask at 380 $^0$C. When equilibrium is reached $3.44 \times 10^{-5}$ mol of $O_2$ is produced. Calculate the amount in mol, of $H_2O$ gas that was originally added to the flask.

**b.** How would the position of equilibrium be affected, if the mixture was cooled down only enough to condense the $H_2O$ into a liquid?

**c.** 1.0 mole of $H_2O$ (g), 0.25 mol of $Cl_2$ (g), $3.12 \times 10^{-3}$ mol of HCl (g) and 0.0015 mol of $O_2$ (g) are placed in a 1.0 L gas jar at 380 K. Is this mixture at equilibrium? If it is not at equilibrium describe how this reaction will get to equilibrium.

**Question 6**

Some $PCl_5$ gas is placed into an empty gas jar and allowed to decompose according to the equation

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

Use collision theory to discuss how the rate of the forward and reverse reactions change as the reaction *approaches* and finally *achieves* equilibrium.

**Question 7**

An important equation in the production of sulfuric acid is

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g) \qquad \Delta H = -196\ \text{KJ mol}^{-1}$$

**a.** What conditions of temperature and pressure would produce a high yield of $SO_3$?

**b.** What conditions of temperature and pressure would produce a fast reaction rate?

**c.** Is there a conflict between the conditions that would give a high yield of $SO_3$ and the conditions that would give a fast reaction rate? Discuss your answer.

**Question 8**

Consider the following system

$$A + B \rightleftharpoons C \qquad \Delta H = -50\ \text{KJ mol}^{-1}$$

If extra A is added to the system:

**a.** How would the position of equilibrium change? Discuss your answer.

**b.** How would the temperature of the system change? Discuss your answer.

**c.** How would the value of K be affected? Discuss your answer.

**Question 9**

Consider the following equilibrium reaction.

$$Co(H_2O)_6^{2+}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons CoCl_4^{2-}\ (aq) + 6H_2O\ (l)$$

Some important information regarding this reaction are

- $Co(H_2O)_6^{2+}$ has a red colour in solution.
- $CoCl_4^{2-}$ has a blue colour in solution.
- $Cl^-$ and $H_2O$ are colourless.

The following changes are made to this equilibrium system.

**a.** the addition of a few drops of concentrated hydrochloric acid.

**b.** the addition of a few drops of concentrated $AgNO_3$ solution.

For each change, discuss how the colour of the mixture at the NEW EQUILIBRIUM compares with the colour at the ORIGINAL EQUILIBRIUM. You should also state whether the concentration of $Cl^-$ ions has increased or decreased at the new equilibrium.

**Question 10**
In terms of equilibrium, explain why a person suffering from carbon monoxide poisoning has a reduction in the concentration of oxyhaemoglobin reaching their cells.

**Question 11**
Some $N_2O_4$ is placed inside a gas syringe and allowed to decompose until equilibrium is reached. The equation describing the reaction is

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

$N_2O_4$ is colourless and $NO_2$ is brown. The volume of the mixture is reduced at constant temperature and allowed to re-establish equilibrium.

**a.** How will the colour of the mixture at the new equilibrium compare with the colour before the volume was reduced? Discuss your answer.
**b.** How will the moles and mass of the $NO_2$ at the new equilibrium compare with the original equilibrium.
**c.** How was the rate of the forward reaction affected by the reduction in volume? Discuss.

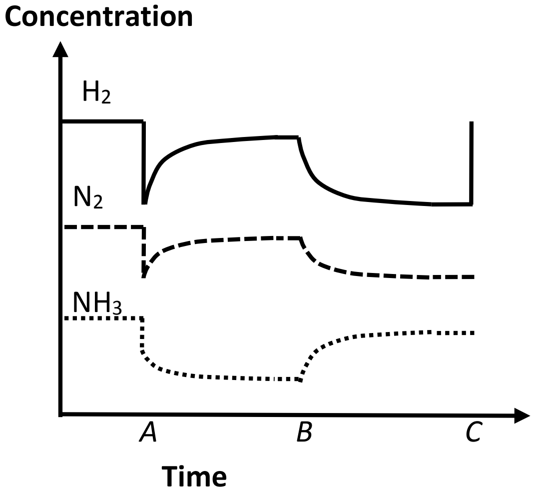
The mixture is allowed to return to the original volume. Then it is placed inside an ice water bath. After a few minutes it is observed that the brown colour has become more intense.

**d.** Is the reaction exothermic or endothermic? Discuss your answer.

**Question 12**
The production of ammonia from nitrogen and hydrogen gas is of great industrial importance. The equation describing this reaction is shown below.

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) \quad \Delta H = -$

The graph below shows the concentration of the reactants and products of an equilibrium mixture formed from this reaction. A number of changes are made to the system and these are shown on the graph.



**a.** How many times was the system at equilibrium?
**b.** What change was made to the system at the point labeled A on the graph?
**c.** What change was made to the system at the point labeled B on the graph. Explain your answer.
**d.** How would the value of the equilibrium constant at point B compare with the value at point A? Discuss your answer.
**e.** A change was made at point C but the response of the system is not shown on the graph. Draw a sketch of a rate versus time graph that shows how the rates of the forward and reverse reactions were affected immediately after the change and when the system went back to equilibrium.

**Question 13**

Draw a rough sketch of a concentration versus time graph showing the reaction

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons$
$CH_3COO^-\ (aq) + H_3O^+\ (aq)$

regaining equilibrium after it has been diluted with a large volume of water. Your graph must show the concentration of $CH_3COOH$, $H_2O$, $CH_3COO^-$ and $H_3O^+$ before and after the dilution.

**Question 14**

The weak acid, benzoic acid, with formula $C_6H_5COOH$ ionises in water according to the following equation:

$C_6H_5COOH\ (aq) + H_2O\ (l) \rightleftharpoons$
$C_6H_5COO^-\ (aq) + H_3O^+\ (aq)$

**a.** Discuss the effect on the equilibrium yield of $C_6H_5COO^-$ if

  **i.** a few drops of concentrated HCl is added to the system.

  **ii.** a few drops of concentrated NaOH are added to the system.

**b.** What would happen to the pH of the acid solution if it was diluted with a large amount of water?

**Question 15**

On planet Earth there is a cyclic movement of carbon dioxide gas between the atmosphere and bodies of water such as the oceans, lakes and rivers.

This can be represented by the following equilibria.

$CO_2\ (g) \rightleftharpoons CO_2\ (aq)$
$CO_2\ (aq) + H_2O\ (l) \rightleftharpoons H^+\ (aq) + HCO_3^-\ (aq)$

Use the above equations to help explain what effect rising levels of $CO_2$ in the atmosphere are having on the pH of the ocean.

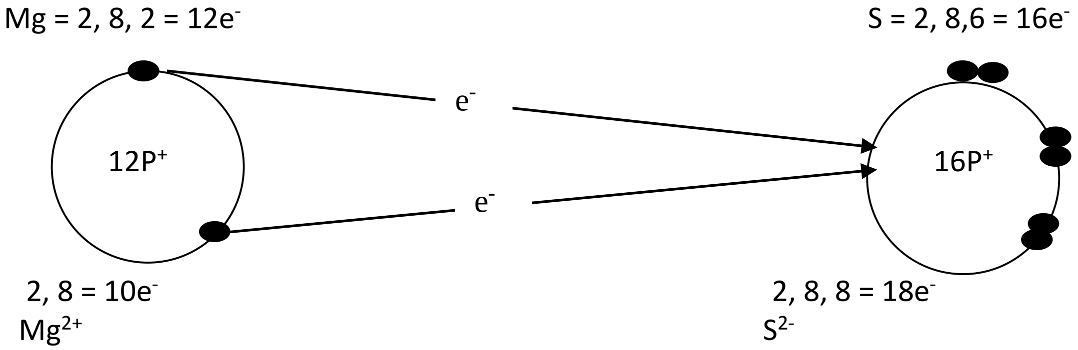
# Chapter 10 – Redox

**REDOX** is derived from the terms **RED**UCTION and **OX**IDATION.

**Oxidation –** Is a loss or donation of electrons.
**Reduction –** Is a gaining or receiving of electrons.

Oxidation also means to **gain oxygen** or **lose hydrogen**. This is a more traditional definition. The definition of reduction in terms of gaining electrons seems contradictory as the general meaning of the word, reduction, is to lose something not gain. It would make more sense to use the term, reduction, to describe a loss of electrons. The more traditional definition of reduction is to **lose oxygen** (hence the use of the term reduction) or **gain hydrogen**. These more traditional definitions of oxidation and reduction will be discussed later on. The loss or gain of electrons is the more fundamental way to define redox. <u>When oxidation occurs electrons are always lost but oxygen is not always gained and hydrogen is not always lost. When reduction occurs electrons are always gained but hydrogen is not always gained and oxygen is not always lost.</u>

You may recognise the electron transfer diagram shown below. This shows the transfer of 2 electrons from the outermost shell of a Mg atom to the outermost shell of a S atom. This occurs because both atoms need to gain a full outer shell of electrons.



After the Mg loses its 2 valence electrons, the number of electrons has decreased from 12 to 10. The number of protons in the nucleus however, is still 12. Now the atom has 12 positively charged protons and 10 negatively charged electrons resulting in an overall charge of +2 (+12 – 10). So the Mg atom is now a $Mg^{2+}$ cation.

In a similar way, after the S gains 2 electrons from the Mg, the number of electrons increases from 16 to 18. The number of protons in the nucleus of this atom is still 16. Now the atom has 16 positively charged protons and 18 negatively charged electrons resulting in an overall charge of -2 (16 – 18). The S atom is now a $S^{2-}$ anion.

The Mg has undergone OXIDATION because it **lost** 2 electrons.
The S atom has undergone REDUCTION because it **gained** 2 electrons.

The processes of oxidation and reduction can be summarised by **half equations.**

The oxidation half equation is

$Mg \rightarrow Mg^{2+} + 2e^-$

The 2 electrons ($2\ e^-$) that the Mg lost are on the right hand side of the equation. The $Mg^{2+}$ ion that was produced in the process is also on the right hand side of the equation.

**An oxidation half equation always has the electrons on the right hand side of the equation.**

The reduction half equation is

$S + 2e^- \rightarrow S^{2-}$

The 2 electrons gained by the S are on the left hand side of the arrow. The $S^{2-}$ ion that was produced in the process is on the right hand side of the arrow.

**A reduction half equation always has the electrons on the left hand side of the equation.**

A **FULL EQUATION** can be written out for the redox reaction between Mg and S by combining all of the reactants from both half equations and all of the products from both half equations. The electrons are left out of the full equation because they cancel each other out.

$Mg + S + 2\cancel{e^-} \rightarrow Mg^{2+} + S^{2-} + 2\cancel{e^-}$

**$Mg + S \rightarrow Mg^{2+} + S^{2-}$ OR $Mg + S \rightarrow MgS$**

REDUCTION AND OXIDATION ALWAYS **OCCUR SIMULTANEOUSLY.** One cannot happen without the other. For example the Mg cannot lose electrons to empty space. There must be another chemical present capable of undergoing reduction to gain the electrons that were lost. In a similar way the S cannot undergo reduction unless it can gain the electrons that were lost by a chemical that has undergone oxidation.

## Worked Example 1

Complete the following half equations by placing the correct number of electrons on the appropriate side of the equation.

**a.** $Na \rightarrow Na^+$
**b.** $Fe^{3+} \rightarrow Fe^{2+}$
**c.** $Ca^{2+} \rightarrow Ca$
**d.** $I^- \rightarrow I_2$
**e.** $Cl_2 \rightarrow Cl^-$
**f.** $O_2 \rightarrow O^{2-}$

## Worked Example 1 Solutions

**a.** The Na atom on the left hand side of the equation is neutral in charge. This means that the atom has the same number of protons and electrons and the negative and positive charges cancel each other out. On the right hand side of the equation the Na now has a charge of +1 ($Na^+$). Under normal circumstances, atoms can only become charged is if they either lose or gain electrons. So if an atom has gone from having a charge of zero to a charge of + 1 it must **have lost an electron**. If it loses an electron, the number of protons will now be one more than the number of electrons.

$Na$ (11 $p^+$ and 11 $e^-$) $\rightarrow$ $Na^+$ (11 $p^+$ and 10 $e^-$) + $e^-$

$Na \rightarrow Na^+ + e^-$

So the Na atom has lost an electron, therefore it has undergone oxidation and the electron is shown on the right hand side of the arrow.

Your equation will be correct if the charges on either side of the arrow are balanced. The Na atom on the left hand side of the arrow has a charge of zero. This is equal to the charge on the right hand side of the arrow which is also zero due to the +1 charge of the $Na^+$ and the -1 charge of the $e^-$ cancelling out.

**b.** The $Fe^{3+}$ ion has lost a +1 charge to become to $Fe^{2+}$. Therefore the ion must have gained an electron and undergone reduction.

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Once again the charges on both sides of the equation are balanced. They are both +2.

**c.** The $Ca^{2+}$ ion has become a neutral atom of Ca. Therefore it must have undergone reduction and gained 2 electrons to cancel out the charge of +2.

$Ca^{2+} + 2e^- \rightarrow Ca$

**d.** With this one before we can put in the electrons we must balance the iodine atoms on both sides of the equation by placing a coefficient of 2 outside the $I^-$.

$2I^- \rightarrow I_2$

The charge on the left hand side of the equation is -2 and the charge on the right hand side is zero. So the 2 negatively charged $I^-$ ions must have lost 2 electrons to produce a neutral $I_2$ molecule.

$2I^- \rightarrow I_2 + 2e^-$

**e.** Once again balance the atoms on both sides of the equation first.

$Cl_2 \rightarrow 2Cl^-$

The $Cl_2$ molecule has no charge and has turned into 2 $Cl^-$ ions with an overall charge of -2. Therefore the $Cl_2$ molecule must have been reduced and gained 2 electrons.

$Cl_2 + 2e^- \rightarrow 2Cl^-$

**f.** Balance the O atoms on both sides of the equation first.

$O_2 \rightarrow 2O^{2-}$

The neutral $O_2$ molecule has become 2 $O^{2-}$ ions with a an overall charge of -4. Therefore the $O_2$ must have gained 4 electrons.

$O_2 + 4e^- \rightarrow 2O^{2-}$

## Combining redox half equations where the electrons are unbalanced

Consider the reaction where Mg is oxidised by $O_2$. That is, Mg undergoes oxidation and $O_2$ undergoes reduction. The 2 half equations are:

$Mg \rightarrow Mg^{2+} + 2e^-$
$O_2 + 4e^- \rightarrow 2O^{2-}$

Unlike the example between Mg and S, the number of electrons given away during oxidation is not equal to the number of electrons gained during reduction. The Mg gives away 2 electrons but the $O_2$ needs to gain 4. When a redox reaction occurs all of the electrons lost during oxidation must be gained by the chemical species undergoing reduction. The $O_2$ will not be satisfied with just gaining the 2 electrons given away by the Mg. It must gain 4 electrons.

The only way this reaction can happen is if 2 Mg atoms give away a combined total of 4 electrons. This way the $O_2$ will be able to gain the 4 electrons it needs to undergo reduction. When combining 2 redox half equations where the electrons are not balanced, you must multiply each equation by an appropriate whole number in order to make the number of electrons lost during oxidation equal to the number of electrons gained during reduction. In other words, you multiply each half equation by a number that will make the number of electrons the same. So for the reaction between Mg and $O_2$:

$Mg \rightarrow Mg^{2+} + 2e^-$ (x2)

$2Mg \rightarrow 2Mg^{2+} + \cancel{4e^-}$
$O_2 + \cancel{4e^-} \rightarrow 2O^{2-}$

Full equation

$2Mg + O_2 \rightarrow 2Mg^{2+} + 2O^{2-}$ or $2Mg + O_2 \rightarrow 2MgO$

## Reductants and Oxidants

Let's go back to the earlier example illustrating the redox reaction between Mg and S. As was discussed earlier, oxidation and reduction must occur simultaneously. One depends on the other occurring. So it is reasonable to say that oxidation causes reduction to occur and reduction causes oxidation to occur.

When the magnesium underwent oxidation, it gave the sulfur 2 electrons. Therefore the magnesium helped the sulfur to undergo reduction. As a consequence the magnesium can be referred to as a **REDUCING AGENT**. The word agent implies help, so the term reducing agent can be defined as a helper of reduction.

In a similar way when the sulfur gained electrons, it helped the magnesium undergo oxidation. The magnesium can't give away its electrons if there is not another atom present to gain them. So the sulfur is referred to as an **OXIDISING AGENT** as it helped oxidation to occur.

The term **reductant** has the same meaning as **reducing agent.**
The term **oxidant** has the same meaning as **oxidising agent.**

A chemical that undergoes oxidation is a **reducing agent / reductant.**
A chemical that undergoes reduction is an **oxidising agent / oxidant.**

One way that might help you wrap your head around this is to look at the term TRAVEL AGENT. A travel agent helps other people to travel. They don't necessarily travel themselves. In a similar way, a **reducing agent** helps other chemicals undergo reduction. It is does not itself undergo reduction.

## Worked Example 2

Write out the half equations for the redox reaction described by this full equation. Then identify the reductant and oxidant.

$Zn\ (s) + Mg^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Mg\ (s)$

## Worked Example 2 Solutions

$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

$Mg^{2+}\ (aq) + 2e^- \rightarrow Mg\ (s)$

Zn has undergone oxidation so it is a reductant.
$Mg^{2+}$ has undergone reduction so it is an oxidant.

## Redox half equations for reactions occurring in acidic media

Most of the redox reactions that will be encountered in units 3 chemistry occur in solutions. The term **acidic media** describes solutions that have acids dissolved in them. As a consequence there are many $H^+$ ions in the solution that can take part in the reactions. Recall that acids produce $H^+(aq)$ ions in solution. Consider the following example:

**Complete the half equation for when $Cr_2O_7^{2-}$ (aq) changes into $Cr^{3+}$ in an acidic solution**.

There is more involved in writing out this half equation than just adding the correct number of electrons on the appropriate side of the equation. The half equations in worked example 1 involved only 1 element. There are 2 elements in this half equation, Cr and O that need to be balanced on both sides of the equation. Below is a list of steps that must be followed when balancing these types of equations.

**Step 1 – Balance any elements other than H and O in the equation.**

$Cr_2O_7^{2-}\ (aq) \rightarrow Cr^{3+}\ (aq)$

In this case it means balance the Cr atoms on either side of the equation. There are two on the left hand side of the equation and one on the right so we need a coefficient of 2 on right hand side of the equation.

$Cr_2O_7^{2-}\ (aq) \rightarrow 2Cr^{3+}\ (aq)$

**Step 2 – Balance O atoms by adding $H_2O$.**

There are 7 O atoms on the left hand side so we need to add 7 $H_2O$ molecules to the right hand side of the equation.

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$

**Step 3 – Balance H atoms by adding $H^+$ ions.**

There are 14 H atoms on the right hand side so we need to add 14 $H^+$ ions to the left hand side of the equation.

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

**Step 4 – Balance the charges on both sides of the equation by adding electrons to the side that has the least negative charge/most positive charge. This will make the charges on both sides of the equation the same.**

This is a step that students can find challenging. You need to very carefully calculate the charges on both sides of the equation.

On the left hand side of the equation the $Cr_2O_7^{2-}$ ion has a charge of -2 and the 14 $H^+$ ions have a charge of +14. -2 + 14 = overall charge of **+12**.

On the right hand side of the equation, $2Cr^{3+}$ has a charge of +6 and the 7 $H_2O$ molecules have no charge. Therefore the overall charge on the product side of the equation = **+6.**

**Overall charge = +12** **Overall charge = +6**

$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

In order to balance the charges on both sides of the equation, 6 electrons must be added to the left hand side of the equation. This will make the overall charge on the left hand side of the equation equal to +6 ( +12 – 6 = +6). Now the overall charge on both sides of the equation is equal to +6.

**Overall charge = +6** **Overall charge = +6**

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

**Step 5 – Add the states of matter.**

All ions are aqueous (aq). $H_2O$ is liquid (l). The electrons are not matter so they don't have any states.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

- These half equations are also known as **ionic equations** because they only show ions that are taking part in the reaction. That is, they don't include the spectator ions.

## Worked Example 3

Write out half equations for the following. Identify the reactant in each half equation as either an oxidant or reductant.

**a.** $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
**b.** $SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq)$
**c.** $H_2O_2(aq) \rightarrow H_2O(l)$
**d.** $H_2S(g) \rightarrow S(s)$

## Worked Example 3 Solutions

**a.**

***overall charge =+ 7 (-1+8)*** ***overall charge = +2 (+2 + 0)***

$MnO_4^- (aq) + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 4H_2O (l)$

$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+} (aq) + 4H_2O (l)$

$MnO_4^-$ has been reduced so it is an OXIDANT.

- *You might be asking the question, how do we know that it is the* $MnO_4^-$ *that is the oxidant and not the other chemical in the equation, the* $H^+$ *ions? This question is best answered after we have covered oxidation numbers later on in this chapter. Refer to question 6 from the short answer section of the chapter review.*

**b.**

***overall charge = -2 (-2+0)*** ***overall charge = 0 (-2 + 2)***

$SO_3^{2-} (aq) + H_2O (l) \rightarrow SO_4^{2-} (aq) + 2H^+ (aq)$

$SO_3^{2-} (aq) + H_2O (l) \rightarrow SO_4^{2-} (aq) + 2H^+ (aq) + 2e^-$

$SO_3^{2-}$ has been oxidised so it is a REDUCTANT.

**c.**

***Overall charge = +4*** ***overall charge = 0***

$H_2O_2 (aq) + 2H^+ (aq) \rightarrow H_2O (l) + H_2O (l)$

$H_2O_2 (aq) + 2H^+ (aq) + 2e^- \rightarrow H_2O (l) + H_2O (l)$

$H_2O_2 (aq) + 2H^+ (aq) + 2e^- \rightarrow 2 H_2O (l)$

$H_2O_2$ has been reduced so it is an OXIDANT.

**d.**

$H_2S (g) \rightarrow S (s)$

There are no O atoms that need balancing so there is no need to add any $H_2O$ molecules.

***Overall charge = 0*** ***Overall charge = +2***

$H_2S (g) \rightarrow S (s) + 2H^+ (aq)$

$H_2S (g) \rightarrow S (s) + 2H^+ (aq) + 2e^-$

$H_2S$ has been oxidised so it is a REDUCTANT.

# Writing full equations for redox reactions in acidic media

Writing full equations for redox reactions occurring in acidic media follows the same rules for the more simple reactions that were covered earlier. That is, after the half equations have been written out they may need to be multiplied by an appropriate coefficient in order to make the electrons lost during oxidation equal to the electrons gained during reduction.

The half equations for redox reactions in acidic media are more complicated and when the half equations are combined there will often be chemicals such as $H_2O$ and $H^+$ present on both sides of the equation. These must be canceled out in order for the full equation to be correct. Consider the following example.

**Potassium dichromate reacts with ethanol to produce a solution of chromium (III) ions and ethanoic acid. Write out the full equation for this reaction.**

Potassium dichromate has the following formula, $K_2Cr_2O_7$. Potassium is a group 1 metal and during redox reactions a $K^+$ ion may be reduced into K metal and K metal may be oxidised into $k^+$ ions. There was no mention however, of the $K^+$ ion having changed during the reaction so it is a spectator ion and must therefore not appear in the half equation.

$Cr_2O_7^{2-}$ (aq) → $Cr^{3+}$ (aq) (K$^+$ has been taken out.)

$Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) + $6e^-$ → $2Cr^{3+}$ (aq) + $7H_2O$ (l) (REDUCTION)

$C_2H_5OH$ (aq) → $CH_3COOH$ (aq)

$C_2H_5OH$ (aq) + $H_2O$ (l) → $CH_3COOH$ (aq) + $4H^+$ (aq) + $4e^-$ (OXIDATION)

The $Cr_2O_7^{2-}$ needs to gain $6e^-$ and the $C_2H_5OH$ needs to lose 4 $e^-$. The only way to make the number of electrons lost during oxidation equal the number of electrons gained during reduction is to first of all find the lowest common multiple of 6 and 4 which is 12. So both half equations will have 12 electrons.

Therefore the reduction half equation must be multiplied by 2:

$Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) + $6e^-$ → $2Cr^{3+}$ (aq) + $7H_2O$ (l) (x2)

$2Cr_2O_7^{2-}$ (aq) + $28H^+$ (aq) + $12e^-$ → $4Cr^{3+}$ (aq) + $14H_2O$ (l)

Therefore the oxidation half equation must be multiplied by 3:

$C_2H_5OH$ (aq) + $H_2O$ (l) → $CH_3COOH$ (aq) + $4H^+$ (aq) + $4e^-$ (x3)

$3C_2H_5OH$ (aq) + $3H_2O$ (l) → $3CH_3COOH$ (aq) + $12H^+$ (aq) + $12e^-$

So now the 2 half equation can be combined:

$2Cr_2O_7^{2-} + \boxed{28H^+} + \cancel{12}e^- + 3C_2H_5OH + \boxed{3H_2O} \rightarrow 4Cr^{3+} + \boxed{14H_2O} + 3CH_3COOH + \boxed{12H^+} + \cancel{12}e^-$

There are 28 $H^+$ on the left hand side of the equation and 12 on the right hand side. Therefore 12 $H^+$ ions are subtracted from both sides of the equation leaving: 28 – 12 = 16 $H^+$ on the left hand side of the equation.

There are 3 $H_2O$ molecules on the left hand side of the equation and 14 on the right. Therefore 3 $H_2O$ molecules are subtracted from both sides of the equation leaving: 14 – 3 = 11 $H_2O$ molecules on the right hand side of the equation. On the left hand side of the equation the $H_2O$ molecules cancel out ($3H_2O – 3H_2O = 0$). So the full equation is

$2Cr_2O_7^{2-}\ (aq) + 16H^+\ (aq) + 3C_2H_5OH\ (l) \rightarrow 4Cr^{3+}\ (aq) + 11H_2O\ (l) + 3CH_3COOH\ (aq)$

## Worked Example 4

Copper metal is placed in a solution containing potassium permanganate. The products of the reaction are permanganate ions and copper (II) ions.

**a.** Give the oxidation half equation.
**b.** Give the reduction half equation.
**c.** Give the formula of the reductant.
**d.** Give the formula of the oxidant.
**e.** Write out the full equation for this reaction.
**f.** What was oxidised during this reaction?
**g.** What was reduced during this reaction.

## Worked Example 4 Solutions

**a.** $Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$
**b.** $MnO_4^-\ (aq) + 8H^+\ (aq) + 5e^- \rightarrow Mn^{2+}\ (aq) + 4H_2O\ (l)$
**c.** Reductant = Cu
**d.** Oxidant = $MnO_4^-$

**e.**

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$ (x5)
$5Cu\ (s) \rightarrow 5Cu^{2+}\ (aq) + 10e^-$

$MnO_4^-\ (aq) + 8H^+\ (aq) + 5e^- \rightarrow Mn^{2+}\ (aq) + 4H_2O\ (l)$ (x2)
$2MnO_4^-\ (aq) + 16H^+\ (aq) + 10e^- \rightarrow 2Mn^{2+}\ (aq) + 8H_2O\ (l)$
$5Cu\ (s) + 2MnO_4^-\ (aq) + 16H^+\ (aq) + \cancel{10}e^- \rightarrow 5Cu^{2+}\ (aq) + 2Mn^{2+}\ (aq) + 8H_2O\ (l) + \cancel{10}e^-$

$5Cu\ (s) + 2MnO_4^-\ (aq) + 16H^+\ (aq) \rightarrow 5Cu^{2+}\ (aq) + 2Mn^{2+}\ (aq) + 8H_2O\ (l)$

**f.** Cu was oxidised. The chemical that has undergone oxidation is oxidised.
**g.** $MnO_4^-$ was reduced. The chemical that has undergone reduction is reduced.

## Oxidation Numbers

The term **oxidation number** simply refers to the charge of an atom or ion. Knowing the oxidation number or charge of the atoms and ions taking part in a chemical reaction can help us identify the reductants and oxidants in a redox reaction.

### OXIDATION NUMBER RULES

**Rule 1 –** Neutral atoms that make up an element have an oxidation number of ZERO.

This is the simplest of the rules. The atoms that make up an element have equal numbers of electrons and protons so the overall charge or oxidation number of the atom is zero.

Eg. Na has 11 $p^+$ and 11 $e^-$ so its oxidation number = 0 (11 $p^+$ + 11 $e^-$ = 0)

The same rule applies to elements that exist as diatomic molecules such as $O_2$. An $O_2$ molecule has 2 O atoms. Each O atom has 8 protons and 8 electrons. Once again the equal number of positive and negative charges cancel each other out ($8p^+ + 8e^- = 0$) and the atoms in the molecule have an overall charge of zero. Some examples of this rule are:

Mg = 0 Fe = 0 $H_2$ = 0 $Cl_2$ = 0 Cr = 0 $S_8$ = 0

**Rule 2 –** The oxidation number of a simple ion is equal to the charge on the ion.

This is the simplest of the oxidation number rules. For example:

The oxidation number of $Na^+$ = + 1
The oxidation number of $Mg^{2+}$ = +2
The oxidation number of $Cl^-$ = -1
The oxidation number of $O^{2-}$ = -2

**Rule 3 –** The oxidation number of an element in an ionic / covalent compound is equal to the charges of the ions. The sum of these charges or oxidation numbers is equal to zero.

Covalent compounds are made from atoms not ions. The atoms in a covalent compound however, can behave as if they have a charge. This is a big rule with lots to think about. An important point to consider is that molecules and the combined ions in the formula of an ionic compound do not have their own oxidation number. For example $H_2O$ does not have an oxidation number and neither does NaCl. The H and O atoms in the $H_2O$ molecule have an oxidation number each and when they are added together they equal zero. Remember that ionic and covalent compounds are neutral.

Unfortunately just learning the valency table in appendix 3 is not enough to work out the oxidation number of elements in compounds. Only a few elements have oxidation numbers that are equal to their charge given in the valency table. For example the valency table states that nitrogen has a charge of -3 ($N^{3-}$) but in reality it can have many different charges depending on the compound it is in. Below is a list of rules that will help you work out the oxidation number of the elements in a compound.

- **All group 1 metals** have an oxidation number of **+1** when in an ionic compound.
- **All group 2 metals** have an oxidation number of **+2** when in an ionic compound.
- **Aluminium** has an oxidation number of **+3** when in an ionic compound.
- **Zinc** has an oxidation number of **+2** when in an ionic compound.
- **Fluorine** always has an oxidation number of **-1** when in an ionic /covalent compound.
- **Chlorine** usually has an oxidation number of **-1** when in an ionic /covalent compound except when it is bonded to either F or O. When bonded to F or O the oxidation number of Cl will not be -1 and it can vary.
- **Oxygen** usually has an oxidation number of -2 when in an ionic /covalent compound except in $H_2O_2$ and $BaO_2$ where it is equal to **-1.** When bonded to fluorine its charge is +2.
- **Hydrogen** usually has an oxidation number of **+1** when in an ionic /covalent compound except in metal hydrides (Eg. NaH, $MgH_2$) where it is **-1.**

Here are some examples of where these rules are applied:

**NaCl**

Na = + 1 and Cl = -1

The sum of the charges will always equal zero (+1 – 1 = 0)

**$MgCl_2$**

Mg = +2 and Cl = -1

The sum of the charges:
+2 + (-1 x2) = 0
Oxidation numbers are only given for one atom regardless of how many appear in the formula of the substance. A common error is to give the oxidation number of the Cl as -2 because there are 2 Cl atoms in the formula of $MgCl_2$. One Cl atom has a charge of -1. Since there are 2 Cl ions in the formula the overall charge of the Cl atoms is -1 x 2 = -2. The charge of one Cl ion however, is -1. It doesn't matter how many Cl atoms are in the formula of a compound, one Cl atom will always have an oxidation number of -1.

**MgO**

Mg = +2 and O = -2

**$H_2O$**

H = +1 and O = -2

**$Al_2O_3$**

Al = +3  and O = -2

Once again, the number of atoms in the formula doesn't matter, the charge of just one Al and one O atom is given.  The fact that there are 2 Al toms and 3 O atoms only becomes significant when working out the overall charge of the compound.

$2 \times Al^{3+} + 3 \times O^{2-}$
$= +6 - 6 = 0$

**$SO_2$**

S = +4 and O = -2

There is no set rule for the oxidation number of sulfur.  Like many elements its charge varies from compound to compound.  It is known that O is -2.  Since there are 2 O atoms in the molecule the overall charge due to the oxygen atoms is -2 x 2 = -4.  Therefore the charge due to the S in order to make the sum of the charges equal to zero must be +4.  Solving a simple equation may help you:

$S + (2 \times -2) = 0$
$S + -4 = 0$
$S - 4 = 0$
$S = 0 + 4$
$S = +4$

**$Cl_2O_7$**

As the Cl is bonded to O its oxidation number will not be -1 and can vary so find the O first.

O = -2

To find Cl solve an equation.

$2\ Cl + 7 \times -2 = 0$
$2\ Cl - 14 = 0$
$2\ Cl = 14$
$Cl = \frac{14}{2} = +7$

**$F_2O$**

F = -1
O = +2 as it is bonded to F.

<u>**Rule 4 –** The sum of the oxidation numbers in a polyatomic ion is equal to the charge of the polyatomic ion.</u>

A polyatomic ion is an ion that has 2 or more elements such as $SO_4^{2--}$, $NO_3^-$ etc. Unlike ionic and covalent compounds, the combined oxidation numbers of the atoms in these ions will not cancel out to zero. Instead, the combined oxidation numbers of the atoms will be equal to the charge on the polyatomic ion. For example,

**$SO_4^{2-}$**

S = +6 and O = -2

Once again solving a simple equation may help you.

$S + (4 \times -2) = -2$
$S + -8 = -2$
$S – 8 = -2$
$S = -2 + 8$
$S = +6$

**$NO_3^-$**

There is no rule for the N so find the O first.

O = -2

Now find N by solving an equation.

$N + (3 \times -2) = -1$

$N + -6 = -1$
$N – 6 = -1$
$N = -1 + 6$
$N = +5$

## Worked Example 5

Give the oxidation number of the underlined element.

**a.** $\underline{N_2}$
**b.** $\underline{N_2}O_4$
**c.** $\underline{N}H_4^+$
**d.** $Mg\underline{H_2}$
**e.** $\underline{Cr_2}O_7^{2-}$

## Worked Example 5 Solutions

**a.** $N = 0$.

**b.** $2N + (4 \times -2) = 0$
$2N - 8 = 0$
$2N = 0 + 8$
$2N = 8$
$N = \frac{8}{2} = +4$

**c.** $N + (4 \times +1) = +1$
$N + 4 = +1$
$N = +1 - 4$
$N = -3$

**d.** This is a metal hydride so the H will have an oxidation number of -1.

**e.** $2Cr + (7 \times -2) = -2$
$2Cr + -14 = -2$
$2Cr - 14 = -2$
$2Cr = -2 + 14$
$2Cr = 12$
$Cr = \frac{12}{2} = +6$

An atom's oxidation number can also be referred to as its **OXIDATION STATE.**

## Using oxidation numbers to identify redox reactions and to identify reductants and oxidants.

When a redox reaction occurs electrons are transferred from the reductant to the oxidant. As a result the atoms involved will experience a change in charge after the reaction. The reductant loses electrons so after the reaction its charge will be either less negative or more positive. That is, its oxidation number will increase. The oxidant gains electrons so after the reaction its charge will be either more negative or less positive. That is its oxidation number will decrease.

An atom that has **an increase in oxidation number** has undergone **OXIDATION.**
An atom that has **a decrease in oxidation number** has undergone **REDUCTION.**

So oxidation numbers can be used to

- classify a reaction as REDOX or NOT REDOX.
- identify the REDUCTANT and OXIDANT in a redox reaction.

Consider the following examples.

**Is the reaction described by the equation, $NaCl\ (aq) + AgNO_3\ (aq) \rightarrow NaNO_3\ (aq) + AgCl\ (s)$ a redox reaction?**

The first step is to assign oxidation numbers to every element in the equation.

$$\underset{+1}{\underset{\downarrow}{\mathrm{Na}}}\,\underset{-1}{\underset{\downarrow}{\mathrm{Cl}}}\ (aq) + \underset{+1}{\underset{\downarrow}{\mathrm{Ag}}}\,\underset{+5}{\underset{\downarrow}{\mathrm{N}}}\,\underset{-2}{\underset{\downarrow}{\mathrm{O}_3}}\ (aq) \rightarrow \underset{+1}{\underset{\downarrow}{\mathrm{Na}}}\,\underset{+5}{\underset{\downarrow}{\mathrm{N}}}\,\underset{-2}{\underset{\downarrow}{\mathrm{O}_3}}\ (aq) + \underset{+1}{\underset{\downarrow}{\mathrm{Ag}}}\,\underset{-1}{\underset{\downarrow}{\mathrm{Cl}}}\ (s)$$

None of the elements have undergone a change in oxidation number so there could not have been any loss or gain of electrons occurring during the reaction. Therefore this is NOT A REDOX REACTION.

**Identify the reducing agent and oxidising agent in the following equation, $2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$.**

Once again the first step is to assign oxidation numbers to the elements in the equation.

$$2\underset{+4}{\underset{\downarrow}{\mathrm{S}}}\,\underset{-2}{\underset{\downarrow}{\mathrm{O}_2}}\ (g) + \underset{0}{\underset{\downarrow}{\mathrm{O}_2}}\ (g) \rightarrow 2\underset{+6}{\underset{\downarrow}{\mathrm{S}}}\,\underset{-2}{\underset{\downarrow}{\mathrm{O}_3}}\ (g)$$

When working out oxidation numbers, the coefficients used to balance an equation are ignored. So the coefficient of 2 outside the $SO_2$ and $SO_3$ is not relevant to the determination of the oxidation number of the S or the O.

At the start of the reaction the oxidation number of S was +4. At the end of the reaction it increased to +6. Therefore S has undergone oxidation. Depending on the wording of the question, it could be acceptable to give either S or $SO_2$ as the REDUCING AGENT. If the question asked for the atom or element that was the reducing agent, the only acceptable answer is **S**. If the question asked for the formula of the reducing agent, the answer should be given as **$SO_2$**. It is only the S not the O that has undergone oxidation but because they are part of the same compound the whole formula, $SO_2$ is given.

At the start of the reaction, $O_2$ has an oxidation number of 0. At the end of the reaction the oxidation number of the oxygen has decreased to -2. Therefore the $O_2$ has undergone reduction and is the OXIDISING AGENT.

Oxidation numbers can be used to illustrate the more traditional definitions of reduction and oxidation in terms of losing/gaining oxygen and hydrogen.

**A chemical that undergoes oxidation can gain oxygen or lose hydrogen.**

$$\underset{0}{C}\,(s) + \underset{0}{O_2}\,(g) \rightarrow \underset{+4}{C}\underset{-2}{O_2}\,(g)$$

The carbon has undergone oxidation and in the process has **gained oxygen** to become $CO_2$. As the carbon has a +4 charge it is now able to bond to 2 O atoms as they each have a charge of -2 (overall charge of -4).

$$2\underset{-3}{N}\underset{+1}{H_3}\,(g) \rightarrow \underset{0}{N_2}\,(g) + 3\underset{0}{H_2}\,(g)$$

The N in $NH_3$ has been oxidised to form $N_2$. Now the N has a zero charge. As a consequence the N has **lost the 3 H atoms** it once had. Without a charge of -3 it cannot hold onto the 3 H atoms that each had a charge of +1. Note that in this example the H atoms lost their +1 charge any way as they were reduced by the N to form $H_2$.

**A chemical that undergoes reduction can lose oxygen or gain hydrogen.**

$$2\underset{+4}{C}\underset{-2}{O_2}\,(g) + \underset{0}{C} \rightarrow 2\underset{+2}{C}\underset{-2}{O}\,(g) + + \underset{0}{O_2}\,(g)$$

Carbon has been reduced and in the process it has **lost an oxygen atom** as $CO_2$ becomes CO. When the C has a charge of +4, it can attract 2 O atoms as they each have a charge of -2. When the C is reduced to a charge of +2, it loses an O because the + 2 charge is only strong enough to attract one O (-2 charge).

$$\underset{0}{N_2}\,(g)\ \ 3\underset{0}{H_2}\,(g) \rightarrow 2\underset{-3}{N}\underset{+1}{H_3}\,(g)$$

The $N_2$ has been reduced and in the process has gained a charge of -3 on the product side of the equation. As a result it can attract 3 H atoms each with a charge of +1.

So to summarise:

- **Oxidation –** A loss of electrons/gain of oxygen/loss of hydrogen.
- **Reduction –** A gain of electrons/loss of oxygen/gain of hydrogen.

# CHAPTER 10 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
The oxidation number of N in $NH_4NO_3$ is

- **A.** -3.
- **B.** +5.
- **C.** +1.
- **D.** -3 and +5.

**Question 2**
Consider the 4 statements below:

- i A reductant donates electrons to an oxidising agent.
- ii An oxidant is oxidised by a reducing agent.
- iii A reducing agent is oxidised by an oxidant.
- iv. A reductant is reduced by an oxidising agent.

Which of these 4 statements are INCORRECT?

- **A.** All 4 statements
- **B.** i and iii
- **C.** ii, iii and iv
- **D.** ii and iv

**Question 3**
The half equation that shows the chemical species A, acting as a reducing agent is

- **A.** $A \rightarrow A^{2-} + 2e^-$
- **B.** $A + 2e^- \rightarrow A^{2-}$
- **C.** $A \rightarrow A^{2+} + 2e^-$
- **D.** $A^{2+} + 2e^- \rightarrow A$

**Question 4**

$$MnO_2\,(s) + 4HCl\,(aq) \rightarrow Cl_2\,(g) + 2H_2O(l) + MnCl_2\,(aq)$$

During this reaction the charge of Mn changes from

- **A.** +4 to +2 and $MnO_2$ is the oxidant.
- **B** +4 to -2 and HCl is the reductant.
- **C.** from +4 to +2 and $MnO_2$ is the reducing agent.
- **D.** +4 to 0 and $Cl_2$ is produced when $Cl^-$ ions are reduced.

**Question 5**
Which of the equations below represents a redox reaction?

- **A.** $Ag^+\,(aq) + Cl^-\,(aq) \rightarrow AgCl\,(s)$
- **B.** $H_2O_2\,(al) \rightarrow H_2\,(g) + O_2\,(g)$
- **C.** $KI\,(aq) + NaCl\,(aq) \rightarrow NaI\,(aq) + KCl\,(aq)$
- **D.** $CuSO_4\,(aq) \rightarrow Cu^{2+}\,(aq) + SO_4^{2-}\,(aq)$

**Question 6**
The oxidation states of chromium in $Cr_2O_7^{2-}$, $CrO_4^{2-}$ and $Cr_2O_3$ are respectively

- **A.** +12, +3 and +3.
- **B.** +3, +6 and +6.
- **C.** +6, +6 and +3
- **D.** +12, +6 and +6.

## Short Answers

**Question 1**
What is the oxidation number of the underlined element?

- **a.** $\underline{Br_2}$
- **b.** $O\underline{Br}^-$
- **c.** $F_2\underline{O}$
- **d.** $\underline{S_2}O_3^{2-}$
- **e.** $Ba\underline{O_2}$

**Question 2**
Write out the oxidation half equation, reduction half equation and overall equation for each of the following.

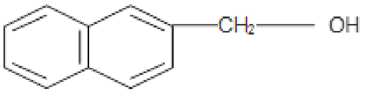
- **a.** A solution of $Fe^{3+}$ions is reduced by iron metal. The product of the reaction is only $Fe^{2+}$ (aq).
- **b.** $CuS$ (s) and nitric acid are allowed to react with each other to produce $CuSO_4$ (aq) and $NO$ (g)
- **c.** A solution of chromium (III) ions is oxidised into $Cr_2O_7^{2-}$ (aq) by $H_2O_2$ (aq) which is reduced into water.

**Question 3**
When hot concentrated sulfuric acid is poured over solid zinc granules, zinc ions and $H_2S$ gas are produced.

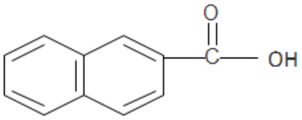
- **a.** Give the ionic oxidation half equation showing states.
- **b.** give the ionic reduction half equation showing states.
- **c.** Give the full equation showing states.
- **d.** Calculate the mass of zinc required to produce 1.0 L of $H_2S$ gas at a temperature of 35 $^0$C and pressure of 2.0 atm.

**Question 4**
An organic molecule, "molecule 1", is transformed into "molecule 2".

**molecule 1**



**Molecule 2**



Is the process of the transformation of molecule 1 into molecule 2 a reduction or oxidation reaction? Discuss your answer.

**Question 5**
Consider the half equation below.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

- **a.** Use oxidation numbers to show that the Cr has been reduced.
- **b.** Show that the Cr has been reduced by discussing the transfer of oxygen atoms.

**Question 6**
Use oxidation numbers to show that manganese atoms have been reduced in this half equation:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

# Chapter 11 – Galvanic Cells

A **Galvanic cell** or **Electrochemical cell** is a device that converts chemical energy into electrical energy. Before starting this chapter, make sure that you have a strong grasp of the following concepts covered in chapter 10.

- oxidation and reduction in terms of electron transfer.
- reductants and oxidants.
- half equations and full equations.
- half equations and full equations of reactions occurring in acidic media.
- oxidation numbers.

Fundamental to the understanding of galvanic cells is the **electrochemical series table.** This table is shown on the next page. This table is basically a list of half equations. When reading the equations from left to right they are **all reduction half equations** as they all involve a gaining of electrons. As they are reduction reactions, the chemicals gaining electrons are known as **oxidants** or **oxidising agents.** For example, the equation at the top of the table is $F_2$ (g) + $2e^-$ $\rightleftharpoons$ $2F^-$ (aq). As the $F_2$ is undergoing reduction it is referred to as an oxidant or oxidising agent.

The order of these half equations in the table is very important. The higher the half equation is in the table the more readily the reduction reaction occurs. In other words, the higher the oxidant is on the table the more readily it gains electrons. $F_2$ is the strongest oxidant as it is at the top of the table. $H_2O_2$ is the next strongest oxidant as it is just underneath $F_2$ on the table. $Li^+$ is at the bottom of the table so it is the weakest oxidant. That is out of all of the oxidants on the table, it is has the weakest ability to attract electrons. The upwards pointing arrow on the left hand side of the electrochemical series table shows that ***when moving up the table the strength of the oxidants increases.***

When reading the equations going backwards, that is from right to left, they are oxidation half equations as the electrons are now on the product side of the equation. When read from right to left, the equation at the top of the table is $2F^-$ (aq) $\rightleftharpoons$ $F_2$ (g) + $2e^-$. $F^-$ is a reductant as it is undergoing oxidation. On the right hand side of the electrochemical series table there is a downwards pointing arrow. This shows ***when going down the table the strength of the reductants increases.*** The next equation when read from right to left is $2H_2O$ (l) $\rightleftharpoons$ $H_2O_2$ (aq) + $2H^+$ (aq) + $2e^-$. $H_2O$ is a stronger reductant than $F^-$ as it is lower on the table. The equation on the bottom of the table when read from right to left is Li (s) $\rightleftharpoons$ $Li^+$ (aq) + $e^-$. Li is the strongest reductant as it is on the bottom of the table.

- ❖ On the left hand side of the table, that is on the left hand side of the arrows ($\rightleftharpoons$), oxidants are found. The higher the oxidant on the table the stronger its ability to undergo reduction.

- ❖ On the right hand side of the table, that is on the right hand side of the arrows ($\rightleftharpoons$), reductants are found. The lower the reductant the stronger its ability to undergo oxidation.

# The Electrochemical series table

**Increasing ability to undergo reduction**. That is, when moving up the table the oxidants become stronger.

*OXIDANTS ARE ON THIS LEFT HAND SIDE OF THE TABLE.*

| Reaction | Standard Electrode Potential ($E^0$) |
|---|---|
| $F_2$ (g) + 2e$^-$ ⇌ 2F$^-$ (aq) | +2.87 V |
| $H_2O_2$ (aq) + 2H$^+$ (aq) + 2e$^-$ ⇌ 2$H_2O$ (l) | +1.77 V |
| Au$^+$ (aq) + e$^-$ ⇌ Au (s) | +1.68 V |
| $Cl_2$ (g) +2e$^-$ ⇌ 2Cl$^-$ (aq) | +1.36 V |
| $O_2$ (g) + 4H$^+$ (aq) + 4e$^-$ ⇌ 2$H_2O$ (l) | +1.23 V |
| $Br_2$ (l) + 2e$^-$ ⇌ 2Br$^-$ (aq) | +1.09 V |
| Ag$^+$ (aq) + e$^-$ ⇌ Ag (s) | +0.80 V |
| Fe$^{3+}$ (aq) + e$^-$ ⇌ Fe$^{2+}$ (aq) | +0.77 V |
| $O_2$ (g) +2H$^+$ (aq) +2e$^-$ ⇌ $H_2O_2$ (aq) | +0.68 V |
| $I_2$ (s) + 2e$^-$ ⇌ 2I$^-$ (aq) | +0.54 V |
| $O_2$ (g) +2$H_2O$ (l) +4e$^-$ ⇌ 4OH$^-$ (aq) | +0.40 V |
| Cu$^{2+}$ (aq) + 2e$^-$ ⇌ Cu (s) | +0.34 V |
| Sn$^{4+}$ (aq) + 2e$^-$ ⇌ Sn$^{2+}$ (aq) | +0.15 V |
| S (s) +2H$^+$ (aq) + 2e$^-$ ⇌ $H_2S$ (g) | +0.14 V |
| 2H$^+$ (aq) + 2e$^-$ ⇌ $H_2$ (g) | 0.00 V |
| Pb$^{2+}$ (aq) + 2e$^-$ ⇌ Pb (s) | -0.13 V |
| Sn$^{2+}$ (aq) + 2e$^-$ ⇌ Sn (s) | -0.14 V |
| Ni$^{2+}$ (aq) + 2e$^-$ ⇌ Ni (s) | -0.25 V |
| Co$^{2+}$ (aq) + 2e$^-$ ⇌ Co (s) | -0.28 V |
| Fe$^{2+}$ (aq) + 2e$^-$ ⇌ Fe (s) | -0.44 V |
| Zn$^{2+}$ (aq) + 2e$^-$ ⇌ Zn (s) | -0.76 V |
| 2$H_2O$ (l) + 2e$^-$ ⇌ $H_2$ (g) + 2OH$^-$ (aq) | -0.83 V |
| Mn$^{2+}$ (aq) + 2e$^-$ ⇌ Mn (s) | -1.18 V |
| Al$^{3+}$ (aq) + 3e$^-$ ⇌ Al (s) | -1.67 V |
| Mg$^{2+}$ (aq) + 2e$^-$ ⇌ Mg (s) | -2.34 V |
| Na$^+$ (aq) + e$^-$ ⇌ Na (s) | -2.71 V |
| Ca$^{2+}$ (aq) + 2e$^-$ ⇌ Ca (s) | -2.87 V |
| K$^+$ (aq) + e$^-$ ⇌ K (s) | -2.93 V |
| Li$^+$ (aq) + e$^-$ ⇌ Li (s) | -3.02 V |

**For a spontaneous redox reaction to occur, a reductant must react with an oxidant.**

***The reductant must be BELOW the oxidant on the table.***

***REDUCTANTS** ARE ON THIS RIGHT HAND SIDE OF THE TABLE.*

**Increasing ability to undergo oxidation**. That is, when moving down the table the reductants become stronger.

- *It is very important to realise that the order of the equations in the electrochemical series table is based on experiments that were performed at standard laboratory conditions (SLC). That is,* ***solution concentrations of 1.0 M, gas pressures of 0.987 atm and temperatures of 25 $^0$C****. The significance of these conditions will be discussed later on when the use of the table for predicting spontaneous redox reactions will be looked at.*

❖ *An electrochemical series table similar to the one on the previous page is provided on page 4 of the end of year exam data book.*

It is best to look at the electrochemical series table as being two tables in one. One that shows the relative strength of oxidants and another table that shows the relative strength of reductants.

The second column of the table shows what is known as the **standard electrode potential ($E^0$).** These values are a numerical measure of the strength of the oxidants. $F_2$ is the strongest oxidant so it has the highest $E^0$ value of +2.87 V. When going down the table the strength of the oxidants decrease and this is shown by the decreasing $E^0$ values. How these values are obtained will be explained later on in the chapter.

## Worked Example 1

Answer the following questions using the electrochemical series.

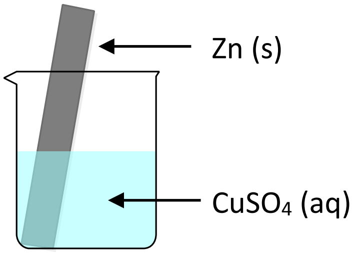
**a.** Is $H_2$ a reductant or oxidant? Explain your answer.
**b.** Which is the stronger oxidant, $Pb^{2+}$ or $I_2$? Explain your answer.
**c.** Is $Sn^{4+}$ a reductant or oxidant? Explain your answer.
**d.** Which is the stronger reductant, Cu or Zn? Explain your answer.
**e.** Are there any chemical species (ions, atoms or molecules) that are both oxidants and reductants? Explain your answer.
**f.** Consider the following statement, "$F_2$ is at the top of the table so it is the strongest oxidant but weakest reductant." Is this statement correct or incorrect? Explain your answer.

## Worked Example 1 Solutions

**a.** $H_2$ is a reductant because it appears on the right hand side of the table.
**b.** $I_2$ is the stronger oxidant because it is higher on the table than $Pb^{2+}$.
**c.** $Sn^{4+}$ is an oxidant because it appears on the left hand side of the table.
**d.** Zn is the stronger reductant because it is lower on the table than Cu.
**e.** Yes there are. There are some chemical species that appear on both the left and right hand side of the table. Some examples include, $H_2O$, $Fe^{2+}$ and $H_2O_2$.
**f.** This statement is incorrect. The first part of the statement is correct as $F_2$ is an oxidant and the higher up the table the oxidants are the stronger they are. The second part of the statement is incorrect because $F_2$ is not a reductant as it is on the left hand side of the table. Reductants are on the right hand side of the table. If the statement claimed that $F^-$ was the weakest reductant, this would be correct as $F^-$ is the highest reductant on the right hand side of the table.

# Predicting spontaneous redox reactions using the electrochemical series table

A **spontaneous reaction** is one that does not require any input of energy. That is, the reaction will occur the moment the chemicals make contact with each other. The major use of the electrochemical series table is to predict if a reductant and oxidant will react spontaneously when mixed together. Consider the following example, where a piece of zinc metal is immersed in a $CuSO_4$ solution as can be seen in the diagram below.



Here are some steps that can be used to predict if a spontaneous redox reaction will occur between 2 chemical species.

**STEP 1 – Identify all the chemical species.**

In this example the chemical species are **Zn (s), $Cu^{2+}$ (aq), $SO_4^{2-}$ (aq) and $H_2O$ (l).**

Any ionic compound in solution such as $CuSO_4$ must be dissociated into its constituent ions:

$CuSO_4 (s) \rightarrow Cu^{2+} (aq) + SO_4^{2-} (aq)$

As the $CuSO_4$ was in solution (aq), water must be present.

The species $SO_4^{2-}$ is not included in the table so it can be ignored.

- A common mistake is to identify Cu instead of $Cu^{2+}$ as the species of copper present in $CuSO_4$. Cu is a solid which is clearly not present in this beaker.

**STEP 2 – Locate the chemical species on the electrochemical series table and classify them as oxidants and reductants.**

Oxidants = **$Cu^{2+}$** and **$H_2O$** as they both appear on the left hand side of the table.

There are 2 equations that show water acting as an oxidant:

$O_2 (g) + 2H_2O (l) + 4e^- \rightleftharpoons 4OH^- (aq)$
$2H_2O (l) + 2e^- \rightleftharpoons H_2 (g) + 2OH^- (aq)$

Only the second equation is relevant to this example because it has $H_2O$ on its own. The first equation has $H_2O$ reacting with $O_2$. This reaction is not possible in this example because there is no $O_2$ present in the beaker, there is only Zn (s), $CuSO_4$ (aq) and $H_2O$ (l).

Reductants = **Zn and $H_2O$.**

There are 2 equations at the top of the table where $H_2O$ is undergoing oxidation. Both of them are relevant as they only involve $H_2O$.

- Since we have chemical species that appear on the right hand side of the table (reductants) and the left hand side of the table (oxidants), a redox reaction may be able to occur. It is not possible to have a reaction when all the chemical species present are reductants. In this case all of the chemicals just want to undergo oxidation, there is no chemical present that is able to undergo reduction. Without an oxidant present to gain the electrons no reaction is possible. The same applies when all of the chemical species present are oxidants. In this case all of the chemicals just want to undergo reduction, there is no chemical present capable of undergoing oxidation. Without a reductant present to lose electrons no reaction is possible.

**STEP 3 – Identify the strongest oxidant and strongest reductant.**

Strongest oxidant = **$Cu^{2+}$** as it is higher on the table than the other oxidant, water.

Strongest reductant = **Zn** as it is lower on the table than water.

When a mixture of reductants and oxidants are exposed to each other, only the strongest reductant present will undergo oxidation and the strongest oxidant will undergo reduction. The weaker reductants and oxidants will not do anything. So if a redox reaction is to occur, it will be the strongest reductant Zn, losing electrons and the strongest oxidant $Cu^{2+}$, that will be gaining the electrons lost by the Zn.

**STEP 4 – Check the position of the reductant and oxidant on the table.**

If a spontaneous redox reaction is to occur, the STRONGEST REDUCTANT must be below the STRONGEST OXIDANT on the table.

In this case the strongest reductant Zn is below the strongest oxidant $Cu^{2+}$, so a spontaneous redox reaction will occur.

**STEP 5 – Write out the 2 half equations and full equation.**

**Oxidation:** $Zn (s) \rightarrow Zn^{2+} (aq) + 2e^-$
**Reduction:** $Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$

**Full equation:** $Zn (s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu (s)$ *don't forget to cancel the electrons.*

When this reaction occurs, the Cu metal produced deposits onto the surface of the Zn metal. The blue colour of the $CuSO_4$ solution fades away as the $Cu^{2+}$ ions are removed from the solution due to their reduction into Cu (s).

- A mistake that students sometimes make is to write out the oxidation half equation from left to write as it appears on the table. This produces a reduction half equation. Remember that the reductants are on the right hand side of the table and the oxidation half equation is therefore written out from right to left.

- When writing out half equations and full equations using the table it is very tempting to use equilibrium arrows (⇌) as every equation in the table uses them. Most redox reactions do not reach equilibrium and you may lose marks on the exam if you write out redox equations using equilibrium arrows. If a question does not give a strong indication that a redox reaction has reached equilibrium, write out the equations using one way arrows (→) only.

A summary of the process of predicting if a reaction will occur between Zn (s) and $CuSO_4$ (aq) is shown below.

| | |
|---|---|
| $H_2O_2$ (aq) + $2H^+$ (aq) + $2e^-$ ⇌ $2H_2O$ (l) | +1.77 V |
| $Au^+$ (aq) + $e^-$ ⇌ Au (s) | +1.68 V |
| $Cl_2$ (g) +$2e^-$ ⇌ $2Cl^-$ (aq) | +1.36 V |
| $O_2$ (g) + $4H^+$ (aq) + $4e^-$ ⇌ $2H_2O$ (l) | +1.23 V |
| $Br_2$ (l) + $2e^-$ ⇌ $Br^-$ (aq) | +1.09 V |
| $Ag^+$ (aq) + $e^-$ ⇌ Ag (s) | +0.80 V |
| $Fe^{3+}$ (aq) + $e^-$ ⇌ $Fe^{2+}$ | +0.77 V |
| $O_2$ (g) +$2H^+$ (aq) +$2e^-$ ⇌ $H_2O_2$ (aq) | +0.68 V |
| $I_2$ (l) + $2e^-$ ⇌ $2I^-$ (aq) | +0.54 V |
| $O_2$ (g) +$2H_2O$ (l) +$4e^-$ ⇌ $4OH^-$ (aq) | +0.40 V |
| $Cu^{2+}$ (aq) + $2e^-$ ⇌ Cu (s) | +0.34 V |
| $Sn^{4+}$ (aq) + $2e^-$ ⇌ $Sn^{2+}$ (aq) | +0.14 V |
| S (s) +$2H^+$ (aq) + $2e^-$ ⇌ $H_2S$ (g) | +0.14 V |
| $2H^+$ (aq) + $2e^-$ ⇌ $H_2$ (g) | 0.00 V |
| $Pb^{2+}$ (aq) + $2e^-$ ⇌ Pb (s) | -0.13 V |
| $Sn^{2+}$ (aq) + $2e^-$ ⇌ Sn (s) | -0.14 V |
| $Ni^{2+}$ (aq) + $2e^-$ ⇌ Ni (s) | -0.23 V |
| $Co^{2+}$ (aq) + $2e^-$ ⇌ Co (s) | -0.28 V |
| $Fe^{2+}$ (aq) + $2e^-$ ⇌ Fe (s) | -0.44 V |
| $Zn^{2+}$ (aq) + $2e^-$ ⇌ Zn (s) | -0.76 V |
| $2H_2O$ (l) + $2e^-$ ⇌ $H_2$ (g) + $2OH^-$ (aq) | -0.83 V |

The reductants are shaded yellow. The strongest reductant is red.

The oxidants are shaded green. The strongest oxidant is red.

A spontaneous redox reaction will occur because the strongest reductant (Zn) is below the strongest oxidant ($Cu^{2+}$).

# Limitations of using the electrochemical series table to predict spontaneous redox reactions

As was mentioned earlier, the electrochemical series table was constructed at standard laboratory conditions (SLC) of gas pressures of **0.987 atm (100 KPa)**, solution concentrations of **1.0 M** and temperatures of **25 $^{0}$C.** In other words, the order of the reactions in the table are based on experiments that were conducted at these standard conditions. If these experiments were conducted at different conditions of pressure, temperature and concentration, the order of the equations in the table could change. So all predictions made by using this table are limited to reactions that are occurring at these SLC conditions. So the prediction of a redox reaction between Zn and $CuSO_4$ based on the electrochemical series table is only valid if the concentration of the $CuSO_4$ solution is 1.0 M and the temperature of the $CuSO_4$ solution and Zn are 25 $^{0}$C.

Another example is the prediction of a reaction between $Sn^{4+}$ (aq) and $H_2$ (g). The table predicts that a spontaneous redox reaction will occur as the reductant $H_2$ (g) is below the $Sn^{4+}$ (aq) oxidant. This prediction is only valid if the pressure of the $H_2$ gas is 1.0 atm, the concentration of the $Sn^{4+}$ is 1.0 M and the temperature of both reactants are 25 $^{0}$C.

- It is possible for 2 chemicals to be mixed together at SLC conditions and show no sign of reaction even though the reductant is below the oxidant on the table. In this case it is likely that the reaction is occurring but the rate of the reaction is so slow that it is not observed.

- The electrochemical series table gives no information regarding the rate of a reaction.

## Worked Example 2

Predict if the following situations will result in a redox reaction. Assume that standard conditions of pressure, concentration and temperature are being met. If a reaction is predicted write out the half equations and the full equation.

**a.** A small piece of sodium metal is dropped into a container filled with distilled water.
**b.** A copper cooking pot is washed out with hydrochloric acid.
**c.** Hydrogen sulfide ($H_2S$) gas is bubbled through a solution of silver nitrate.

## Worked Example 2 Solutions

**a.** The chemical species are Na (s) and $H_2O$ (l). The strongest reductant Na (s) is below the strongest oxidant, $H_2O$ so a spontaneous redox reaction will occur.

Oxidation half equation: $Na\ (s) \rightarrow Na^{+}\ (aq) + e^{-}$
Reduction half equation: $2H_2O\ (l) + 2e^{-} \rightarrow H_2\ (g) + 2OH^{-}\ (aq)$

Multiply the oxidation half equation by 2 to balance out the electrons.
$2Na\ (s) \rightarrow 2Na^{+}\ (aq) + 2e^{-}$

Now combine this equation with the reduction half equation to get the full equation.

$2Na\ (s) + 2H_2O\ (l) \rightarrow 2Na^+\ (aq) + H_2\ (g) + 2OH^-\ (aq)$ OR
$2Na\ (s) + 2H_2O\ (l) \rightarrow 2NaOH\ (aq) + H_2\ (g)$

**b.** The chemical species present are $Cu$ (s), $H^+$ (aq), $Cl^-$ (aq) and $H_2O$ (l).

The hydrochloric acid is a solution so water is present. The $H^+$ and $Cl^-$ are from the dissociation of $HCl$.

Reductants = $H_2O$, $Cl^-$ and $Cu$.
Oxidants = $H_2O$ and $H^+$.

The strongest reductant $Cu$ is above the strongest oxidant, $H^+$. Therefore a spontaneous redox reaction will not occur.

**c.** The chemical species are $H_2S$ (g), $Ag^+$ (aq), $NO_3^-$ (aq) and $H_2O$ (l).

$NO_3^-$ does not appear in the table so it is ignored.

Reductants = $H_2O$ and $H_2S$.
Oxidants = $H_2O$ and $Ag^+$.

The strongest reductant, $H_2S$ is below the strongest oxidant, $Ag^+$ so a spontaneous redox reaction will occur.

Oxidation half equation: $H_2S\ (g) \rightarrow S\ (s) + 2H^+\ (aq) + 2e^-$
Reduction half equation: $Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$

Multiply reduction half equation by 2 to balance electrons.

$2Ag^+\ (aq) + 2e^- \rightarrow 2Ag\ (s)$

Now combine this equation with the oxidation half equation.

$H_2S\ (g) + 2Ag^+\ (aq) \rightarrow 2Ag\ (s) + S(s) + 2H^+\ (aq)$

## Extent of a redox reaction

It was stated earlier that most redox reactions do not reach equilibrium. If they do however, reach equilibrium, the extent of the reaction is related to the difference between the reductant and oxidant on the table. That is the bigger the gap between the reductant and oxidant on the table the greater the equilibrium constant for that reaction. So the reaction between $F_2$ (g) and $Li$ (s) will occur to a greater extent than the reaction between $Br_2$ (l) and $Ag$ (s).

# Galvanic Cells

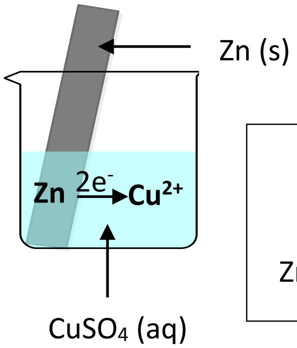
As was mentioned at the start of this chapter, a galvanic or electrochemical cell is a device that converts chemical energy directly into electrical energy or electricity. Electricity or an electric current is basically a flow of charge. This flow of charge can be in the form of

- electrons moving through a wire or
- positive and negative ions moving through a solution.

This flow of charge must be able to make a complete circuit in order to produce electricity. That is, it must be able to get back to where it started from. Since redox reactions involve a flow of negative charge in the form of electrons from reductant to oxidant, they are a potential source of electricity.

The examples of redox reactions looked at so far in this chapter have involved a direct transfer of electrons from the reductant to the oxidant. That is, the reductant and oxidant atoms make direct contact with each other and when the reductant undergoes oxidation the electrons lost are instantly and directly gained by the oxidant.

For example, when Zn is immersed in a solution of $CuSO_4$ (aq), $Cu^{2+}$ ions make direct contact with Zn atoms. When the Zn atoms undergo oxidation the electrons they lose are directly picked up by the $Cu^{2+}$ ions in the solution.



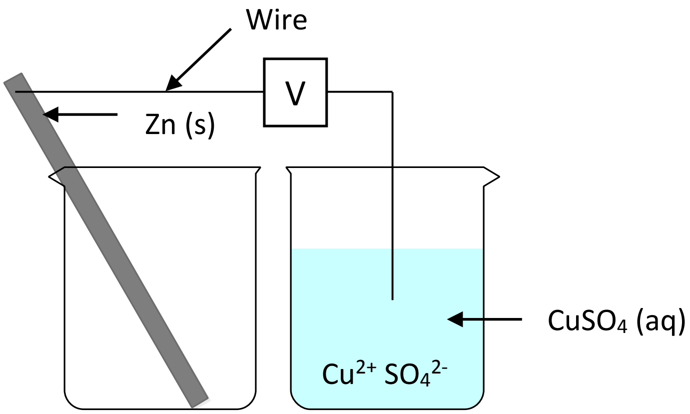
$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$$
$$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$$

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

This simple redox reaction can produce an electric current if it is made into a GALVANIC CELL or ELECTROCHEMICAL CELL. To do this the above set up showing the Zn metal immersed in a $CuSO_4$ solution needs some major modifications.

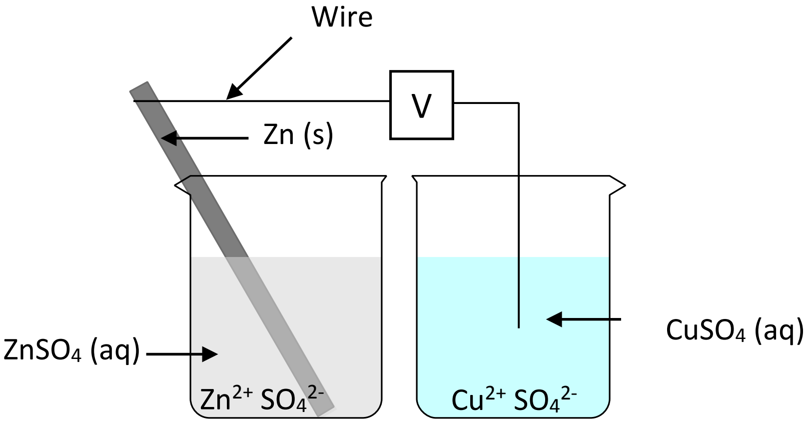
- The strongest reductant, Zn, must be separated from the strongest oxidant, $Cu^{2+}$. That is, they can no longer be in direct contact with each other. They must be placed in 2 separate beakers and connected with a wire so that when the Zn undergoes oxidation, the electrons are forced to pass through the wire before they are eventually gained by the $Cu^{2+}$.

The diagram below shows the Zn (s) and $CuSO_4$ (aq) in 2 separate beakers. The Zn and $CuSO_4$ are connected with a wire. If the Zn (s) undergoes oxidation the electrons can pass through the wire and into the beaker containing the $CuSO_4$ where the $Cu^{2+}$ ions can gain the electrons and undergo reduction. If an appliance such as a light globe is placed in the wire it can use the energy from the electrons and convert it into light, sound etc. depending on the function of the appliance.

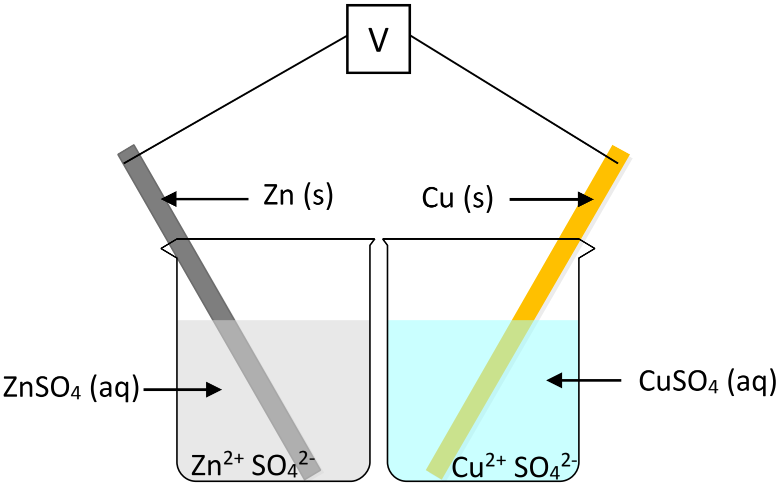


This current set up however, will not produce any electricity. Simply connecting the Zn (s) and $Cu^{2+}$ (aq) with a wire is not enough to force the Zn to undergo oxidation. So the voltmeter (V), which is a device used to measure the voltage of an electric current will show a zero reading.

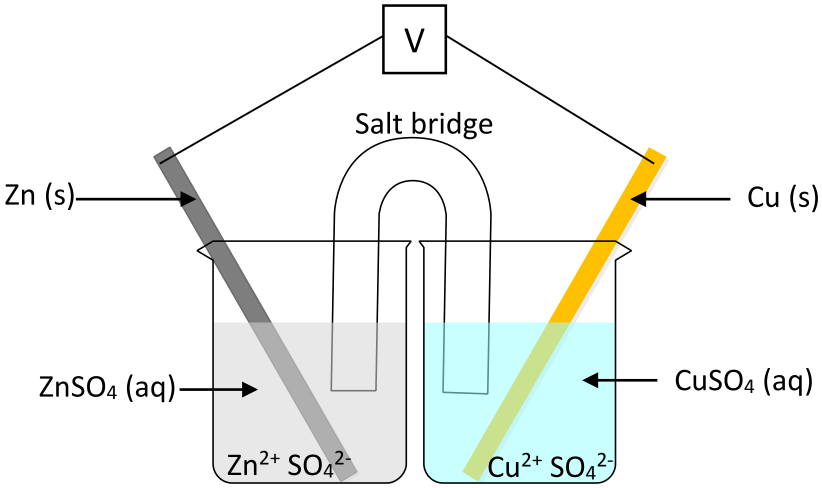
The zinc metal needs to be immersed in a solution containing free moving positive and negative ions. Such a solution is called an **electrolyte.** An appropriate electrolyte for this beaker is $ZnSO_4$ (aq). Since there is already Zn (s) in this beaker the electrolyte should contain $Zn^{2+}$ ions. The significance of having the electrolyte containing the cation of the metal will be discussed later on. So this electrolyte contains free moving $Zn^{2+}$ and $SO_4^{2-}$ ions. The $CuSO_4$ in the other beaker will act as the electrolyte as it contains free moving $Cu^{2+}$ and $SO_4^{2-}$ ions.



The end of the wire is currently immersed in the $CuSO_4$ solution. As was the case with the other beaker, this beaker should also contain a solid metal and its cation. So a rod made from Cu (s) is placed in the beaker with $Cu^{2+}$ (aq).



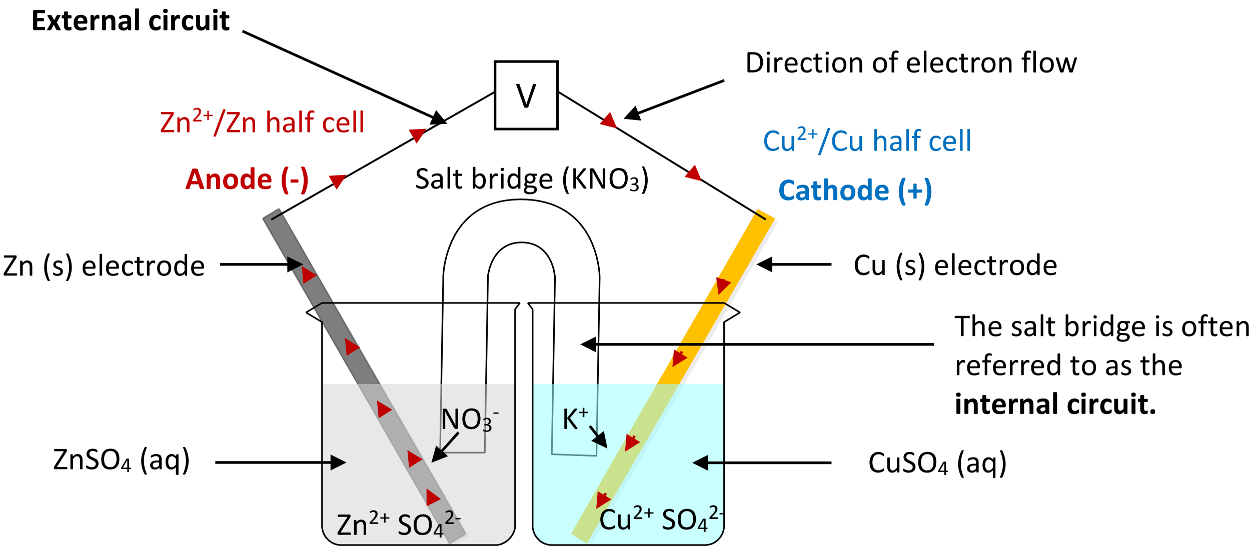
This is starting to look more like an electrochemical cell but it still won't produce electricity as it is not a complete circuit. The 2 beakers are connected with wires but there needs to be another path for the electricity to take in order for it to return back to the Zn and complete the circuit. A "salt bridge" is placed between the 2 beakers to complete the circuit. The salt bridge in the diagram resembles an upside down U.



Now the galvanic cell is complete. The Zn will undergo oxidation and the $Cu^{2+}$ will undergo reduction. The electrons lost by the Zn will pass through the wire, through the voltmeter and through the Cu. The $Cu^{2+}$ ions will make contact with the Cu metal and gain the electrons as they pass through. Electricity will flow around the cell and the voltmeter will give a positive reading indicating the presence of an electric current.

The specific details of how this galvanic cell works are explained below. For the sake of clarification some information that has already been discussed will be repeated.

The set up shown below shows an electrochemical cell / galvanic cell for the redox reaction occurring between Zn and $Cu^{2+}$.



**Anode half equation**
$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

**Cathode half equation**
$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

**Full Equation**
$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

There is obviously a lot going on in this diagram! The reaction occurring in this galvanic cell is the same as the reaction that was occurring in the beaker where the Zn (s) was immersed in the $CuSO_4$ (aq). In the galvanic cell however, the reductant, Zn (s) is one beaker and the oxidant $Cu^{2+}$ is in another one. The Zn is in the beaker on the left and the $Cu^{2+}$ ($CuSO_4$) is in the beaker on the right. So the reductant and oxidant are in separate beakers.

The Zn rod is known as an electrode. An **electrode** is a piece of material that allows electrons to pass through it. That is, it is a conductor of electricity. When the Zn undergoes oxidation,

$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

The $Zn^{2+}$ ion produced when each Zn atom is oxidised dissolves into the surrounding solution of $ZnSO_4$. The 2 electrons produced from the oxidation of each Zn atom are pushed through the Zn electrode, through the wire and through the Cu electrode. The Zn electrode is known as the **anode** because it is the electrode where oxidation has occurred. The $Cu^{2+}$ ions from the $CuSO_4$ solution are attracted to the electrons moving through the Cu electrode and make contact with it. Each $Cu^{2+}$ ion making contact with the Cu metal will gain 2 electrons. The Cu electrode is known as the **cathode** because it is the electrode where reduction is occurring. This does not mean that the Cu electrode itself has undergone reduction. Rather it is the $Cu^{2+}$ ions that have been reduced on the surface of the Cu metal. Cu is a reductant (on the right hand side of electrochemical series table) so it cannot be reduced. The Cu cathode is the site or surface where reduction is happening. The reduction reaction is

$Cu^{2+}$ (aq) + $2e^-$ → Cu (s)

Now we get to the role of the salt bridge. When looking at the diagram of the galvanic cell it would seem that the electrons that have just gone through the Cu electrode will now travel through the salt bridge and into the Zn electrode in the other beaker, thus completing the circuit. **Electrons do not move through the salt bridge.**

To understand how the salt bridge works we need to look at what it's made of. A salt bridge is usually a piece of filter paper that has been soaked in a salt solution such as potassium nitrate ($KNO_3$). As was mentioned before, free moving positive and negative ions must be present in each beaker in order for the cell to produce electricity. These positive and negative ions must balance each other out. If one of the beakers gains a positive or negative charge the galvanic cell will not work. The salt bridge will maintain neutrality of charge (prevent the buildup of charge) in each beaker.

Now let's discuss how the salt bridge maintains the neutrality of charge in each beaker. As was discussed previously, when the Zn anode undergoes oxidation, the $Zn^{2+}$ ions produced dissolve into the surrounding electrolyte of $ZnSO_4$. This solution initially contains $Zn^{2+}$ and $SO_4^{2-}$ ions that are equal in number so it has a neutral charge as the negative and positive ions balance each other out. These new $Zn^{2+}$ ions that are dissolving into the solution from the oxidation of Zn will not be able to find a $SO_4^{2-}$ ion to balance out their charge. So these $Zn^{2+}$ ions from the oxidation of Zn have the potential to make this beaker accumulate a positive charge which would prevent electricity from flowing in this cell. The $NO_3^-$ ions from the salt bridge will be attracted by the positive charge of the new $Zn^{2+}$ ions that have just dissolved into the solution. $2NO_3^-$ ions from the salt bridge will balance out the charge of one $Zn^{2+}$ ion so the charge in this beaker will remain neutral.

Over in the other beaker at the cathode, the $CuSO_4$ electrolyte is neutral in charge as the $Cu^{2+}$ ions are balanced out by the $SO_4^{2-}$ ions. The reduction reaction causes $Cu^{2+}$ ions to turn into Cu metal atoms which deposit onto the surface of the Cu electrode. The reduction of $Cu^{2+}$ ions removes positive charges from the beaker but the number of $SO_4^{2-}$ ions does not change. So the removal of $Cu^{2+}$ ions has the potential to cause this beaker to accumulate a negative charge. The $K^+$ ions from the salt bridge are attracted to the negative charge of the $SO_4^{2-}$ ions that no longer have a $Cu^{2+}$ to balance out their charge. $2K^+$ ions from the salt bridge will balance out the charge of one $SO_4^{2-}$ ion so the charge in this beaker will remain neutral.

So the salt bridge completes the circuit by keeping the charges at the anode and cathode neutral by allowing anions (-) to flow towards the anode and cations towards the cathode (+)

Here are some other important points that relate to the functioning of an electrochemical cell.

- When a galvanic cell is functioning and producing electricity, it is said to be **discharging.** Each beaker containing the anode and cathode is known as a **half cell.** A half cell contains what is known as a conjugate redox pair. For example the $Zn^{2+}/Zn$ half cell contains the oxidant $Zn^{2+}$ and the reductant Zn. They are referred to as a conjugate redox pair because when the oxidant, $Zn^{2+}$ undergoes reduction it becomes the reductant, Zn. The other beaker containing the Cu metal in $CuSO_4$ is referred to as the $Cu^{2+}/Cu$ half cell. Not every chemical in a half cell will take part in the redox reactions. For example in the $Zn^{2+}/Zn$ half cell it is only the Zn that undergoes oxidation. The oxidant, $Zn^{2+}$ does not undergo any reaction. In the other half cell, $Cu^{2+}/Cu$, it is the $Cu^{2+}$ that undergoes reduction. The Cu does not react. You should avoid referring to a whole half cell as being the anode or the cathode. For example, in the $Cu^{2+}/Cu$ half cell it is only the Cu metal that is acting as the cathode.

  $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $Zn^{2+}/Zn$ conjugate redox pair
  Oxidant Reductant

  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Cu^{2+}/Cu$ conjugate redox pair
  Oxidant Reductant

Half cell containing anode + half cell containing cathode = 1 galvanic cell

The main reason why conjugate redox pairs are used in galvanic cells is because there is no risk of having the redox reaction occurring in the same beaker. This will be discussed later on in worked example 4.

- The movement of electrons from the anode to the cathode via the wires is known as the **external circuit.**

- The movement of cations from the salt bridge into the cathode and anions from the salt bridge into the anode is known as the **internal circuit.**

- The compound that is going to be used to make the solution for a salt bridge should be: highly soluble in water; cheap; readily available; a weak reductant and or oxidant. The last characteristic is very important because the salt bridge should not take part in the redox reactions. It is the chemicals in the half cells that should only take part in the redox reactions. $KNO_3$ is often chosen for the salt bridge because on the electrochemical series table, $K^+$ is a very weak oxidant and $NO_3^-$ is so weak as a reductant or an oxidant that it does not appear on the table. $KNO_3$ is also cheap and readily available.

- Quite often the anode electrode will lose mass when the cell is discharging. For example, the Zn atoms in the anode are oxidised into $Zn^{2+}$ ions which dissolve into the surrounding solution. As a consequence the Zn anode is gradually dissolving into the surrounding electrolyte and losing mass.

- Quite often the cathode electrode will gain mass when the cell is discharging. For example, when the $Cu^{2+}$ ions undergo reduction they turn into Cu atoms which deposit onto the surface of the Cu cathode. As a consequence the Cu cathode gains mass while the cell is discharging.

- When a galvanic cell is discharging, electrons will always flow from **anode** to **cathode** through the external circuit.

- The anode is given a **negative (-) polarity**. A good way to remember this is that negatively charged ions ***(anions)*** are attracted to the ***anode.*** The cathode is given a **positive polarity (+).** A good way to remember this is that positively charged ions ***(cations)*** are attracted to the ***cathode.***

## Worked Example 3

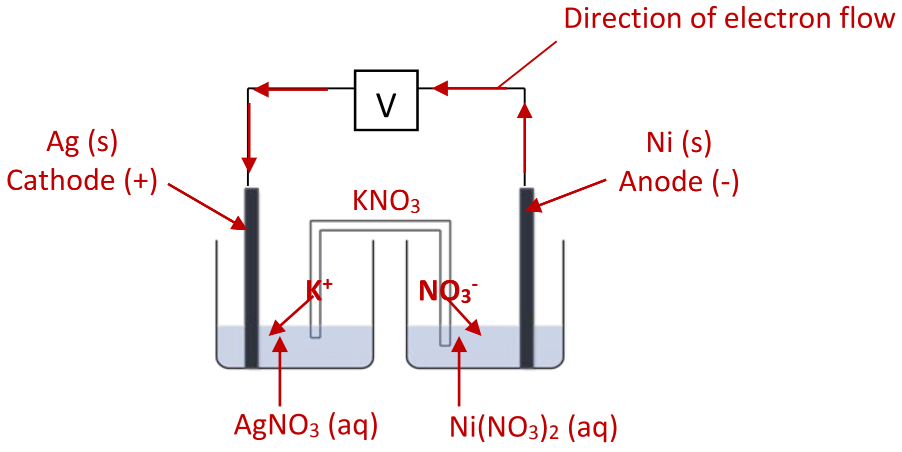
Draw a galvanic cell consisting of a $Ag^+/Ag$ half cell and a $Ni^{2+}/Ni$ half cell. In your diagram you must show and label the following.

- The anode and cathode including their composition.
- The formula of the electrolyte in each half cell.
- A suitable salt bridge.
- The movement of ions from the salt bridge into each half cell.
- The direction of electron flow.

When this galvanic cell is discharging give the

- anode half equation.
- oxidation half equation.
- full equation.
- name of the electrode that loses mass.
- name of the electrode that gains mass.

## Worked Example 3 Solutions



*The beaker on the left is the $Ag^+/Ag$ half cell. This half cell cannot just contain $Ag^+$ ions. As was mentioned before if there is a positive or negative charge in a half cell there will be no production of electricity. There must be a negative ion such as $NO_3^-$ present to keep the charge in the beaker neutral. $NO_3^-$ is a good choice of a negative ion in a half cell because it will not take part in the redox reactions and will always form a soluble ionic compound, regardless of the cation it is combined with. $NO_3^-$ was also chosen as the negative ion to combine with $Ni^{2+}$ in the other half cell. In order to work out where the anode and cathode is, all of the chemicals in the 2 half cells need to be located on the electrochemical series table.*

*Reductants = $H_2O$, Ag (s) and Ni (s)*
*Oxidants = $H_2O$, $Ag^+$ (aq) and $Ni^{2+}$ (aq)*

*Strongest reductant = Ni (s) as it is the lowest reductant on the table.*
*Strongest oxidant = $Ag^+$ (aq) as it is the highest oxidant on the table.*

*Therefore the strongest reductant, Ni (s), will undergo oxidation and give its electrons away to the strongest oxidant, $Ag^+$ (aq) which is in the other beaker. So the* ***anode must be the Ni electrode*** *and the* ***cathode must be the Ag electrode.***

*The electrons will always flow from anode to cathode. Another way of working out which half cell will contain the anode and cathode is to locate the half cells on the table. The lower half cell will always contain the strongest reductant and the higher half cell will always contain the strongest oxidant.* ***So the higher half cell will always contain the cathode and the lower half cell will always contain the anode.***

Higher half cell containing strongest oxidant, $Ag^+$ (aq)

| | |
|---|---|
| **$Ag^+$** (aq) + $e^-$ ⇌ Ag (s) | +0.80 V |
| $Fe^{3+}$ (aq) + $e^-$ ⇌ $Fe^{2+}$ | +0.77 V |
| $O_2$ (g) +$2H^+$ (aq) +$2e^-$ ⇌ $H_2O_2$ (aq) | +0.68 V |
| $I_2$ (l) + $2e^-$ ⇌ $2I^-$ (aq) | +0.54 V |
| $O_2$ (g) +$2H_2O$ (l) +$4e^-$ ⇌ $4OH^-$ (aq) | +0.40 V |
| $Cu^{2+}$ (aq) + $2e^-$ ⇌ Cu (s) | +0.34 V |
| $Sn^{4+}$ (aq) + $2e^-$ ⇌ $Sn^{2+}$ (aq) | +0.14 V |
| S (s) +$2H^+$ (aq) + $2e^-$ ⇌ $H_2S$ (g) | +0.14 V |
| $2H^+$ (aq) + $2e^-$ ⇌ $H_2$ (g) | 0.00 V |
| $Pb^{2+}$ (aq) + $2e^-$ ⇌ Pb (s) | -0.13 V |
| $Sn^{2+}$ (aq) + $2e^-$ ⇌ Sn (s) | -0.14 V |
| $Ni^{2+}$ (aq) + $2e^-$ ⇌ **Ni (s)** | -0.23 V |

Lower half cell containing strongest reductant, Ni (s)

**Anode half equation:** $Ni\ (s) \rightarrow Ni^{2+}\ (aq) + 2e^-$

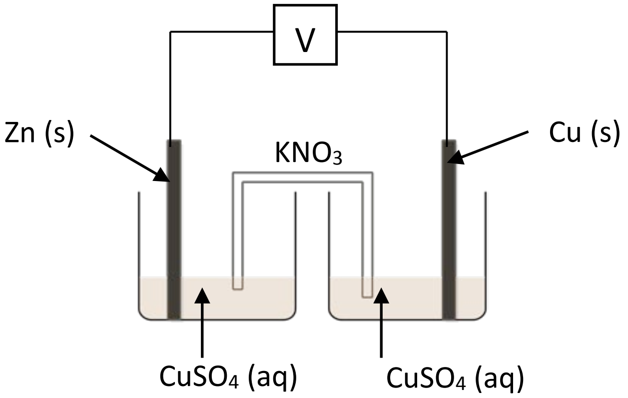
**Cathode half equation:** $Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$ x 2

**Full equation:** $Ni\ (s) + 2Ag^+\ (aq) \rightarrow Ni^{2+}\ (aq) + 2Ag\ (s)$

The Ni electrode loses mass due to the oxidation of Ni atoms into $Ni^{2+}$ ions which dissolve into the surrounding electrolyte. The Ag electrode gains mass because the $Ag^+$ ions in the electrolyte are reduced into Ag atoms which deposit onto the surface of the Ag electrode.

## Worked Example 4

Explain why this galvanic cell will not produce electricity.



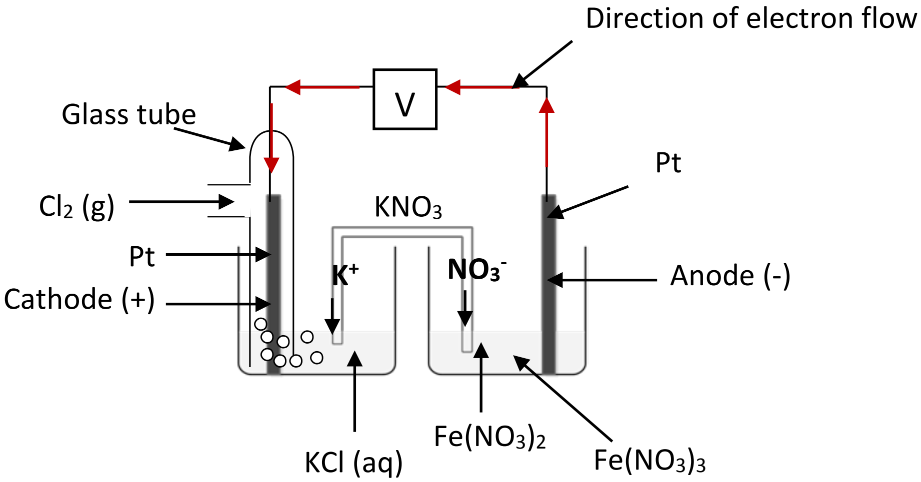
## Worked Example 4 Solutions

In the half cell on the left, a Zn electrode is immersed in a $CuSO_4$ electrolyte. On the electrochemical series table, the reductant, Zn is below the $Cu^{2+}$ oxidant. Therefore a spontaneous redox reaction will occur in the beaker. Electrons will always take what is known as the path of least resistance. A simple way of looking at this is to view electrons as being lazy. When the Zn undergoes oxidation, it is easier for the electrons to be gained by the $Cu^{2+}$ ions making direct contact with the Zn as opposed to the $Cu^{2+}$ions in the other beaker. This would be a much more difficult journey for the electrons as they have to travel through the external circuit (wires) to get to the $Cu^{2+}$ oxidant.

- Worked example 4 shows the reason why it is sensible to use conjugate redox pairs in half cells. If a metal is immersed in a solution containing its cation it will never react with the cation. For example, in the $Zn^{2+}/Zn$ half cell, Zn (s) is immersed in a solution of $Zn^{2+}$ ions. No reaction will occur because the reductant must be below the oxidant on the table. In this case the Zn reductant is directly across the $Zn^{2+}$ oxidant on the electrochemical series table.

## Inert electrodes

The 2 examples of galvanic cells investigated so far have both had solids as part of each half cell. For example the cell made from $Cu^{2+}$ (aq) /Cu (s) contained solid Cu metal and the $Zn^{2+}$ (aq) / Zn(s) contained solid Zn metal. As a consequence the electrodes in these half cells were made from Zn and Cu metal. Sometimes a galvanic cell may contain half cells where none of the chemicals are in solid form. For example a $Cl_2$ (g) / $Cl^-$ (aq) half cell does not have any solid chemicals. $Cl_2$ is a gas and $Cl^-$ is an aqueous ion so neither of these 2 materials can form a solid electrode. As a consequence half cells such as these require **inert** or **unreactive electrodes** to sit in the half cell**.** An **inert electrode** is usually made from either carbon in the form of graphite or platinum metal (Pt). It provides a surface for oxidation and reduction reactions to occur. The electrode is inert so it does not take part in the redox reactions. Inert electrodes just allow electrons to pass through them so they must be good conductors of electricity. The $Cl_2$ (g) / $Cl^-$ (aq) has another problem other than needing an inert electrode. The $Cl_2$ gas has very low solubility in water so it will easily bubble out of solution. To stop this from happening a glass tube is used to keep the $Cl_2$ gas in the half cell and in contact with an inert electrode. Consider the galvanic cell shown below which is constructed from a $Cl_2$ (g) / $Cl^-$ (aq) half cell and a $Fe^{3+}$ (aq) / $Fe^{2+}$ (aq) half cell.



**Cathode half equation:** $Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq)$
**Anode half equation:** $Fe^{2+} (aq) \rightarrow Fe^{3+} (aq) + e^-$

The beaker on the right contains the $Fe^{3+}$ (aq)/ $Fe^{2+}$ (aq) half cell. $Fe^{3+}$ and $Fe^{2+}$ are both aqueous ions and cannot physically form an electrode. Therefore the $Fe^{3+}$/ $Fe^{2+}$ half cell requires an inert electrode. The $Fe(NO_3)_2$ provides the $Fe^{2+}$ and the $Fe(NO_3)_3$ provides the $Fe^{3+}$. $Fe^{2+}$ is the strongest reductant in the cell so it undergoes oxidation. The $Fe^{2+}$ ions make contact with the Pt inert electrode and when they undergo oxidation the electrons are passed into the electrode where they travel through the external circuit and into the cathode which is also a Pt inert electrode.

The beaker on the left contains the $Cl_2$ (g) / $Cl^-$ (aq) half cell. The $Cl_2$ gas is bubbled into the solution through the glass tube which helps trap the $Cl_2$ gas. The $Cl_2$ gas is the strongest oxidant so the inert electrode will act as the cathode. The $Cl_2$ gas molecules will make contact with the Pt electrode and gain the electrons that have just come in from the anode. Unlike the previous 2 examples of electrochemical cells the anode will not lose mass. The Pt anode did not take part in the oxidation reaction so it has not been oxidised into ions that have dissolved in solution. Similarly, the cathode has not gained mass because the reduction reaction occurring on its surface did not produce a solid. When the $Cl_2$ molecules were reduced, $Cl^-$ (aq) ions were produced which just dissolved into the surrounding electrolyte.

## Calculating the voltage of a cell

The voltage of the electricity produced from a galvanic cell can be calculated using the formula:

**Voltage = $E^0$ oxidant – $E^0$ reductant**

OR

**Voltage = $E^0$ (higher half cell) – $E^0$ (lower half cell)**

As an example let us calculate the voltage of the cell using $Cl_2/Cl^-$ and $Fe^{3+}/Fe^{2+}$. From the electrochemical series table, the $E^0$ of the oxidant ($Cl_2/Cl^-$) is +1.36 v and the $E^0$ of the reductant, $Fe^{3+}/Fe^{2+}$ is +0.77 v.

Voltage = +1.36 - +0.77 = +0.59 v

The voltage gives an indication of the energy of the electricity that the galvanic cell can produce. For example the greater the voltage of the electricity the greater the brightness of a globe that is connected to the external circuit. Voltage is also known as **emf, cell potential** and **potential difference.**

The $E^0$ values in the electrochemical series table can only be used to calculate the voltage of a cell if the half cells are at standard conditions (0.987 atm, 25 $^0$C and 1.0 M).

## Summary of galvanic cells

- **Anode** is the electrode where oxidation occurs and has a negative (-) polarity.
- **Cathode** is the electrode where reduction occurs and has a positive (+) polarity.
- The higher half cell will always act as the cathode and the lower half cell will always act as the anode.
- Electrons always flow through the external circuit from **anode** to **cathode.**
- Cations from the salt bridge move towards the cathode and anions move towards the anode.
- Galvanic cells convert chemical energy directly into electricity.

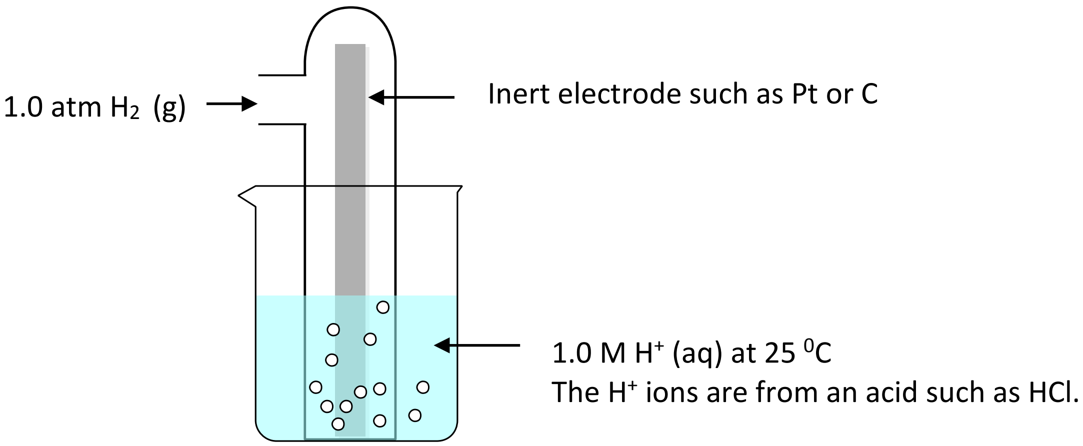
# The standard hydrogen half cell

The standard hydrogen half cell, $H^+/H_2$ is unusual compared to the other half cells in that it has an $E^0$ value of 0.00 v. Recall that the $E^0$ values are a numerical measure of the ability of an oxidant to undergo reduction. For example, the $Cu^{2+}/Cu$ half cell has an $E^0$ of +0.34 V. This is a measure of the ability of $Cu^{2+}$ to be reduced into Cu, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The standard hydrogen half cell is so called because it has been assigned an $E^0$ of 0.00 and is <u>the standard used to derive the $E^0$ values of the other half cells.</u>

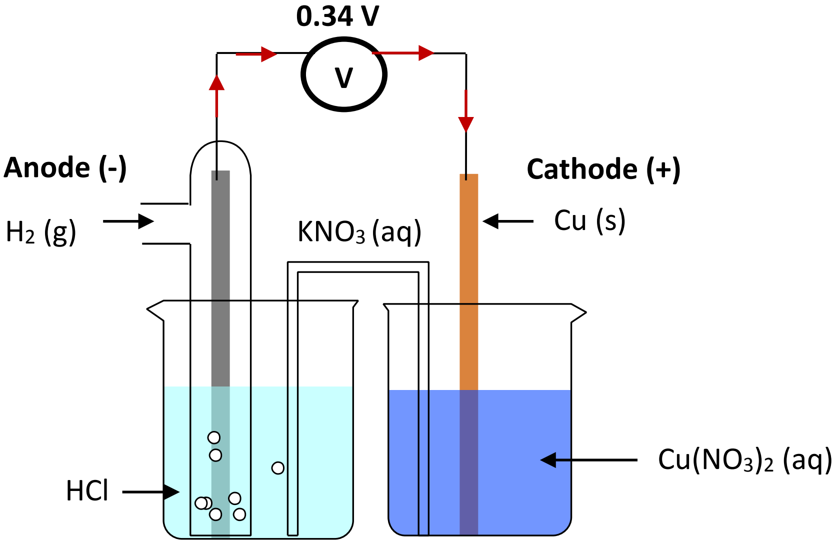
**Standard $H^+/H_2$ half cell ($E^0$ = 0.00 v)**

$2H^+(aq) + 2e^- \rightarrow H_2(g)$



Let us look at how the $H^+/H_2$ standard half cell is used to determine the $E^0$ of the $Cu^{2+}/Cu$ half cell.

The 2 half cells are connected with a voltmeter in order to measure the voltage of electricity produced.



Standard conditions must be used so the $H_2$ gas must be at 0.987 atm pressure, $H^+$ and $Cu^{2+}$ concentrations must be at 1.0 M. The temperature of the contents of both half cells must be 25 $^{0}$C. The reading on this voltmeter is **0.34 v.** The reading in isolation doesn't indicate which half cell is the higher or lower one. That is, it doesn't show which half cell has the anode and which has the cathode. Observations of changes in each half cell need to be made in order to determine which half cell underwent oxidation and which one underwent reduction.

If a pH meter was placed in the $H^+/H_2$ half cell it would show that the pH of the electrolyte is decreasing as the cell discharges. <u>A decrease in pH is indicative of an increase in $H^+$ ions.</u> Therefore it can be reasonably concluded that while the cell is discharging the $H^+$ ions in the half cell are increasing due to the oxidation of $H_2$ gas into $H^+$ ions [$H_2\ (g) \rightarrow 2H^+\ (aq) + 2e^-$]. In the $Cu^{2+}/Cu$ half cell, the mass of the Cu electrode would increase. This would be due to the reduction of $Cu^{2+}$ into solid Cu metal which would deposit onto the Cu electrode [$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$]. The blue colour of this solution would gradually fade as the cell discharges due to the lowering in concentration of the $Cu^{2+}$ ions.

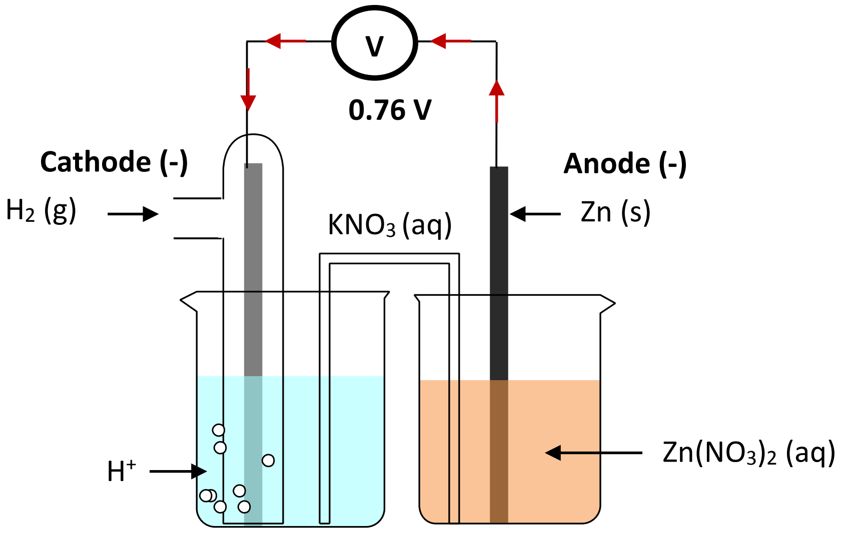
So when the $H^+/H_2$ and $Cu^{2+}/Cu$ half cells are joined together, the $H^+/H_2$ half cell contains the strongest reductant and the $Cu^{2+}/Cu$ half cell contains the strongest oxidant. Therefore the $Cu^{2+}/Cu$ half cell is the higher one and will be given a positive $E^0$ value:

$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$ $\quad$ $E^0 = +0.34$ v

$2H^+\ (aq) + 2e^- \rightarrow H_2\ (g)$ $\quad$ $E^0 = 0.00$ v

Remember that $E^0$ values are a measure of the ability of the oxidants in the table to undergo reduction. Therefore the $Cu^{2+}/Cu$ half cell must be given the higher $E^0$ value since $Cu^{2+}$ is a stronger oxidant than $H^+$ in the $H^+/H_2$ half cell.

Now let us connect the standard $H^+/H_2$ half cell to the $Zn^{2+}/Zn$ half cell.



When these 2 half cells are connected and the cell discharges, the voltmeter gives a reading of

0.76 v. If a pH meter was placed in the $H^+/H_2$ half cell it would show an increase in pH as the concentration of $H^+$ ions becomes lower as they are reduced into $H_2$ gas [$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$]. In the $Zn^{2+}/Zn$ half cell the concentration of $Zn^{2+}$ ions would increase as the Zn electrode is oxidised into $Zn^{2+}$[$Zn (s) \rightarrow Zn^{2+} (aq) + 2e^-$]. The mass of the Zn electrode would also decrease. These observations show that when these 2 half cells are connected, the $H^+$ from the $H^+/H_2$ half cell is a stronger oxidant than $Zn^{2+}$ in the $Zn^{2+}/Zn$ half cell. Therefore the $H^+/H_2$ half cell must be above the $Zn^{2+}/Zn$ half cell. As a consequence the $E^0$ value of the $Zn^{2+}/Zn$ half cell must be -0.76 v.

$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$ $E^0 = +0.34$ v

$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$ $E^0 = 0.00$ v

$Zn^{2+} (aq) + 2e^- \rightarrow Zn (s)$ $E^0 = -0.76$ v

So all of the half cells in the electrochemical series table can be placed in the table according to the voltage they produce when connected to the standard $H^+/H_2$ half cell. Observations made when the cells discharge are used to determine if the half cell is above or below $H^+/H_2$ on the table. Of course SLC conditions must be used when the half cells are connected.

- *Note that when a reductant and oxidant are in contact with each other, heat energy can be produced when the electrons flow from reductant to oxidant. So spontaneous redox reactions can be seen as* ***exothermic reactions*** *as they release heat energy. When the reductant and oxidant are separated in an electrochemical cell however, the heat produced is considerably less. In an electrochemical cell the energy produced is predominantly electrical (a flow of electrons through the external circuit and ions through the internal circuit.).*

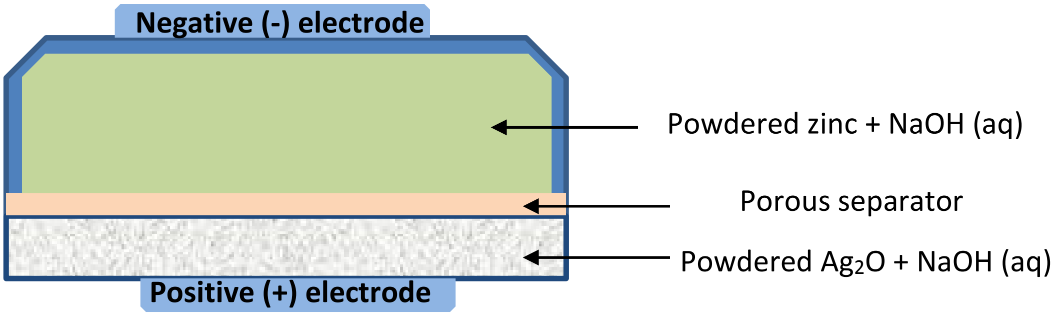
# Commercial Cells

The principles that apply to galvanic cells also apply to the cells and batteries used to power everyday appliances such as calculators, ipads, computers, mobile phones, torches etc. The structures and reactions occurring in these cells can be more complicated than the simple electrochemical cells encountered so far. For the end of year exam you do not need to have any prior knowledge of these commercial cells. You may however, be asked questions where you will need to apply your knowledge of galvanic cells to these commercial cells. Worked example 5 is an example of such a question.

- The term battery is used when 2 or more cells are working together to deliver electrical energy into an appliance.

## Worked Example 5

A silver button cell is an efficient and portable energy source for small devices such as digital thermometers, watches and hearing aids. A cross-section of a silver button cell is shown below.



The porous separator only allows the movement of $OH^-$ ions. $OH^-$ ions are able to move freely through the separator. When the negative and positive electrodes are connected to a load (appliance that uses electricity), the cell will discharge and produce electrical energy. The full equation when the cell is discharging is shown below.

$Zn (s) + Ag_2O (s) + H_2O (l) \rightarrow Zn(OH)_2 (s) + 2Ag (s)$

**a.** Give the anode half equation for when the cell is discharging.
**b.** Give the cathode reaction for the when the cell is discharging.
**c.** Give the formula of the electrolyte used for this cell.
**d.** Discuss the movement of $Na^+$ and $OH^-$ ions through this cell.
**e.** Why is the porous separator needed?

## Worked Example 5 Solutions

*This cell does not seem to resemble at all, the galvanic cells investigated so far. As we go through this question you will see that it does have the same basic features of more simple galvanic cells. In the diagram of the cell the anode is above the porous separator and the cathode is below it.*

**a.**

*The half equations for this cell do not appear in the electrochemical series table. It is possible to work out the anode half equation from the full equation. When using oxidation numbers it can be seen that Zn (s) is the reductant as it has undergone an increase in oxidation number.*

$$\underset{\mathbf{0}}{\mathrm{Zn}}\ (s) + \underset{+1}{\mathrm{Ag}_2}\underset{-2}{\mathrm{O}}\ (s) + \underset{+1}{\mathrm{H}_2}\underset{-2}{\mathrm{O}}\ (l) \rightarrow \underset{\mathbf{+2}}{\mathrm{Zn}}(\underset{-2}{\mathrm{O}}\underset{+1}{\mathrm{H}})_2\ (s) + 2\underset{0}{\mathrm{Ag}}\ (s)$$

*The oxidation number of Zn has increased from 0 to +2 so Zn (s) must be the reductant undergoing oxidation at the anode.*

*In the electrochemical series table the oxidation half equation of zinc is*

*$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$*

*This equation is not quite correct for this cell because the full equation doesn't have $Zn^{2+}$ (aq) as a product but rather $Zn(OH)_2$ (s). This shows that when the Zn was oxidised into $Zn^{2+}$, the $Zn^{2+}$ reacted with the $OH^-$ in the electrolyte: $Zn^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Zn(OH)_2\ (s)$. If the state of matter for the $Zn(OH)_2$ was aqueous (aq), it would be acceptable to leave out the $OH^-$ and give the equation showing the oxidation of Zn from the electrochemical series table. This is because the $OH^-$ would be a spectator ion (not taking part in the reaction). It is not a spectator ion in this case because it has changed from aqueous to solid after the reaction has occurred. The correct half equation is shown below.*

$$\mathbf{Zn\ (s) + 2OH^-\ (aq) \rightarrow Zn(OH)_2\ (s) + 2e^-}$$

The state of $OH^-$ has changed from aqueous to solid so it must be shown in the half equation.

**b.** *The oxidation numbers in the full equation show that Ag from $Ag_2O$ has undergone a decrease in oxidation number from +1 to 0. Therefore the $Ag_2O$ must be the oxidant reacting at the cathode. This equation is more difficult to work out than the anode equation. There is no assistance from the electrochemical series table with this one. One way to approach working out the cathode reaction is to remove Zn (s) and $Zn(OH)_2$ (aq) from the full equation as they have already been used in the anode half equation. What is left over from the full equation is*

$Ag_2O\ (s) + H_2O\ (l) \rightarrow 2Ag\ (s)$

*There are 2 O and 2 H atoms on the left hand side of the equation and none on the right hand side. With these commercial cells, it is very common for one of the ions in the electrolyte to be used up by one of the electrode reactions and produced by the other electrode reaction. For example, the anode reaction may use up (react with) one of the ions from the electrolyte and the cathode reaction may produce it. With this cell, the anode reacted with $OH^-$ ions from the electrolyte so it is very likely that the cathode reaction will produce $OH^-$ ions. The equation can be balanced by placing $2OH^-$ ions on the product side of the equation.*

$Ag_2O\ (s) + H_2O\ (l) \rightarrow 2Ag\ (s) + 2OH^-\ (aq)$

*In order to balance the -2 charge on the product side of the equation, 2 electrons must be added to the reactant side to complete the reduction half equation.*

**$Ag_2O\ (s) + H_2O\ (l) + 2e^- \rightarrow 2Ag\ (s) + 2OH^-\ (aq)$**

*Another way to obtain the reduction half equation is to* ***subtract the anode half equation from the full equation.***

If **oxidation half equation + reduction half equation = full equation,**

then **reduction half equation = full equation – oxidation half equation**

Before the oxidation half equation is subtracted from the full equation, check that the coefficients in the oxidation half equation are the same as the coefficients in the full equation. In this example the Zn and $Zn(OH)_2$ have a coefficient of 1 in both the full equation and the half equation. If however, the full equation showed 2Zn and $2Zn(OH)_2$, then that would indicate that the anode half equation was multiplied by 2 in order to balance out the electrons with the cathode reaction. So in this case you would have to multiply the anode half equation by 2 before it is subtracted from the full equation. In this example it is not necessary.

So subtract the reactants from the anode equation away from the reactants on the full equation and the products from the anode equation away from the products of the full equation:

$Zn$ (s) **– $Zn$ (s) – $2OH^-$ (aq)** + $Ag_2O$ (s) + $H_2O$ (l) → $Zn(OH)_2$ (s) **– $Zn(OH)_2$ (s)** + 2Ag (s) **– $2e^-$**

The Zn (s) and $Zn(OH)_2$ are now eliminated from the equation. The – $2e^-$ electrons on the product side of the equation should be brought over to the reactant side of the equation so the sign will change to + $2e^-$. The – 2 $OH^-$ on the reactant side must be moved over to the product side of the equation where it becomes + $2OH^-$. So the cathode half equation is

**$Ag_2O$ (s) + $H_2O$ (l) + $2e^-$ → 2Ag (s) + $2OH^-$ (aq)**

Another way of obtaining the oxidation and reduction half equations for this cell is to use what is known as the "fake acid" method. This method is used for balancing redox half equations that are occurring in alkaline ($OH^-$) environments as is the case with this commercial cell.

## "FAKE ACID" METHOD FOR BALANCING REDOX HALF EQUATIONS IN ALKALINE/BASIC ($OH^-$) MEDIA

First of all balance the half equation as if it was in acidic media ($H^+$).

**1.** Balance all atoms except for H and O.
**2.** Balance O atoms by adding $H_2O$.
**3.** Balance H atoms by adding $H^+$ ions.
**4.** Balance the charges by adding electrons.

Now follow these steps so that the equation will be adjusted to show that the reaction was occurring in an alkaline environment.

- Add $OH^-$ ions in order to balance out the $H^+$ ions. For example if there are $2H^+$ ions add $2OH^-$ ions.
- Combine the $OH^-$ and $H^+$ ions to make $H_2O$.
- Add the same number of $OH^-$ ions to the other side of the equation.
- Finally complete the half equation by cancelling out any species that appear on both sides of the equation. This will usually involve cancelling water molecules.

Let's use this fake acid method to get the oxidation half equation.

Steps 1 to 4
$Zn(s) \rightarrow Zn(OH)_2\ (s)$
$Zn(s) + 2H_2O\ (l) \rightarrow Zn(OH)_2\ (s)$
$Zn\ (s) + 2H_2O\ (l) \rightarrow Zn(OH)_2\ (s) + 2H^+\ (aq) + 2e^-$

- Add $OH^-$ ions in order to balance out the $H^+$ ions. For example if there are $2H^+$ ions add $2OH^-$ ions.

$Zn(s) + 2H_2O\ (l) \rightarrow Zn(OH)_2\ (s) + 2H^+\ (aq) + 2OH^-\ (aq) + 2e^-$

- Combine the $OH^-$ and $H^+$ ions to make $H_2O$.

$Zn(s) + 2H_2O(l) \rightarrow Zn(OH)_2(s) + 2H_2O(l) + 2e^-$

- Add the same number of $OH^-$ ions to the other side of the equation.

$Zn(s) + 2H_2O(l) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2H_2O(l) + 2e^-$

- Finally complete the half equation by cancelling out any species that appear on both sides of the equation. This will usually involve cancelling water molecules.

$Zn(s) + 2H_2O(l) - 2H_2O(l) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2H_2O(l) - 2H_2O(l) + 2e^-$

$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$

Now let's use this fake acid method to get the reduction half equation.

$Ag_2O(s) \rightarrow Ag(s)$
$Ag_2O(s) \rightarrow 2Ag(s)$
$Ag_2O(s) \rightarrow 2Ag(s) + H_2O(l)$
$Ag_2O(s) + 2H^+(aq) \rightarrow 2Ag(s) + H_2O(l)$
$Ag_2O(s) + 2H^+(aq) + 2e^- \rightarrow 2Ag(s) + H_2O(l)$

$Ag_2O(s) + 2H^+(aq) + 2OH^-(aq) + 2e^- \rightarrow 2Ag(s) + H_2O(l)$
$Ag_2O(s) + 2H_2O(l) + 2e^- \rightarrow 2Ag(s) + H_2O(l)$
$Ag_2O(s) + 2H_2O(l) + 2e^- \rightarrow 2Ag(s) + H_2O(l) + 2OH^-(aq)$
$Ag_2O(s) + 2H_2O(l) - H_2O(l) + 2e^- \rightarrow 2Ag(s) + H_2O(l) - H_2O(l) + 2OH^-(aq)$

$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

**c.** The electrolyte is NaOH (aq). *It is the only chemical in the cell that is in aqueous solution. Unlike the other electrochemical cells in this chapter, the anode and cathode have the same electrolyte of NaOH (aq).*

**d.** *It is impractical for commercial cells like this one to have a salt bridge. Instead they usually have a porous separator that allows ions from the electrolyte to move from the anode into the cathode or vice versa.*

*When looking at the anode reaction, it can be seen that $OH^-$ ions from the electrolyte are removed as $OH^-$ (aq) react with $Zn^{2+}$ (aq) to produce $Zn(OH)_2$ (s). Remember that before the cell was discharging, $Na^+$ and $OH^-$ ions were perfectly balanced and the charge at the anode was neutral. Every time an $OH^-$ ion is removed by the anode reaction, a $Na^+$ ion no longer has an $OH^-$ to balance out its positive charge. As a consequence $OH^-$ ions produced at the cathode can cross the separator and move into the anode where they will replace the $OH^-$ ions that were lost and hence cancel out the positive charge of the now unpartnered $Na^+$*

*ions. It would seem reasonable to expect that $Na^+$ ions should migrate from the anode to the cathode since cations from the salt bridge migrate to the cathode in order to balance out the negative charges that build up there. This is not necessary because when the $OH^-$ ions move from the cathode to the anode, this also balances out the charges at the cathode. The moment an $OH^-$ ion is produced at the cathode it moves away to the anode so the cathode does not build up any negative charge and does not need $Na^+$ to come in and balance out the charges. So during the operation of this cell the $Na^+$ ions do not move across the separator (this was already stated in the question).*

- *A different type of separator might only allow the movement of $Na^+$ ions between the electrodes. In this case $Na^+$ ions would move from the anode to the cathode. Movement of $Na^+$ ions away from the anode would prevent the accumulation of positive charge at the anode as $OH^-$ ions are used up resulting in the buildup of unpartnered $Na^+$ ions. As $Na^+$ ions enter the cathode they will prevent the buildup of negative charge as they will balance out the negative charge produced as $OH^-$ are made by the cathode reaction.*

**e.** The porous separator is needed to allow the movement of anions ($OH^-$) between the half cells in order to complete the circuit by preventing the accumulation of charge. It does a similar job to the salt bridge in simple galvanic cells. The porous separator also prevents the Zn reductant at the anode and $Ag_2O$ oxidant at the cathode from making direct contact with each other. If this happens the electrons will be transferred directly from the Zn to $Ag_2O$ and there will be no electric current passing through the external circuit.

## Secondary and Primary Cells

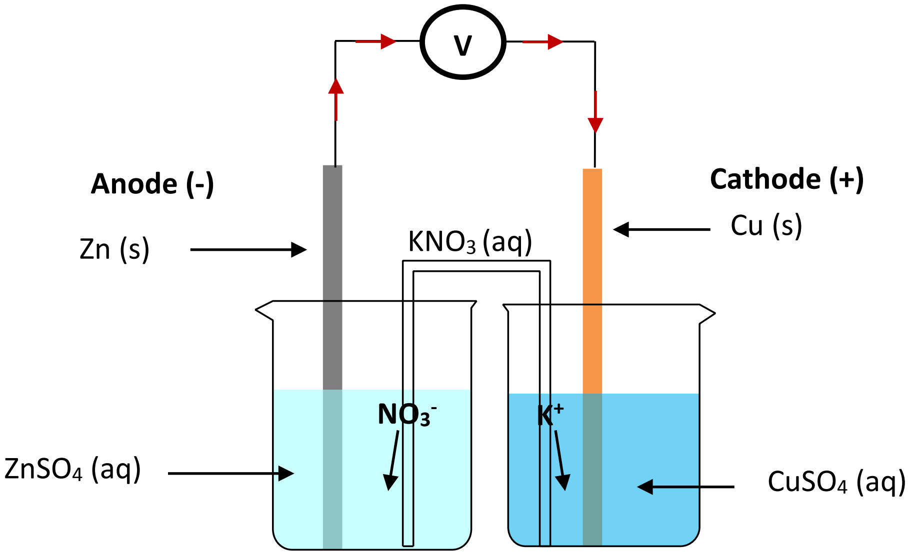
A **secondary cell** _is one that is able to be recharged._ In order for a cell to be recharged the products of the anode and cathode reactions must make contact with the electrodes. It is also necessary for the ions in the electrolyte that are maintaining the neutrality of charge to be able to move to the opposite electrode to that which they were moving towards during discharge. Refer to worked example 6 part c on pages 253 and 254 for further clarification on this point.

A **primary cell** _is one that cannot be recharged._ This is mainly due to the products of the anode and cathode either not remaining in contact with the electrodes or being consumed by side reactions occurring in the cell. A side reaction is an unwanted chemical reaction that can occur in a cell.

### Recharging secondary cells

The best way to understand both secondary and primary cells is to investigate how secondary cells are recharged.

Earlier in the chapter the electrochemical cell formed by connecting $Zn^{2+}/Zn$ to $Cu^{2+}/Cu$ was investigated. The diagram below shows this cell discharging. This cell will be used as an example to show how a cell can be recharged.



$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$ $Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

**Full equation:** $Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$

Before we look at how this cell can be recharged, we need to know what happens when a cell goes **flat.** When a cell goes flat, either the reductant or oxidant has been totally used up. This is the case with a simple galvanic cell like the one shown above or a commercial cell used in a computer, mobile phone etc. If the above cell has gone flat, it could be because all of the Zn that was immersed in the electrolyte has been oxidised. If the Zn no longer makes contact with the electrolyte the cell will not discharge. It is also possible that all of the $Cu^{2+}$ oxidant at the cathode half cell has been reduced into Cu metal. If there is no $Cu^{2+}$ left to undergo reduction the cell will not discharge. The purpose of recharging this cell is simply to reform the Zn reductant and $Cu^{2+}$ oxidant. Once this happens the cell can go back to discharging again. The only way to reform the Zn reductant and $Cu^{2+}$ oxidant is to reverse the oxidation and reduction reactions that were occurring when the cell was discharging.

If the oxidation reaction is reversed, the $Zn^{2+}$ ions that were produced when the cell was discharging will be converted back into Zn (s). That is the $Zn^{2+}$ ions will be reduced into Zn (s).

$Zn^{2+}$ (aq) + $2e^-$ → Zn (s)

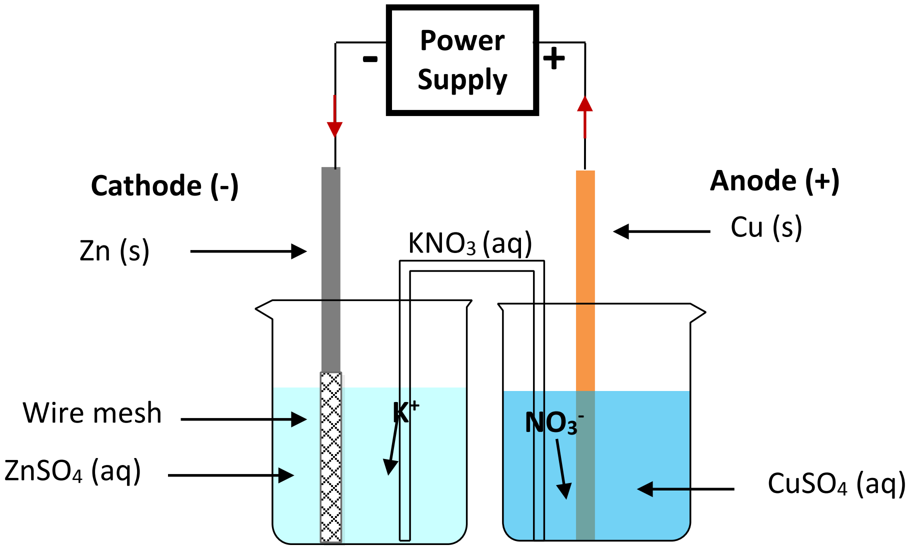
*This means that what used to be the anode during DISCHARGING will now act as a cathode during RECHARGING.*

If the reduction reaction is reversed, the Cu solid that was produced when the cell was discharging will be converted back into $Cu^{2+}$ ions. That is, Cu solid will be oxidised into $Cu^{2+}$ (aq).

Cu (s) → $Cu^{2+}$ (aq) + $2e^-$

*This means that what used to be the cathode during DISCHARGING will now act as an ANODE during RECHARGING.*

The diagram below shows how this electrochemical cell is recharged.



$Zn^{2+}$ (aq) + $2e^-$ → Zn (s)

Cu (s) → $Cu^{2+}$ (aq) + $2e^-$

**Full equation:** $Zn^{2+}$ (aq) + Cu (s) → Zn (s) + $Cu^{2+}$ (aq)

The first thing that must be done is to remove the voltmeter or any appliance that was using the electricity when the cell was discharging. This must be replaced with a **power supply.** A power supply is a device that produces electricity. Another functioning galvanic cell can acts as a power supply. It is more likely that the power supply will be a power pack that is connected to mains electricity.

The electrode that was acting as the anode during discharge, in this case the Zn, must be connected to the negative terminal of the power supply. When the power supply is turned on, electrons will leave the negative of the power supply and pass through the Zn electrode and the wire mesh immersed in the electrolyte. The wire mesh that is connected to the Zn electrode has replaced the part of the electrode that was immersed in the solution. This part of the electrode was totally consumed when the cell went flat. As electrons have entered this electrode, it would make sense that reduction can occur here. The strongest oxidant in the beaker, $Zn^{2+}(aq)$, will be attracted to the wire mesh and gain the electrons as they come in. As a consequence, $Zn^{2+}$ ions will be reduced into Zn atoms on the surface of the wire mesh.

$Zn^{2+} (aq) + 2e^- \rightarrow Zn (s)$ *Zn reductant of the galvanic cell is reformed.*

The Zn (s) atoms deposit onto the surface of the wire mesh and rebuild the part of the electrode immersed in the solution. The Zn electrode is now a **cathode (-)** since reduction is occurring on its surface during recharging. The polarity of the cathode during recharging is negative because it is attached to the negative of the power supply.

The Cu electrode which was the cathode during discharging is connected to the positive of the power supply. The positive of the power supply will force oxidation to occur at this electrode. The Cu solid that was deposited on this electrode during discharge, is the strongest reductant in this half cell and will be oxidised back into $Cu^{2+}$ (aq).

$Cu (s) \rightarrow Cu^{2+} (aq) + 2e^-$ *The $Cu^{2+}$ oxidant of the galvanic cell has just been reformed.*

The Cu electrode during recharging is an anode (+) and is given a positive polarity because it is connected to the positive of the power supply.

During recharging the cations from the salt bridge still migrate to the cathode and the anions still migrate to the anode in order to complete the circuit by preventing the accumulation of charge in the half cells.

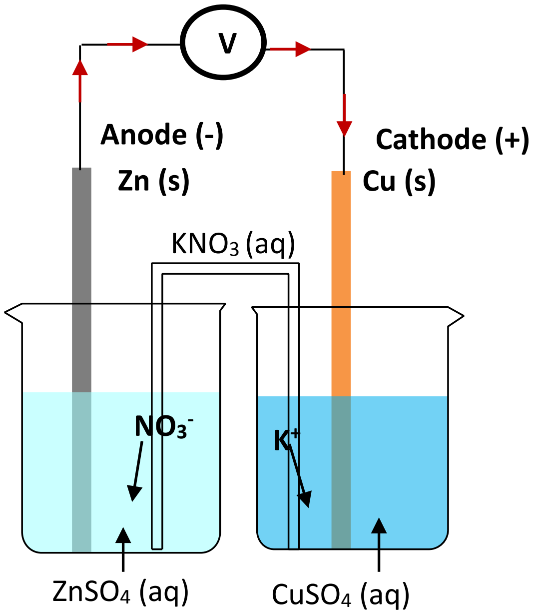
In order to fully recharge the cell, the power supply must deliver electricity with a voltage that is slightly higher than the voltage delivered by the cell when it was discharging. The voltage of the electricity delivered by this cell when it was discharging is:

Voltage = $E^0$ higher half cell – $E^0$ lower half cell
= +0.34 – -0.76
= +0.34 + 0.76 = 1.10 v

This cell should be recharged with a voltage of just over 1.10 v. Eg. 1.20 v. During recharging some energy and hence voltage is lost as the electrons pass through the wires. Recharging the cell using a voltage of electricity that is slightly greater than the voltage produced when the cell was discharging will compensate for this loss of voltage.

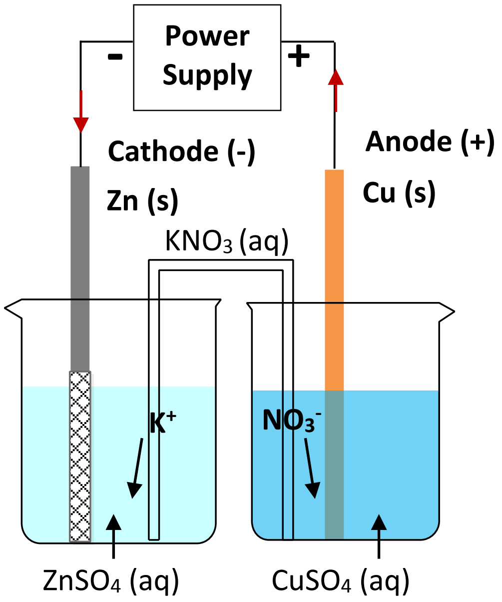
# Summary of discharging and recharging

## Discharging



- Oxidation occurs at the anode.
- Reduction occurs at the cathode.
- Anode (-) has a negative polarity.
- Cathode (+) has a positive polarity.
- Electrons flow from anode to cathode through the external circuit.
- Electrons flow from the negative electrode to the positive electrode through the external circuit.
- Anions from the salt bridge flow to the anode.
- Cations from the salt bridge flow to the cathode.
- Chemical energy is converted into electrical energy.

## Recharging



- Oxidation occurs at the anode.
- Reduction occurs at the cathode.
- Anode (+) has a positive polarity.
- Cathode (-) has a negative polarity.
- Electrons flow from anode to cathode through the external circuit.
- Electrons flow from the positive electrode to the negative electrode through the external circuit.
- Anions from the salt bridge flow to the anode.
- Cations from the salt bridge flow to the cathode.
- Electrical energy is converted into chemical energy.
- Negative of power supply connected to anode (during discharge). Positive of power supply connected to cathode (during discharge).

Once a galvanic cell has been recharged it can be disconnected from the power supply and allowed to discharge again.

The reason why this galvanic cell was able to be recharged is that during discharge the products at The anode and cathode remained in contact with the electrodes. So when the power supply was turned on, the $Zn^{2+}$ ions that were produced at the anode during discharge were able to touch the electrode, gain the electrons and undergo reduction. The Cu metal that was produced at the cathode during discharge remained in contact with the Cu electrode. As a consequence when the power supply was turned on the Cu was able to undergo oxidation and reform the $Cu^{2+}$ oxidant. If the Cu did not remain in contact with the electrode it would not have been oxidised as it would not have been connected to the power supply.

- *Note that when a cell is recharging or discharging, the polarity of the electrodes never changes. It is just what happens at that electrode that changes. So during discharging the negative electrode is the anode but that same negative electrode during recharging is the cathode. During discharging the positive electrode is the cathode but that same positive electrode is the anode during recharging.*

- *Recharging a galvanic cell like the one in this example is impractical. This example was used to make the process easier to follow. Commercial cells are recharged all the time. Worked example 6 shows the recharging of a car battery.*

## Worked Example 6

A car battery is a secondary cell that is used to power the electric components in a car such as the radio, heater, air conditioning etc. The electrode reactions when a car battery discharges are shown below.

**anode (-):** $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$
**cathode (+):** $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

**a.** When the car battery is recharging,

  **i.** give the half equation for the reaction occurring at the negative electrode.
  **ii.** give the half equation for the reaction occurring at the positive electrode.

**b.** By referring to the information given in the question, explain why a car battery is a secondary cell.

**c.** In a car battery, $H^+$ ions from the electrolyte maintain the neutrality of charge at both the anode and cathode. Membranes known as porous separators are placed between the anode and cathode electrodes to prevent them from making contact with each other. These separators must also allow $H^+$ ions to move freely between the electrodes in both directions. Discuss why this movement of $H^+$ ions in both directions between the electrodes is necessary for the car battery to be rechargeable.

## Worked Example 6 Solutions

**a.**

**i.** *During recharging, the anode reaction that occurred during discharging is reversed. The electrode that used to be the anode is now the cathode and it still has a negative polarity. The reaction is:*

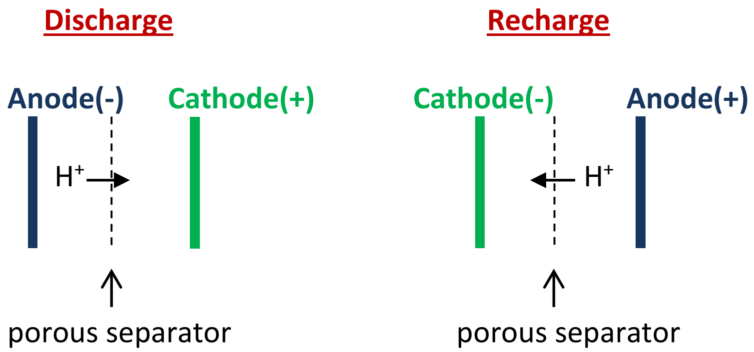
$PbSO_4\text{ (s)} + 2e^- \rightarrow Pb\text{ (s)} + SO_4^{2-}\text{ (aq)}$

**ii.** *During recharging, the cathode reaction that occurred during discharging is reversed. The electrode that used to be the cathode is now the anode and it still has a positive polarity. The reaction is*

$PbSO_4\text{ (s)} + 2H_2O\text{ (l)} \rightarrow PbO_2\text{ (s)} + SO_4^{2-}\text{ (aq)} + 4H^+\text{ (aq)} + 2e^-$

**b.** The car battery is a secondary cell because the product at the anode and cathode is $PbSO_4$ (s). As this is a solid it will remain in contact with the electrodes enabling the car battery to be recharged.

**c.** During the discharge of the car battery, $H^+$ ions from the anode move to the cathode to replace the $H^+$ ions that were used up by the cathode reaction. This prevents the anode from accumulating a positive charge and the cathode from accumulating a negative charge. These $H^+$ ions must be able to move through the porous separator between the electrodes in order for this to happen. When the car battery is recharged, the electrode that used to be anode becomes the cathode and vice versa. Now the $H^+$ ions have to move to the other electrode and in the opposite direction in order to keep the charges at both electrodes neutral. The $H^+$ ions are still moving from anode to cathode but in the opposite direction due to the changing functions of the electrodes. If the porous separator didn't allow the movement of $H^+$ ions in both of these directions the cell would be unable to be recharged. Refer to the diagrams below.



- *Always remember, cations migrate to the cathode and anions to the anode.*

## Factors affecting the life of a battery / commercial cell

The life of a primary cell and secondary cell is limited. Even a secondary cell which can be recharged has a finite life. A secondary cell cannot be discharged and recharged “forever”. Below is a list of some of the factors that limit the life of both primary and secondary cells.

- Important chemicals such as the reductant, oxidant and electrolyte can leak out of a cell. After a while the main structure of the cell can corrode (rust out) resulting in the leakage of these important materials.

- Important chemicals such as the reductant, oxidant and electrolyte can become consumed in side reactions. Side reactions are unwanted reactions that can occur in a cell over time. Many commercial cells are a big cocktail of chemicals that over time may react in ways that are unexpected or unwanted.

- In secondary cells, solid electrode products may detach from the electrodes or become consumed by side reactions. Once the products at the anode and cathode lose contact with the electrodes the cell can no longer be recharged.

- Impurities in the cell may form a barrier between the electrodes and the electrolyte. Once this happens the cell may no longer discharge or be rechargeable.

- Most commercial cells should be stored at low temperatures, usually at room temperature (25 $^0$C) or lower. If the temperature of a cell is too high the rate of the redox reactions occurring when it is discharging will be high and it will go flat quickly. At lower temperatures, the side reactions that can limit the life of a cell will occur at a slower rate and the cell will last longer. For secondary cells, the number of charge cycles (the number of times the cell can be recharged during its life time) will be higher at lower temperatures. *So low temperatures will help increase the life and number of charge cycles of a cell, but low temperatures are not good for the performance of a cell.* At low temperatures the slow rate of the redox reactions means that the current of electricity produced in a given amount of time is lower than at higher temperatures. As the cell is delivering less electrical energy at lower temperatures, the appliance may not perform at its optimum (best) level.

## Fuel Cells

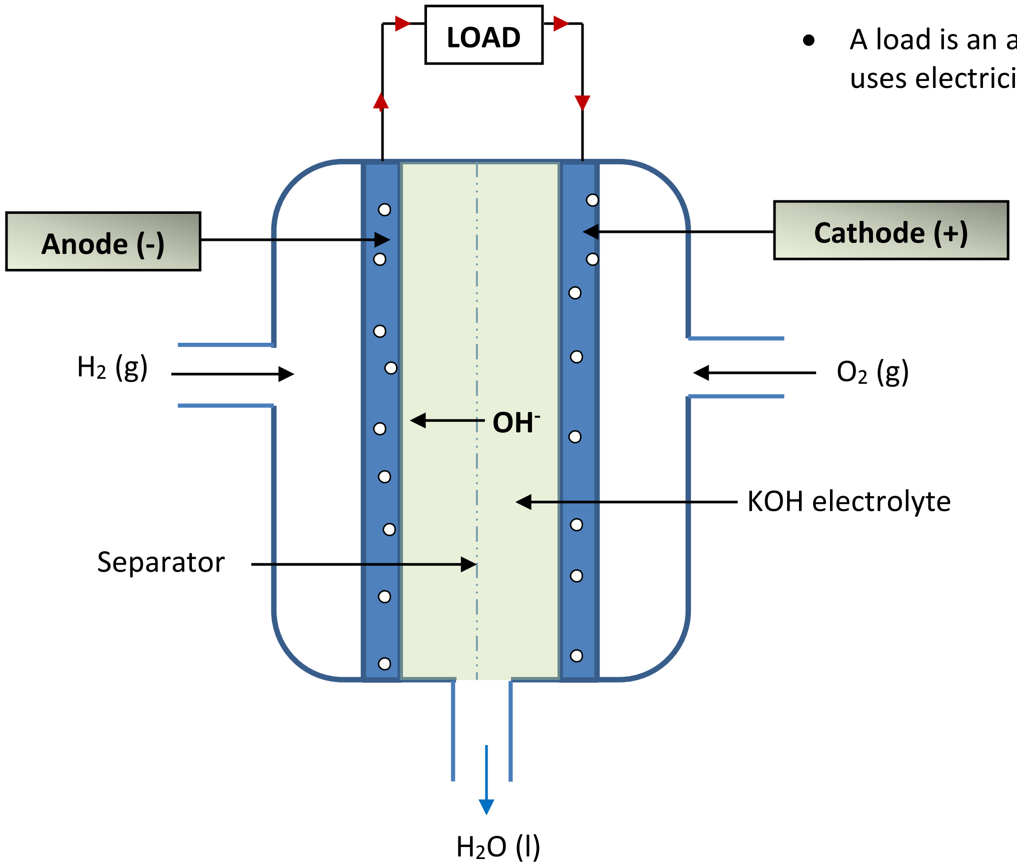
A **fuel cell** is a galvanic cell but is neither a primary nor a secondary cell. Unlike a traditional electrochemical cell, a fuel cell has the ability to receive a continuous supply of reductant and oxidant. As a consequence it does not need to be recharged. If the reductant or oxidant runs out you just add more. This cannot be done with the more traditional galvanic cells. When they go flat they are thrown out if they are primary cells or recharged if they are secondary cells. They do not have the capacity to take in more reductant or oxidant as the reactants are totally enclosed within the cell.

Fuel cells are not used anywhere near as much as primary and secondary cells. Some applications of fuel cells include, alcohol breathalysers, electric vehicles and power supplies for spacecraft and other facilities.

The 2 main types of fuel cell are the **alkaline hydrogen/oxygen fuel cell** and **the acid hydrogen/oxygen fuel cell.**

### Alkaline hydrogen/oxygen fuel

The diagram below shows the main features of an alkaline hydrogen/oxygen fuel cell.



- A load is an appliance that uses electricity.

**Anode half equation**
$H_2 (g) + 2OH^- (aq) \rightarrow 2H_2O (l) + 2e^-$

**Cathode half equation**
$O_2 (g) + 2H_2O (l) + 4e^- \rightarrow 4OH^- (aq)$

**Full equation**
$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

The name of this fuel cell pretty much gives its main features away. It has an alkaline or basic electrolyte of potassium hydroxide (KOH). Other bases such as NaOH can be used. Hydrogen gas is the reductant that is fed into the anode through an inlet. Oxygen gas is the oxidant that is fed into the cathode through the inlet on the opposite side of the cell. The anode and cathode electrodes are both inert. They are also **porous** which means that they contain tiny little holes that increase the surface area of the electrode exposed to the reactant gases. This helps to increase the rate of the reduction and oxidation reactions which in turn helps to increase the current of electricity produced in a given amount of time. Unlike the electrodes in most other galvanic cells, the electrodes in fuel cells contain chemicals that helps them to catalyse the oxidation and reduction reactions occurring on their surface. This helps to increase the rate of oxidation and reduction. When the $H_2$ gas makes contact with the electrode at the anode, it is oxidised and the $OH^-$ ions in the electrolyte are part of the reaction:

**Anode:** $H_2 (g) + 2OH^- (aq) \rightarrow 2H_2O (l) + 2e^-$

The electrons get pushed through the external circuit and enter the cathode. $O_2$ gas in contact with the cathode electrode gains these electrons and undergoes reduction. Water in the electrolyte takes part in the reaction.

**Cathode half equation:** $O_2 (g) + 2H_2O (l) + 4e^- \rightarrow 4OH^- (aq)$

Notice how the oxidation reaction uses up $OH^-$ ions and the reduction reaction produces $OH^-$ ions. As was mentioned previously, many commercial galvanic cells have anode and cathode reactions where an ion from the electrolyte is produced by one reaction but used up by the other one.

The full equation is very simple: $2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

Here is how this equation is derived from the 2 half equations.

**Anode half equation:** $H_2 (g) + 2OH^- (aq) \rightarrow 2H_2O (l) + 2e^-$ **x 2**
$2H_2 (g) + 4OH^- (aq) \rightarrow 4H_2O (l) + 4e^-$

Combine with cathode half equation

$2H_2 (g) + 4OH^- (aq) + O_2 (g) + 2H_2O (l) \rightarrow 4OH^- (aq) + 4H_2O (l)$

Subtract $4OH^-$ and $2H_2O$ from both sides of the equation.

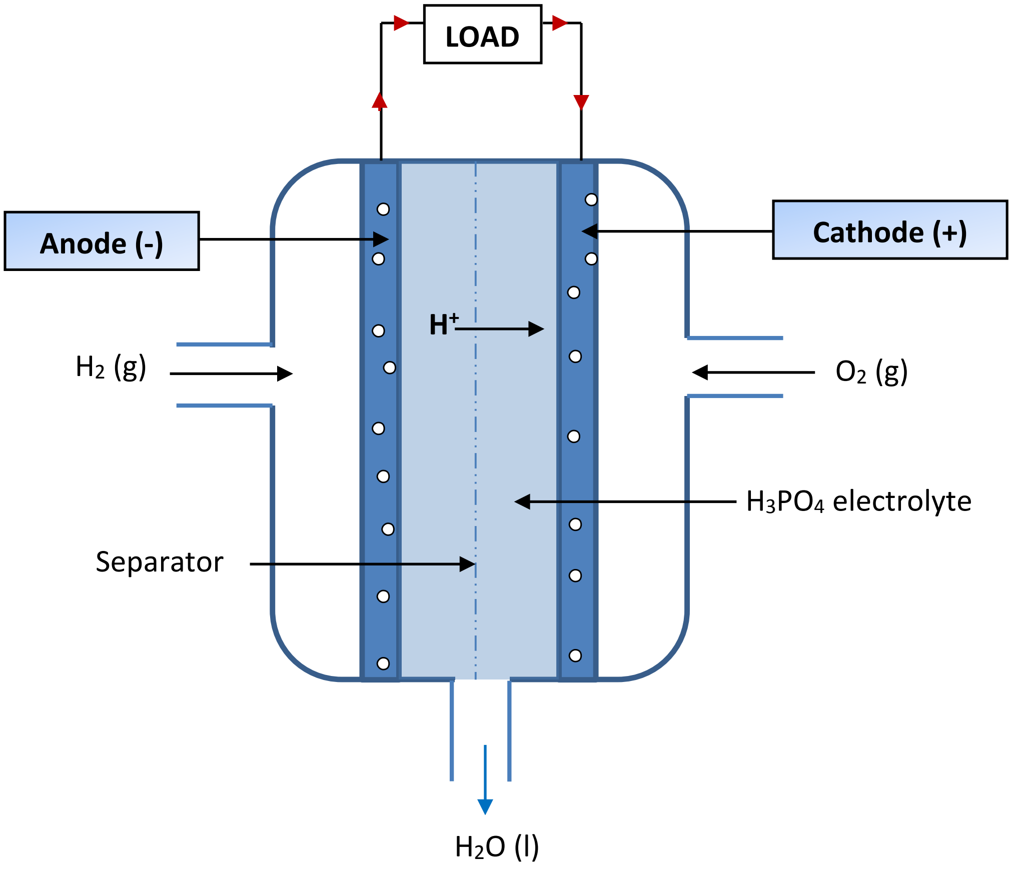
$2H_2 (g) + 4OH^- (aq)$ **– $4OH^- (aq)$** $+ O_2 (g) + 2H_2O (l)$ **– $2H_2O (l)$** $\rightarrow 4H_2O (l)$ **– $2H_2O (l)$** $+ 4OH^- (aq)$ **– $4OH^- (aq)$**

**$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$** *The $H_2O$ produced by the fuel cell is allowed out through the bottom outlet.*

As is the case with most commercial cells there is no salt bridge in fuel cells and it is the job of the electrolyte to keep the 2 half cells neutral in charge. The anode reaction uses up $OH^-$ ions from the electrolyte which used to be attracted to and balanced out by $K^+$ ions. As a consequence, $OH^-$ ions produced at the cathode can migrate through the separator and into the anode where they replace the $OH^-$ ions that just reacted and balance out the positive charges of the $K^+$ ions. Over at the cathode the reduction reaction is producing $OH^-$ ions. The moment these ions are produced they migrate over to the anode so there is no accumulation of negative charge at the cathode. As a consequence there is no need for $K^+$ ions to migrate to the cathode to balance out the charges. The separator will not allow the movement of $K^+$ ions from anode and cathode and vice versa. It is possible however, for the separator to maintain the neutrality of charges by allowing only the movement of $K^+$ ions from anode to the cathode. The $OH^-$ ions used up at the anode can result in an accumulation of positive charge due the presence of $K^+$ ions which no longer have an $OH^-$ to balance out their positive charge. The movement of $K^+$ ions out of the anode will prevent the buildup of positive charge at this electrode. As $K^+$ ions move into the cathode they balance out the negative charge of the $OH^-$ ions produced at the cathode.

## Acid hydrogen/oxygen fuel

The diagram below shows the main features of an acid hydrogen/oxygen fuel cell.



**Anode half equation**

$H_2 (g) \rightarrow 2H^+ (aq) + 2e^-$

**Cathode half equation**

$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$

**Full equation**
$2H_2$ (g) + $O_2$ (g) → $2H_2O$ (l)

The acid hydrogen fuel cell is almost identical to the alkaline fuel cell. The main difference is that the acid fuel cell uses an acid electrolyte. The above diagram shows a fuel cell using phosphoric acid ($H_3PO_4$) but it is possible to use other acids such as $HNO_3$ and HCl.

The half equations are different due to the use of the acid electrolyte. The full equation however is the same. Here is how the full equation is derived for the acid fuel cell.

Multiply the anode half equation by 2.

$H_2$ (g) → $2H^+$ (aq) + $2e^-$ **x 2**
$2H_2$ (g) → $4H^+$ (aq) + $4e^-$

Combine with cathode half equation.

$2H_2$ (g) + $O_2$ (g) + $4H^+$ (aq) → $4H^+$ (aq) + $2H_2O$ (l)

Subtract $4H^+$ from both sides of the equation.

$2H_2$ (g) + $O_2$ (g) + $4H^+$ (aq) **– $4H^+$ (aq)** → $4H^+$ (aq) **– $4H^+$ (aq)** + $2H_2O$ (l)

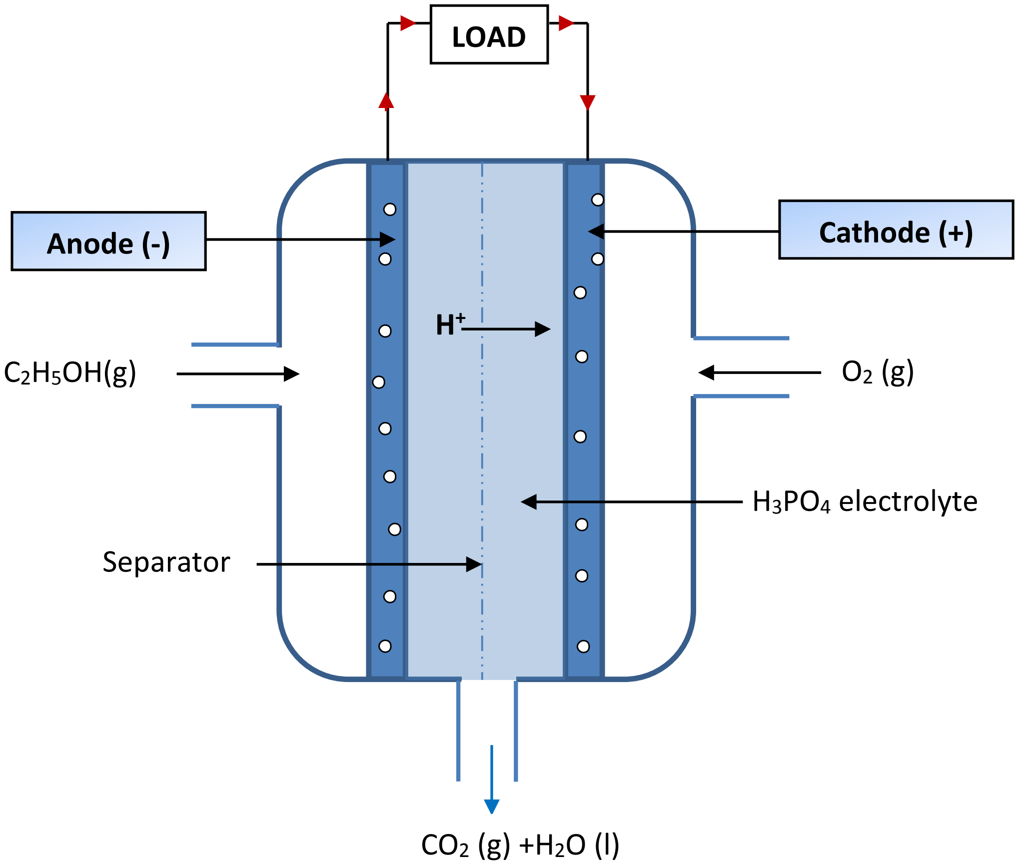
**$2H_2$ (g) + $O_2$ (g) → $2H_2O$ (l)**

The acid electrolyte contains dissolved $H^+$ ions. Often the separator will allow the $H^+$ ions produced at the anode to migrate to the cathode. This will prevent the accumulation of positive charge at the anode and negative charge at the cathode.

The half equations for both the alkaline and acid fuel cells are found in the electrochemical series table.

| | | |
|---|---|---|
| **Cathode:** acid fuel cell | $O_2\ (g) + 4H^+\ (aq) + 4e^- \rightleftharpoons 2H_2O\ (l)$ | |
| | $Br_2\ (l) + 2e^- \rightleftharpoons Br^-\ (aq)$ | |
| | $Ag^+\ (aq) + e^- \rightleftharpoons Ag\ (s)$ | |
| | $Fe^{3+}\ (aq) + e^- \rightleftharpoons Fe^{2+}$ | |
| | $O_2\ (g) + 2H^+\ (aq) + 2e^- \rightleftharpoons H_2O_2\ (aq)$ | |
| | $I_2\ (l) + 2e^- \rightleftharpoons 2I^-\ (aq)$ | |
| **Cathode:** alkaline fuel cell | $O_2\ (g) + 2H_2O\ (l) + 4e^- \rightleftharpoons 4OH^-\ (aq)$ | |
| | $Cu^{2+}\ (aq) + 2e^- \rightleftharpoons Cu\ (s)$ | |
| | $Sn^{4+}\ (aq) + 2e^- \rightleftharpoons Sn^{2+}\ (aq)$ | |
| | $S\ (s) + 2H^+\ (aq) + 2e^- \rightleftharpoons H_2S\ (g)$ | |
| | $2H^+\ (aq) + 2e^- \rightleftharpoons H_2\ (g)$ | **Anode:** acid fuel cell |
| | $Pb^{2+}\ (aq) + 2e^- \rightleftharpoons Pb\ (s)$ | |
| | $Sn^{2+}\ (aq) + 2e^- \rightleftharpoons Sn\ (s)$ | |
| | $Ni^{2+}\ (aq) + 2e^- \rightleftharpoons Ni\ (s)$ | |
| | $Co^{2+}\ (aq) + 2e^- \rightleftharpoons Co\ (s)$ | |
| | $Fe^{2+}\ (aq) + 2e^- \rightleftharpoons Fe\ (s)$ | |
| | $Zn^{2+}\ (aq) + 2e^- \rightleftharpoons Zn\ (s)$ | |
| | $2H_2O\ (l) + 2e^- \rightleftharpoons H_2\ (g) + 2OH^-\ (aq)$ | **Anode:** alkaline fuel cell |

It is possible to have an acid fuel cell that has a reductant other than $H_2$ gas fed into the anode. Any compound that can be combusted in oxygen can react at the anode of an acid fuel cell. For example, $CH_4$, $C_2H_5OH$, $C_4H_{10}$ etc. Shown below is an acid fuel cell with ethanol undergoing oxidation at the anode.



**Anode half equation**

$C_2H_5OH (g) + 3H_2O (l) \rightarrow 2CO_2 (g) + 12H^+ (aq)+ 12e^-$

**Cathode half equation**

$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$

**Full equation**

$C_2H_5OH (g) + 3O_2 (g) \rightarrow 2CO_2 (g) + 3H_2O (l)$

The cathode equation is the same as for the $H_2/O_2$ fuel cell as it is just $O_2$ gas that is fed at the cathode.

$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$

The anode reaction for $C_2H_5OH$ is not on the electrochemical series table. Since we know that $CO_2$ and $H_2O$ are the products, the rules for balancing equations in acidic media can be used. Start the equation off with:

$C_2H_5OH (g) \rightarrow CO_2 (g)$

Balance the C atoms first.

$C_2H_5OH\ (g) \rightarrow 2CO_2\ (g)$

Balance the O atoms by adding 3 $H_2O$ on the left had side of the equation.

$C_2H_5OH\ (g) + 3H_2O\ (l) \rightarrow 2CO_2\ (g)$

Balance the H atoms by adding 12 $H^+$ on the right hand side of the equation.

$C_2H_5OH\ (g) + 3H_2O\ (l) \rightarrow 2CO_2\ (g) + 12H^+\ (aq)$

There are zero charges on the left had side of the equation and a charge of +12 on the right hand side of the equation. Balance the charges by adding 12 $e^-$ to the right hand side of the equation.

$C_2H_5OH\ (g) + 3H_2O\ (l) \rightarrow 2CO_2\ (g) + 12H^+\ (aq) + 12e^-$

To derive the full equation, multiply the cathode half equation by 3 in order to balance the electrons.

$O_2\ (g) + 4H^+\ (aq) + 4e^- \rightarrow 2H_2O\ (l)$ **x 3**

$3O_2\ (g) + 12H^+\ (aq) + 12e^- \rightarrow 6H_2O\ (l)$

Combine this with the anode half equation.

$C_2H_5OH\ (g) + 3H_2O\ (l) + 3O_2\ (g) + 12H^+\ (aq) \rightarrow 6H_2O\ (l) + 2CO_2\ (g) + 12H^+\ (aq)$

Subtract $12H^+$ and $3H_2O$ from both sides of the equation.

$C_2H_5OH\ (g) + 3H_2O\ (l)$ **$- 3H_2O\ (l)$** $+ 3O_2\ (g) + 12H^+\ (aq)$ **$- 12H^+\ (aq)$** $\rightarrow 6H_2O\ (l)$ **$- 3H_2O\ (l)$** $+ 2CO_2\ (g) + 12H^+\ (aq)$ **$- 12H^+\ (aq)$**

**$C_2H_5OH\ (g) + 3O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (l)$**

- If $CO_2$ is produced at the anode of an acid fuel cell, the full equation will be the same as the equation for when the reductant is completely combusted in $O_2$. All combustion reactions are redox reactions. If a fuel is placed at the anode of a fuel cell, when it is oxidised an electric current will be produced as the electrons flow to the $O_2$ at the cathode as opposed to the great amount of heat (evident by the flame) produced when the fuel is directly oxidised by oxygen during combustion. The same can be said for the $H_2/O_2$ fuel cell. The full equation of $H_2\ (g) + O_2\ (g) \rightarrow H_2O\ (g)$ is the same as the equation for when $H_2$ is combusted to produce heat.

Fuel cells are seen as a possible alternative to the burning of fossil fuels such as coal for the production of electricity. Some **advantages** that fuel cells have over the burning of fossil fuels to produce electricity are:

- They are more efficient because they convert chemical energy directly into electricity. When fossil fuels are combusted, chemical energy is converted into heat energy which is finally converted into electricity. Heat energy is very easily lost and this greatly minimises the amount of electricity that can be derived from a given amount of chemical energy from a fossil fuel.

  **<u>Energy conversions when fossil fuels are combusted</u>**

  Chemical energy → Heat energy → Electricity

  **<u>Energy conversions when fuel cells discharge</u>**

  Chemical energy → Electricity

  *No heat produced so a greater % of the chemical energy in the reactants is converted into electricity.*

- If a $H_2/O_2$ fuel cell is used to produce electricity, the only product emitted is harmless $H_2O$ as opposed to the harmful emissions such as $CO_2$ from the combustion of fossil fuels. The use of $H_2/O_2$ fuel cells to produce electricity does not contribute to global warming. *Be aware that water vapour is actually a greenhouse gas. The water produced by a fuel cell however is in the form of a liquid so it would not be expected to contribute to globally warming.*

The biggest **disadvantage** that fuel cells have for the production of electricity on a large scale is their HIGH COST. The systems required to continuously feed reactants into the anode and cathode are very expensive. It is also very expensive to maintain their operating conditions which can include very high temperatures. The storage of hydrogen gas for fuel cells is a disadvantage because it is a highly flammable gas which may explode or cause fires.

# CHAPTER 11 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
When Pb metal is placed in a $H_2O_2$ solution at standard conditions, the most likely outcome will be that

- **A.** the $H_2O_2$ will decompose into $O_2$ and $H^+$ ions.
- **B.** the Pb metal will increase in mass and the concentration of $H_2O_2$ will decrease.
- **C.** the Pb metal will decrease in mass.
- **D.** the concentration of $Pb^{2+}$ ions surrounding the Pb metal will decrease.

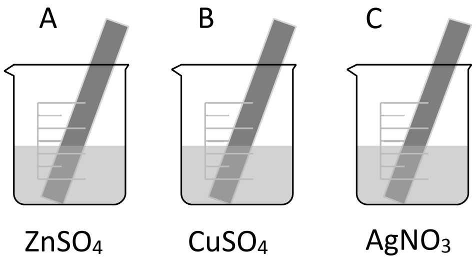
**Question 2**
Which combination will all reduce a solution of $Sn^{4+}$ ions?

- **A.** Sn (s), Li (s), Ni (s) and $H_2$ (g)
- **B.** $F^-$ (aq), $H_2O$ (l), $Br^-$ (aq) and $I^-$ (aq)
- **C.** $F_2$ (g), $H_2O_2$ (aq), $Au^+$ (aq) and $Cl_2$ (g)
- **D.** Cu (s), $Sn^{2+}$, $I^-$ (aq) and S (s)

**Question 3**
Storing pieces of silver metal in a solution of $Sn(NO_3)_2$ (aq) will

- **A.** result in the loss of the silver metal through oxidation.
- **B.** prevent the reduction of silver ions into silver metal.
- **C.** cause the concentration of $Sn^{2+}$ ions to increase.
- **D.** prevent the silver metal from being oxidised by $Cl_2$ gas.

**Question 4**
The 3 beakers shown below labelled A, B and C have a piece of Zn metal immersed in a solution.



The beakers that will produce a coating of metal on the Zn after a period of time are

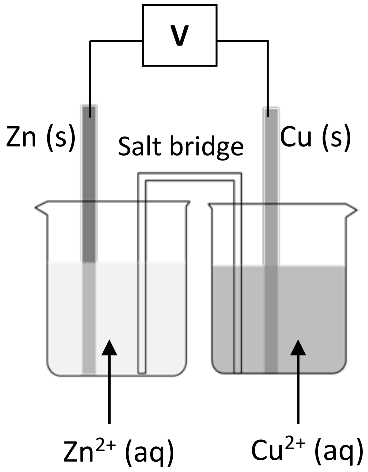
- **A.** A, B and C
- **B.** A and B.
- **C.** B and C.
- **D.** C only.

**Question 5**
A half cell contains $Fe(NO_3)_2$ and $Fe(NO_3)_3$ solutions. An appropriate electrode for this half cell would be

- **A.** Fe (s)
- **B.** graphite
- **C.** $Fe^{2+}$ (aq)
- **D.** $Fe^{3+}$ (aq)

*Questions 6 and 7 refer to the following information.*

The galvanic cell shown below is known as the Daniel cell. It contains the $Zn^{2+}$/Zn half cell and the $Cu^{2+}$/Cu half cell.



**Question 6**
While this cell is discharging, the salt bridge allows

**A.** electrons to pass through it from the anode through to the cathode.
**B.** cations to pass into the cathode through the external circuit.
**C.** anions to migrate towards the anode.
**D.** cations to neutralise the negative charge accumulating around the anode.

**Question 7**
In order to change the direction of electron flow through the external circuit, the $Zn^{2+}$/ Zn half cell should be replaced with a

**A.** $Ag^{+}$/Ag half cell.
**B.** $Mn^{2+}$/Mn half cell.
**C.** $Ca^{2+}$/Ca half cell.
**D.** None of the above.

**Question 8**
The information below relates to the following half cells:

$A^{+}$ (aq) / A (s)
$B^{2+}$ (aq) / B (s)
$C^{2+}$ (aq )/ C (s)
$D^{3+}$ (aq) / D (s)

- When A (s) is immersed in a solution of $C^{2+}$ (aq), the solid C is produced.
- When A (s) is placed in a solution of
- $B^{2+}$ (aq), no changes are observed.
- D (s) loses mass when placed in a solution of $B^{2+}$ (aq).

The list that shows the oxidants in order of increasing oxidising strength is

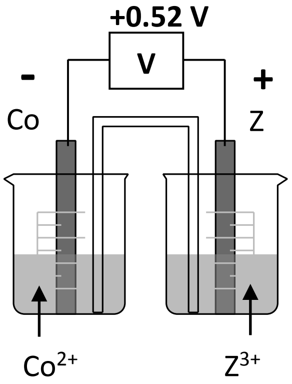
**A.** C, A, B and D.
**B.** D, B, A and C.
**C.** $C^{2+}$, $A^{2+}$, $B^{2+}$ and $D^{3+}$.
**D.** $D^{3+}$, $B^{2+}$, $A^{2+}$ and $C^{2+}$.

**Question 9**
When connected to the standard $H^{+}/H_2$ half cell, half cell Z causes the pH in the $H^{+}/H_2$ half cell to increase. When half cell Z is placed in the $Fe^{2+}$/Fe half cell, the mass of the Fe electrode increases. Half cell Z is

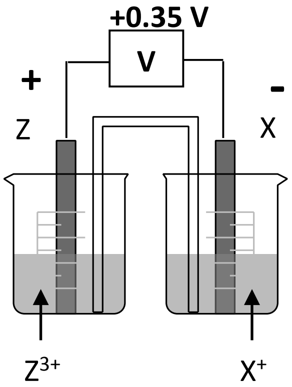
**A.** $Cu^{2+}$/ Cu
**B.** $Mn^{2+}$/ Mn
**C.** $Ag^{+}$/ Ag
**D.** $Br_2$ / $2Br^{-}$

*Questions 10 and 11 relate to the following information.*

The galvanic cell shown below is constructed from the half cells $Co^{2+}/Co$ and $Z^{3+}/Z$.



This galvanic cell is constructed from the half cells $Z^{3+}/Z$ and $X^{+}/X$.



**Question 10**
Which list contains the reductants from these 2 galvanic cells ordered in increasing reducing strength?

**A.** Co, X and Z.
**B.** Z, X and Co.
**C.** Co, X and Z.
**D.** X, Co and Z

**Question 11**
The $E^0$ value of the $X^+/X$ half cell is

A. + 0.35 V
B. + 0.59 V
C. + 0.52 V
D. - 0.11 V

**Question 12**
Methane gas is fed into a fuel cell using an acidic electrolyte. While this cell is discharging the reaction occurring at the positive electrode is

**A.** $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$
**B.** $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
**C.** $2H^+ + 2e^- \rightarrow H_2$
**D.** $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

*Questions 13 and 14 refer to the following:*

Nickel cadmium cells are secondary cells that are used as a power supply for many portable devices such as power tools. The full equation when this cell is discharging is

$Cd + 2NiOH + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

**Question 13**
When this cell is discharging, the reaction occurring at the negative electrode is

**A.** $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
**B.** $2NiOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$
**C.** $2Ni(OH)_2 + 2OH^- \rightarrow 2NiOH + 2H_2O$
**D.** $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$

**Question 14**
When this cell is recharging, the reaction occurring at the negative electrode is

**A.** $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
**B.** $2NiOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$
**C.** $2Ni(OH)_2 + 2OH^- \rightarrow 2NiOH + 2H_2O$
**D.** $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$

**Question 15**
A year 12 chemistry student constructs an electrochemical cell in the lab. This cell consists of the following.

- A half cell made from Cu (s) and $Cu(NO_3)_2$ (aq).
- A half cell made from $CuSO_4$ (aq) and Zn (s).
- A salt bridge made from a piece of filter paper that was soaked in potassium nitrate solution.

When these 2 half cells are connected by wires and the salt bridge, the main energy transformation that is occurring is

**A.** Chemical → Electrical
**B.** Chemical → Heat
**C.** Electrical → Chemical
**D.** Chemical → Heat → Electrical

**Question 16**
A lithium-ion cell is stored in a refrigerator. As a consequence of these storage conditions it is expected that

**A.** when the cell is taken out of the refrigerator and placed straight into an appliance, the appliance will operate at its best performance.
**B.** this cell will be able to be recharged only a small number of times.
**C.** the life of this cell will be prolonged.
**D.** when the cell is taken out of the refrigerator and placed straight into an appliance, the appliance will operate at its best performance but will go flat very quickly.

## Short Answers

**Question 1**

Explain the following observations.

**a.** A gold ring that has been immersed in water for years shows very little sign of corrosion (rust).

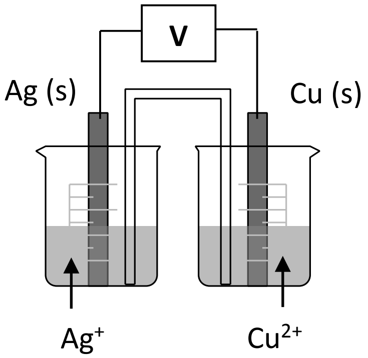
**b.** Lithium metal and fluorine gas react explosively when mixed together.

**c.** A piece of Cu is immersed in $Ag^+$ (aq) and shows no sign of reaction even though the electrochemical series table predicts that a reaction should occur.

**d.** At SLC conditions, a piece of Mg is allowed to stand in a solution of $Fe(NO_3)_3$ and no reaction is observed.

**Question 2**

The galvanic cell shown below consists of a $Cu^{2+}/Cu$ half cell and a $Ag^+/ag$ half cell.



**a.** Give the name of the anode.

**b.** Give the name of the cathode.

**c.** Give the anode half equation showing states.

**d.** Give the cathode half equation showing states.

**e.** Give the full equation showing states.

**f.** Give the formulae of suitable electrolytes for each half cell.

**g.** Explain why the anode loses mass and the cathode gains mass.

**Question 3**

An electrochemical cell is to be constructed from a $Fe^{3+}/Fe^{2+}$ half cell and a $Cl_2/Cl^-$ half cell.

**a.** Draw a labelled sketch of this cell. Your sketch must include the following.

- Anode and cathode including polarities.
- Names of materials used for the electrodes.
- Formulae of appropriate solutions for each half cell.
- The formulae of the solution used for the salt bridge.
- The direction of movement of electrons through the external circuit.
- The direction of movement of cations and anions from the salt bridge.

**b.** Give the electrode half equations and the full equation.

**c.** Give 3 reasons why the solution you chose for the salt bridge was suitable.

**d.** Calculate the predicted cell potential for this cell.

**Question 4**

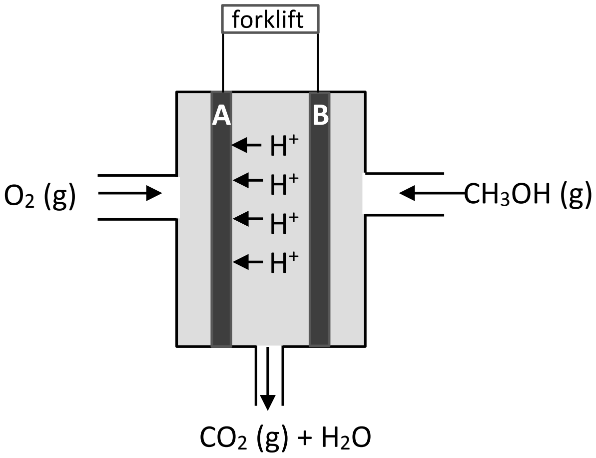
With reference to the electrochemical series table, explain why silver nitrate is not an appropriate solution to use for a salt bridge.

**Question 5**

What are the factors that have prevented the use of fuel cells for the large scale generation of electrical energy?

**Question 6**

A direct methanol fuel cell (DMFC) can be used to power vehicles such as forklifts. Methanol is fed into the anode and oxygen gas into the cathode. A proton exchange membrane allows for the movement of $H^+$ ions into the cathode area.



**a.** Which electrode, A or B is positive?

**b.** Give the half equation for the reaction occurring at the anode.

**c.** Give the half equation for the reaction occurring at the cathode.

**d.** Give the full equation.

**e.** Why is it important for $H^+$ ions to be allowed to flow from electrodes B to A?

**f.** It is possible for the membrane to only allow the movement of negative ions. Explain how this would maintain the neutrality of charges at the anode and cathode. Assume the electrolyte contains $HNO_3$.

**g.** Give one advantage that a fuel cell has over a traditional combustion engine as the power source for the forklift.

**h.** Give one advantage that a traditional combustion engine has over a fuel cell as the power source for the forklift.

**Question 7**

A special type of hydrogen / oxygen fuel cell has molten $Li_2CO_3$ as the electrolyte. The separator between the anode and cathode allows for the movement of $CO_3^{2-}$ ions.

The full equation and anode half equation for when this cell discharges are shown below.

Full equation

$2H_2 + O_2 \rightarrow 2H_2O$

Anode half equation

$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

**a.** Write out the cathode half equation. States of matter do not need to be shown.

**b.** Describe and justify the movement of $CO_3^{2-}$ ions through this fuel cell.

**Question 8**

A nickel metal hydride battery is a special type of secondary cell that uses a hydrogen absorbing alloy as the negative electrode (MH) when the cell is discharging. The full equation for when the cell is recharging is shown below.

$$M (s) + H_2O (l) + Ni(OH)_2 (s) + OH^- (aq) \rightarrow MH(s) + OH^- (aq) + NiOOH (s) + H_2O (l)$$

The oxidation half equation for when the cell is discharging is shown below.

$$MH (s) + OH^- (aq) \rightarrow M (s) + H_2O (l) + e^-$$

**a.** Give the full formula of the reductant during the recharging process.

**b.** Write out the half equation for the reaction occurring at the positive electrode when the cell is recharging. States of matter must be shown.

**c.** Give the formula of the oxidant when the cell is discharging.

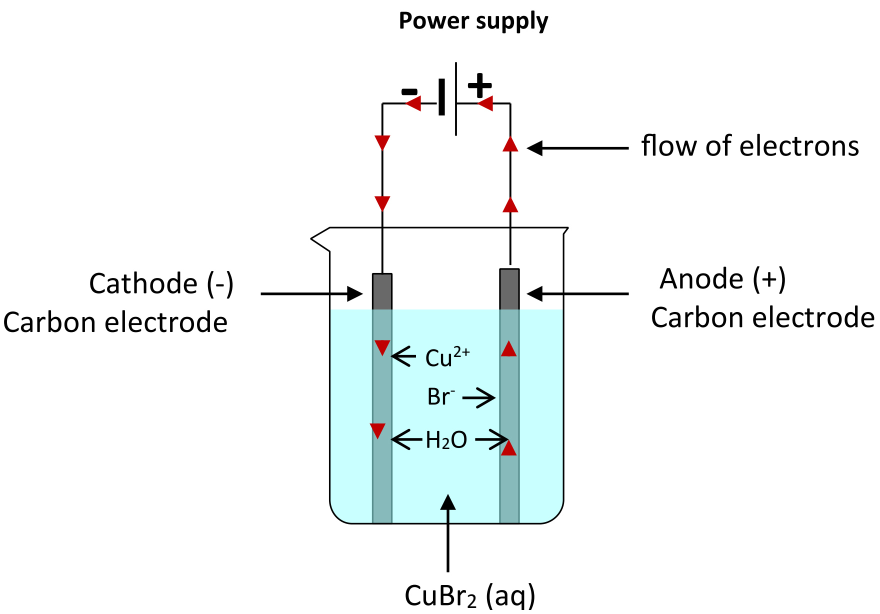
# Chapter 12 – Electrolysis

Electrolysis is a similar process to that going on in electrochemical cells in that it involves oxidation at an anode and reduction at a cathode. There are however, some major differences. **Electrolysis** is a process where **electrical energy** is used to force the oxidation of a reductant at an anode and the reduction of an oxidant at a cathode. Electrolysis can force redox reactions to occur where the reductant is above the oxidant on the electrochemical series table. Recall that for a spontaneous reaction to occur, the reductant must be below the oxidant. Electrolysis uses electrical energy to make non-spontaneous reactions happen.

**Energy transformation in a galvanic cell:** Chemical Energy → Electrical Energy
**Energy transformation in an electrolysis cell:** Electrical Energy → Chemical Energy

The best way to understand how electrolysis works is to look at a simple **electrolysis** or **electrolytic cell.**

**Electrolytic cell**



**Cathode (-) half equation**
$Cu^{2+}$ (aq) + $2e^-$ → Cu (s)

**Anode (+) half equation**
$2Br^-$ (aq) → $Br_2$(l) + $2e^-$

**Full equation**
$Cu^{2+}$ (aq) + $2Br^-$ (aq) → Cu (s) + $Br_2$ (l)

This simple electrolysis cell contains a solution of $CuBr_2$. Immersed in this solution are 2 inert carbon electrodes. One electrode is connected to the negative (-) terminal of a power supply and the other one is connected to the positive (+) terminal of the same power supply. This is the most fundamental difference between electrolysis and electrochemical cells. There is no power supply in electrochemical cells.

The chemical species present in this solution are $Cu^{2+}$, $Br^-$ and $H_2O$. The strongest reductant is $Br^-$ and the strongest oxidant is $Cu^{2+}$. On the electrochemical chemical series table $Br^-$ is above $Cu^{2+}$ so no spontaneous reaction is expected to occur at standard laboratory conditions.

| | | |
|---|---|---|
| | $H_2O_2$ (aq) + $2H^+$ (aq) + $2e^-$ ⇌ $2H_2O$ (l) | |
| | $Au^+$ (aq) + $e^-$ ⇌ Au (s) | |
| | $Cl_2$ (g) +$2e^-$ ⇌ $2Cl^-$ (aq) | |
| | $O_2$ (g) + $4H^+$ (aq) + $4e^-$ ⇌ $2H_2O$ (l) | |
| | $Br_2$ (l) + $2e^-$ ⇌ **$Br^-$ (aq)** ← | Strongest reductant |
| | $Ag^+$ (aq) + $e^-$ ⇌ Ag (s) | |
| | $Fe^{3+}$ (aq) + $e^-$ ⇌ $Fe^{2+}$ | |
| | $O_2$ (g) +$2H^+$ (aq) +$2e^-$ ⇌ $H_2O_2$ (aq) | |
| | $I_2$ (l) + $2e^-$ ⇌ $2I^-$ (aq) | |
| | $O_2$ (g) +$2H_2O$ (l) +$4e^-$ ⇌ $4OH^-$ (aq) | |
| Strongest oxidant → | **$Cu^{2+}$ (aq)** + $2e^-$ ⇌ Cu (s) | |

When the power supply is turned on, electrons come out of the negative terminal and pass through the wire and into the electrode. Since electrons are passing through this electrode, it would make sense that a chemical in the solution could gain these electrons and undergo reduction. So the 2 oxidants in the solution, $Cu^{2+}$ and $H_2O$ are attracted to the electrode connected to the negative terminal. It is only the $cu^{2+}$ however, that will gain the electrons and undergo reduction as it is the stronger oxidant.

$Cu^{2+}$ (aq) + $2e^-$ → Cu (s)

This electrode is the cathode as reduction is occurring on its surface. It is given a **negative polarity** because it is connected to the negative of the power supply. Recall that the cathode in electrochemical cells is positive.

The other electrode is connected to the positive terminal of the power supply which forces oxidation to occur on its surface. The reductants from the solution, $Br^-$ and $H_2O$ are attracted to the positive electrode but it is only the stronger reductant, $Br^-$, that is oxidised there.

$2Br^-$ (aq) → $Br_2$ (l) + $2e^-$

<u>So the power supply has forced the strongest oxidant, $Cu^{2+}$ to be reduced at the negative electrode and the strongest reductant, $Br^-$ to be oxidised at the positive terminal.</u> As the $Br^-$ reductant is above the $Cu^{2+}$ oxidant, the redox reaction cannot happen spontaneously. It can only happen if electrical energy is passed through the solution.

Unlike electrochemical cells, there is no salt bridge required in electrolytic cells. This is because the reduction and oxidation reactions occur in the same container and as a consequence the products of the reactions balance out each other's charges. Let's use the above cell as an example. When the $Cu^{2+}$ ions undergo reduction they become Cu atoms which deposit onto the surface of the inert electrode. This has the potential to cause the beaker to accumulate a negative charge because every time a $Cu^{2+}$ ion is reduced, $2Br^-$ ions no longer have their negative charge balanced out. This does not happen however because at the same time at the anode, $2Br^-$ ions are reduced into $Br_2$. So every time the cathode removes a +2 charge when the $Cu^{2+}$ ions are reduced, the anode balances this out by removing a -2 charge when $2Br^-$ ions are oxdised into $Br_2$. As a consequence there is no need for a salt bridge to add anions or cations to keep the charge in the solution neutral. *If the electrolyte accumulates a charge (- or +) in either electrochemical or galvanic cells, there will be no flow of electricity.*

**Steps for determining anode and cathode reactions in electrolysis**

**1.** Work out which electrode is the anode and the cathode. The electrode connected at the negative terminal of the power supply is always the cathode. The electrode connected at the positive of the power supply is always the anode.

**2.** Use the electrochemical series table to determine which chemical species is the strongest oxidant and which chemical species is the strongest reductant.

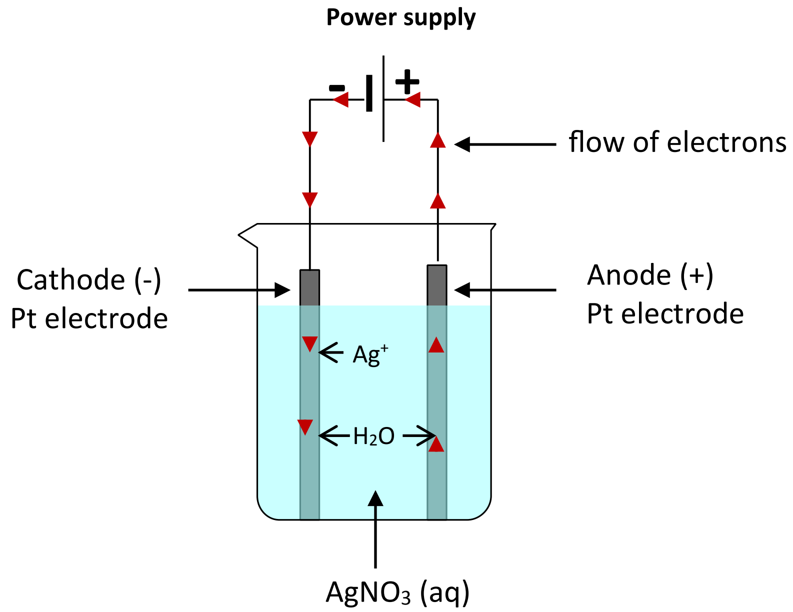
**3.** From the table, write out the half equations for the reduction of the strongest oxidant at the cathode and the oxidation of the strongest reductant at the anode.

## Worked Example 1

Give the electrode equations for the electrolysis of a 1.0 M solution of $AgNO_3$. The electrodes are made from platinum (Pt).

## Worked Example 1 Solutions

*It is helpful to draw the cell out.*



**Anode half equation:** $2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$
**Cathode half equation:** $Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$

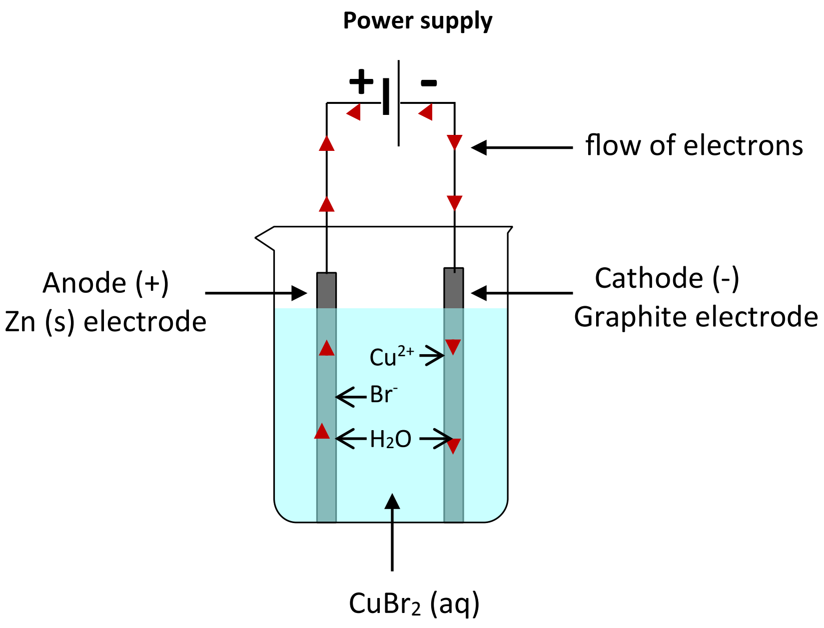
*The cathode (-) is always the electrode connected to the negative terminal of the power supply. There are 2 oxidants in this beaker, $Ag^+$ and $H_2O$. They will both be attracted to the cathode but it is only $Ag^+$ that will be reduced at the cathode because it is the stronger oxidant. $H_2O$ is the only reductant present in this beaker so it will be oxidised at the anode.*

- *Remember that $NO_3^-$ and $SO_4^{2-}$ do not appear on the electrochemical series table so they can be ignored.*

## Reactive electrodes

The electrolytic cells looked at so far have used inert electrodes made from either graphite (C) or platinum (Pt). It is possible to have electrodes from metals that are reactive. That is, metals that appear on the electrochemical series table. The approach to working out the anode and cathode reactions is the same as when inert electrodes are used. The only difference is that the electrode connected at the anode will be oxidised if it is the strongest reductant present.

The cell on the next page shows the electrolysis of a $CuBr_2$ (aq) solution using a zinc (Zn) electrode at the anode and a graphite electrode at the cathode.



**Anode (+) half equation**
$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^-$

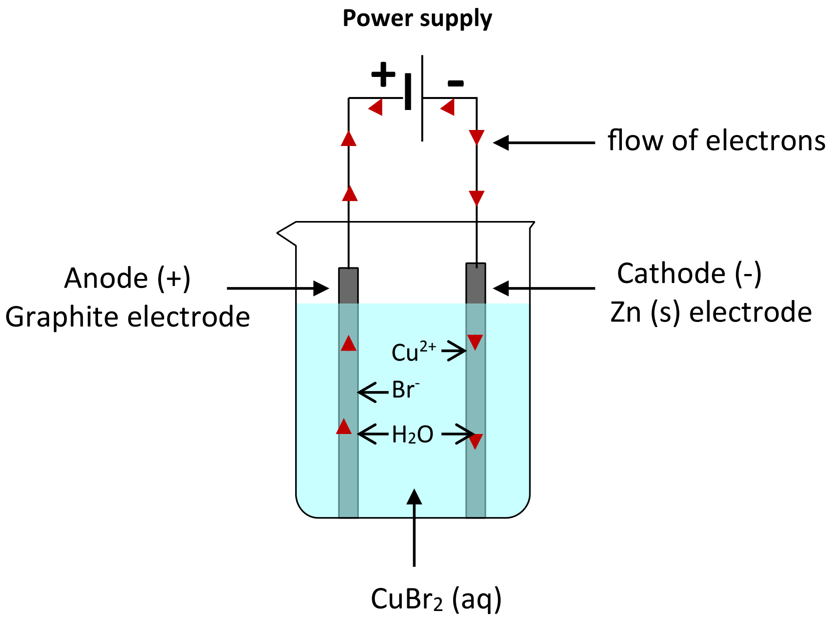
**Cathode (-) half equation**
$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ \ (s)$

**Full equation**
$Cu^{2+}\ (aq) + Zn\ (s) \rightarrow Cu\ (s) + Zn^{2+}\ (aq)$

There are 3 reductants in this beaker, $H_2O$ (l), $Br^-$ (aq) and the Zn (s) electrode. Zn (s) is the lowest reductant on the electrochemical series table so it is the strongest and will be oxidised.

There are 2 oxidants in this beaker, $Cu^{2+}$ (aq) and $H_2O$l (l). $Cu^{2+}$ (aq) will be reduced at the cathode because it is the stronger oxidant.

The cell on the next page is almost identical to the one that was just investigated. The only difference is that the electrodes have been swapped around. Now the Zn (s) is connected to the negative electrode and the graphite is connected to the positive electrode.



**Anode (+) half equation**
$2Br^- (aq) \rightarrow Br_2 (l) + 2e^-$

**Cathode (+) half equation**
$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$

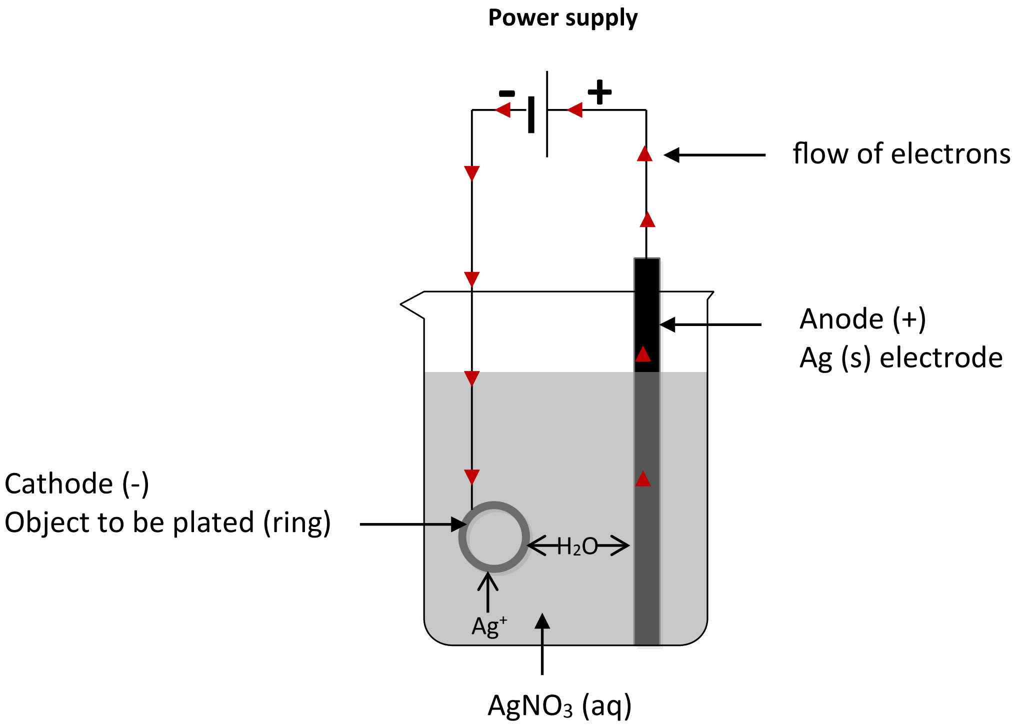
**Full equation**
$Cu^{2+} (aq) + 2Br^- (aq) \rightarrow Cu (s) + Br_2 (l)$

Notice how the anode and cathode equations are identical to those at the start of the chapter where the $CuBr_2$ was electrolysed using inert carbon electrodes. The Zn (s) may be the strongest reductant present in the beaker but it is incapable of undergoing oxidation when connected to the negative electrode. Remember that with electrolysis it is the power supply that forces oxidation to occur at the positive electrode and reduction at the negative electrode. As long as the Zn (s) is connected at the negative electrode it will never be oxidised. Instead electrons from the negative terminal of the power supply will pass through the Zn electrode and the strongest oxidant present in the solution, $Cu^{2+}$, will gain the electrons and undergo reduction on the surface of the Zn electrode. When attached to the negative terminal of the power supply, the Zn acts like an inert electrode allowing electrons to flow through it. An electrode made from a reductant metal such as Zn can only be oxidised if it is connected to the positive terminal of the power supply. As the Zn is unable to be oxidised at the anode, the next strongest reductant in the beaker, $Br^-$, will be oxidised at the anode.

# Electroplating

**Electroplating** or **metal plating** is a process where electrolysis is used to coat a metal onto the surface of a different metal. This is how gold plated and silver plated jewellery is made. For example a ring made from a cheap metal such as tin can be coated with a thin layer of a more expensive metal such as gold or silver. As the ring contains only a fine coating of the expensive metal it is much cheaper than a ring made only from gold or silver. The diagram below shows an electroplating cell where silver metal is plated onto a ring.

**Silver plating cell**



**Cathode (-) half equation**
$Ag^+ (aq) + e^- \rightarrow Ag (s)$

**Anode (+) half equation**
$Ag (s) \rightarrow Ag^+ (aq) + e^-$

**Full equation**
$Ag^+ (aq) + Ag (s) \rightarrow Ag (s) + Ag^+ (aq)$

The object to be plated with a metal, in this case a ring must be attached to the negative of the power supply. That is, the object to be plated must be the cathode.

The electrolyte must contain the cation of the metal that is to be plated onto the surface of the object. Since the ring is to be plated with silver, the electrolyte must contain $Ag^+$ ions. The anode must be an electrode made from the metal that is to be plated onto the object. In this case the electrode must be silver.

When the power supply is turned on, electrons will flow into the ring attached at the negative terminal. The oxidants from the solution, $Ag^+$ and $H_2O$ will both be attracted to the electrode. Since $Ag^+$ is the stronger oxidant, it will gain the electrons from the surface of the ring and undergo reduction to form Ag solid.

$Ag^+ (aq) + e^- \rightarrow Ag (s)$

The Ag (s) will deposit onto the surface of the ring and form a thin layer of silver. This is the reason why the object to be plated must be attached to the negative of the power supply. The cation of the metal to be plated onto the object will only be reduced into solid metal at a cathode. Therefore the object to be plated must be attached at the cathode.

The Ag (s) at the anode (+) is the strongest reductant in the beaker. It will undergo oxidation and form $Ag^+$ ions.

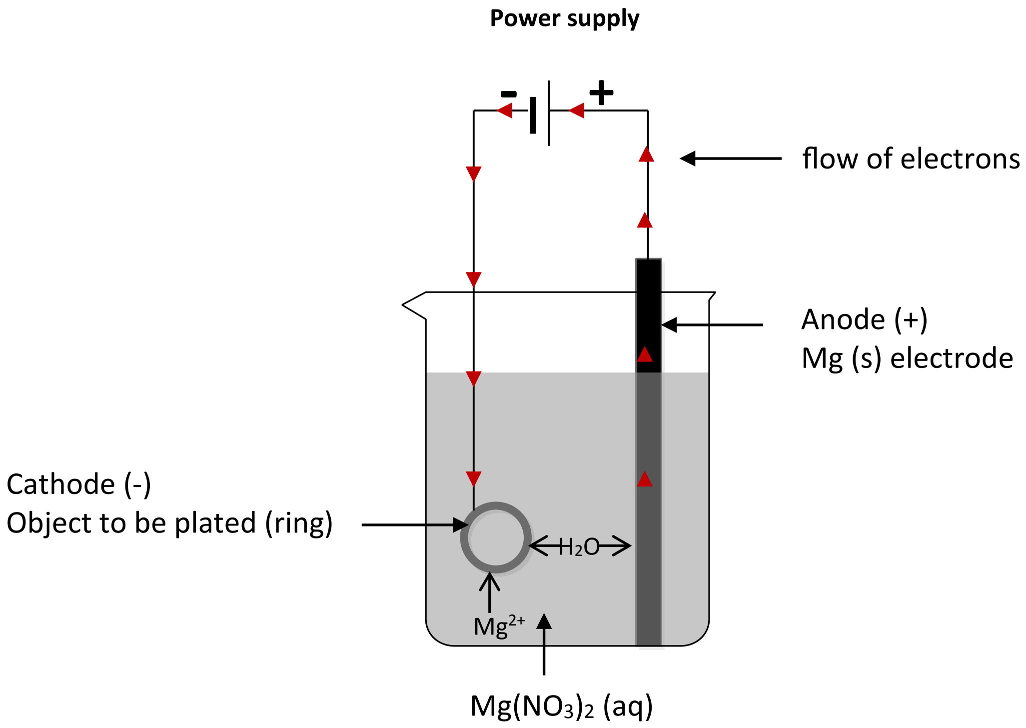
$Ag (s) \rightarrow Ag^+ (aq) + e^-$

When electroplating is performed, the conditions that will produce a smooth and permanent coating of metal on the object are very specific and vary depending on the metal that is to be produced. Some of these conditions include temperature, voltage, current and electrolyte concentration. The concentration of the electrolyte is able to be maintained at the optimum level if the anode contains the same metal as the cations in the electrolyte. With this silver plating cell, every time an $Ag^+$ ion is removed by reduction at the cathode, an Ag atom is oxidised into an $Ag^+$ ion at the anode. So the oxidation of Ag at the anode replaces the $Ag^+$ ions that are lost by the reduction reaction at the cathode. As a consequence the concentration of $Ag^+$ and hence $AgNO_3$ will remain constant while the cell is in operation. This ensures that the concentration of the electrolyte will be maintained at the level required for the smoothest and most permanent coating of metal.

**Summary of electroplating**

- The object to be plated with metal must be attached to the negative of the power supply. That is, it must be the cathode.
- The cation of the metal to be plated onto the object must be present in the electrolyte.
- The anode must be made from the same metal as the metal that is to be plated onto the object.
- The concentration of the electrolyte remains constant during the operation of an electroplating cell.
- The object to be plated must be a metal or some other material that allows electrons to pass through it (an electrical conductor).

Not all metals can be coated onto the surface of an object through the electrolysis of an aqueous solution of the metal cation. It works for Ag but it doesn't work for all metals. Consider the cell below which has been set up to coat a ring with a layer of Mg metal.



**Cathode (-) half equation**
$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$

**Anode (+) half equation**
$Mg (s) \rightarrow Mg^{2+} (aq) + 2e^-$

**Full equation**
$Mg (s) + 2H_2O (l) \rightarrow Mg^{2+} (aq) + H_2 (g) + 2OH^- (aq)$

This cell seems to be following correctly all the rules for electroplating. The electrolyte contains $Mg^{2+}$which is the cation of the metal to be plated onto the object. The anode is made from Mg, which is the metal that is to be plated onto the object. The reaction at the cathode however, produces $H_2$ (g) and $OH^-$ (aq) instead of Mg metal. This is because $H_2O$ (l) is a stronger oxidant than $Mg^{2+}$ (aq) as can be seen on the electrochemical series table where $H_2O$ (l) is higher than $Mg^{2+}$ (aq). As a consequence $H_2O$ is reduced at the cathode in preference to $Mg^{2+}$ ions. Instead of Mg metal being deposited onto the surface of the ring, there will be $OH^-$ ions and $H_2$ gas bubbles forming around the ring.

Metals whose cations are beneath $H_2O$ on the electrochemical series table cannot be produced from the electrolysis of an aqueous solution of the cation. These metals include **Li, K, Ca, Na, Mg, Al and Mn.**

| |
|---|
| $2H_2O$ (l) + $2e^-$ $\rightleftharpoons$ $H_2$ (g) + $2OH^-$ (aq) |
| $Mn^{2+}$ (aq) + $2e^-$ $\rightleftharpoons$ Mn (s) |
| $Al^{3+}$ (aq) + $3e^-$ $\rightleftharpoons$ Al (s) |
| $Mg^{2+}$ (aq) + $2e^-$ $\rightleftharpoons$ Mg (s) |
| $Na^+$ (aq) + $e^-$ $\rightleftharpoons$ Na (s) |
| $Ca^{2+}$ (aq) + $2e^-$ $\rightleftharpoons$ Ca (s) |
| $K^+$ (aq) + $e^-$ $\rightleftharpoons$ K (s) |
| $Li^+$ (aq) + $e^-$ $\rightleftharpoons$ Li (s) |

- Any metal cation that is under $H_2O$ on the electrochemical series table cannot be reduced into a solid metal at a cathode. This is because $H_2O$ is a stronger oxidant and will be preferentially reduced at a cathode.

It is possible to reduce these cations into solid metals if they are in molten (melted into a liquid) form or dissolved in a solvent other than water.

For example, if the cell on the previous page contained $Mg(NO_3)_2$ (l) instead of $Mg(NO_3)_2$ (aq), there would be no water present in the cell. Now the only oxidant present in the electrolyte is $Mg^{2+}$ which can undergo reduction at the cathode without any interference from water. Producing metals through the electrolysis of a molten electrolyte can be very costly as it can take a lot of heat energy to melt ionic compounds containing metal cations. For example, the melting temperature of aluminium oxide is over 2,000 $^0$C. A lot of energy is required to maintain the cell operating conditions at such a high temperature.

# COMPARING ELECTROCHEMICAL & ELECTROLYSIS CELLS

| Electrochemical | Electrolysis |
|---|---|
| Convert chemical energy to electrical | Convert electrical energy to chemical |
| Not connected to a power supply (they are a power supply) | Connected to a power supply |
| Reactions are spontaneous and produce electrical energy | Reactions are non-spontaneous and need to absorb electrical energy |
| Oxidation occurs at the anode (-) | Oxidation occurs at the anode (+) |
| Reduction occurs at the cathode (+) | Reduction occurs at the cathode (-) |
| Anode has a negative (-) polarity | Anode has a positive (+) polarity |
| Cathode has a positive (+) polarity | Cathode has a negative (-) polarity |
| Electrons flow from anode (-) to cathode (+) through the external circuit | Electrons flow from anode (+) to cathode (-) through the external circuit |
| Electrons flow from – to + through the external circuit | Electrons flow from + to – through the external circuit |
| Needs a salt bridge | Does not need a salt bridge |
| Produce electricity | Produce chemicals |

- The process of recharging covered in chapter 11 is an application of electrolysis.

# Calculations in electrochemistry

**Electrochemistry** is a broad term which includes both electrochemical and electrolytic cells. The calculations of masses, moles, concentrations etc. that we have become familiar with in VCE chemistry can all be applied to electrochemistry. Not surprisingly, many calculations in electrochemistry revolve around the electrons passing through either an electrolysis or galvanic cell.

A **Faraday** is the charge in coulomb (c), carried by 1.0 mole of electrons. Coulombs are the units used to measure the negative charge carried by electrons. 1.0 mol of electrons carries 96,500 coulombs of charge. This can be expressed as 96,500 c $mol^{-1}$.

**1 Faraday or 1 F =** 96,500 c $mol^{-1}$ *This value is provided on page 5 of the end of year exam data book.*

As 1 F is the charge carried by 1.0 mol of electrons, it is must be true that the number of moles of electrons passing through a cell is equal to the number of faradays passing through that cell. That is, 1 F = 1 mol of electrons, 2 F = 2 mol of electrons etc.

If 1.0 mol of electrons carries a charge of 96,500 c and 1.0 mol of electrons is equal to $6.02 \times 10^{23}$ electrons, then the charge carried by just one single electron is:

$6.02 \times 10^{23}$ electrons → 96,500 c
1.0 electron → **X**

$\mathbf{X} \times 6.02 \times 10^{23} = 96{,}500 \times 1.0$

$$\mathbf{X} = \frac{96{,}500 \times 1.0}{6.02 \times 10^{23}} = 1.6 \times 10^{-19} \text{ c}$$

**Charge carried by one electron =** $-1.6 \times 10^{-19}$ c *This value is provided on page 5 of the end of year exam data book.*

If 1.0 mole of electrons carries a charge of 96,500 c, then the charge carried by any number of moles of electrons can be calculated by:

**$Q = n(e^-) \times 96{,}500$** *Q = charge in coulomb.*

If a current of electricity measured in amps passes through an electrolytic or galvanic cell in a given amount of time, the charge in coulomb of the electrons passing through the cell can be calculated by:

**$Q = I \times t$**

*Q = charge in coulomb*
*I = current measured in amps (A)*
*t = time measured in seconds (s)*

**$E = Q \times V$**

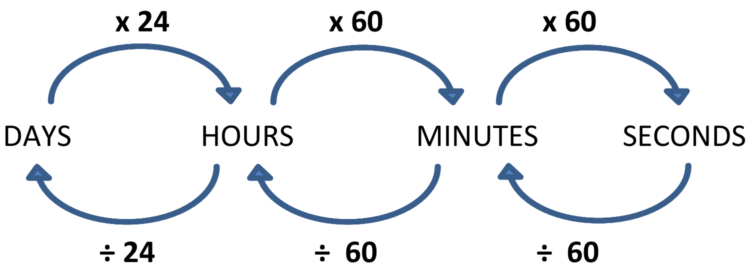
*E = energy in joule (J)*
*Q = charge in coulomb*
*V = measured in volts*

This equation is produced by combining the equation $Q = I \times t$ with the equation $E = V \times I \times t$ which will be encountered in chapter 14 of Unit 4 Chemistry Tutor.

$E = V \times (\underset{\substack{\uparrow \\ Q\ (Q = I \times t)}}{I \times t})$ Therefore $E = V \times Q$

- *These formulas used for calculations in electrochemistry are often referred to **as Faraday's Laws.***

When doing calculations in electrochemistry it is important to be able to convert between different units of time.



## Worked Example 2

A copper plating cell has been operating for 30.0 minutes. If a current of 4.98 A has passed through the cell, what would be the predicted mass of copper coated onto the surface of the object connected at the cathode?

## Worked Example 2 solutions

*Write out the half equation from the electrochemical series table showing the reduction of $Cu^{2+}$ (aq) into Cu (s).*

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

*We need to use stoichiometry to calculate the mass of Cu deposited at the cathode. Before we can do that we need to calculate the moles of the electrons that passed through the cell.*

Q = I x t
= 4.98 x( 30.0 x 60) *multiply by 60 to convert minutes into seconds.*
= 8,964 c

Q = n($e^-$) x 96,500

$$n\,(e^-) = \frac{Q}{96{,}500}$$

$$= \frac{8{,}964}{96{,}500} = 0.092891 \text{ mol}$$

n (Cu) = 0.092891 x ½ = 0.0464455 mol
*The mole ratio in a balanced equation can be applied to electrons.*

m (Cu) = 0.0464455 x 63.5 = 2.949289 = 2.95 g

## Worked Example 3

How many Faradays of charge are required to produce 2.0 mol of $Cl_2$ gas from the electrolysis of molten sodium chloride?

## Worked Example 3 Solutions

*The number of Faradays of charge required is equal to the number of moles of electrons required to produce 2.0 mol of $Cl_2$ gas. The molten sodium chloride has $Cl^-$ ions that can be oxidised into $Cl_2$ gas. The half equation for this reaction is on the electrochemical series table.*

$2Cl^- (l) \rightarrow Cl_2 (g) + 2e^-$

*According to the ratio in the equation,*

n ($e^-$) = n ($Cl_2$) x 2
= 2.0 x 2 = 4.0 mol

*Therefore 4.0 Faraday's of charge are required.*

## Worked Example 4

11.738 g of Ni is collected at the cathode of an electrolysis cell. 10.74 A of current passed through this cell for a time of 3,589 seconds.

**a.** Use the data provided to calculate a value for Faraday's constant.
**b.** Use the data provided to calculate a value for Avogadro's constant.

## Worked Example 4 Solutions

**a.** *At first impression this question can seem very obscure. A good strategy is to just use the data in any way that you can.*

*You have been given the mass of Ni so a good start would be to calculate the moles of the Ni.*

$$\text{n (Ni)} = \frac{11.738}{58.7} = 0.19997 \text{ mol}$$

*From this you can work out the moles of electrons that passed through the cell.*

$Ni^{2+} (aq) + 2e^{-} \rightarrow Ni (s)$

$\text{n} (e^{-}) = 0.19997 \times 2 = 0.39994$ mol

*We have the current in amps and the time in seconds so we can work out the charge in coulomb that passed through the cell.*

$Q = I \times t$

$= 10.74 \times 3{,}589 = 38{,}545.86$ c

*The temptation is to divide this Q value by 96,500 to work out the moles of electrons. This can't be done as the question requires us to work out Faraday's constant. You have to pretend that you don't know its value of 96,500 c! The only acceptable way to work out the moles of the electrons is to use the moles of Ni. This has already been done.*

*We have calculated all that we can with the data provided in the question. Now we have to link the moles of electrons and charge that have just been calculated.*

*The calculations tell us that* 0.39994 *mol of electrons carries 38,545.86 c of charge. So to find Faraday's number we have to calculate the charge of 1.0 mol of electrons. This can be done by cross multiplying:*

0.39994 mol of electrons → 38,545.86 c
1.0 electron → **X c**

$\mathbf{X} \times 0.39994 = 38{,}545.86 \times 1.0$

$$\mathbf{X} = \frac{38{,}545.86 \times 1.0}{0.39994} = 96{,}379.11 = 9.638 \times 10^{4} \text{ c mol}^{-1}$$

*The alternative way to work this out is to the use the formula*

*$Q = n (e^{-}) \times 96{,}500$*

*Make 96,500 the unknown (F). Remember we are trying to find Faraday's constant (F)*

$Q = n(e^-) \times F$

$$F = \frac{Q}{n\,(e^-)} = \frac{38{,}545.86}{0.39994} = 96{,}379.11 = 9.638 \times 10^4 \text{ c mol}^{-1}$$

**b.** *The value of Faraday's constant, $9.638 \times 10^4$ c mol$^{-1}$ is the charge of one mole of electrons. If this value is divided by the charge of just one electron, the answer obtained will be the number of electrons in 1.0 mol which is Avogadro's number.*

$$\frac{96{,}379.11}{1.6 \times 10^{-19}} = 6.02369 \times 10^{23} = 6.0 \times 10^{23}$$

Or use cross multiplying.

96,379.11c → **X** number of electrons
1.6 x $10^{-19}$ c → 1.0 electron

**X** x 1.6 x $10^{-19}$ = 96,379.11x 1.0

$$\mathbf{X} = \frac{96{,}379.11 \times 1.0}{1.6 \times 10^{-19}} = 6.02356 \times 10^{23} = 6.0 \times 10^{23}$$

## Worked Example 5

During the electrolysis of an aqueous solution, 0.00063367 mol of a metal is deposited at the cathode. What is the oxidation state of the cation of this metal in the electrolyte if 1.019 amps of electricity passes through this cell for a time of 180 seconds?

## Worked Example 5 Solutions

*No formula was given for this metal so let's just call it "M". A general equation showing the reduction of any metal cation into a solid metal can be expressed as:*

$M^{x+}(aq) + xe^- \rightarrow M(s)$

*The charge of the cation and the number of electrons that the cation needs to gain to become a metal are both represented by "x". This is because they have the same value. For example, if a cation has a charge of +1 (eg. $Na^+$) it must gain 1 $e^-$ in order to become a solid metal:*

$Na^+(aq) + e^- \rightarrow Na(s)$

*In order to calculate the oxidation state (charge) of the metal cation a mole ratio between the electrons and the metal or metal cation needs to be established.*

*Q = I x t*

*= 1.019 x 180 = 183.42 c*

$Q = n(e^-) \times 96{,}500$

$n(e^-) = \dfrac{Q}{96{,}500}$

$= \dfrac{183.42}{96{,}500} = 0.001901$ mol

$M^{x+}(aq) + xe^- \rightarrow M(s)$

0.0019 01mol : 0.00063367 mol

*Ratio* 3 : 1

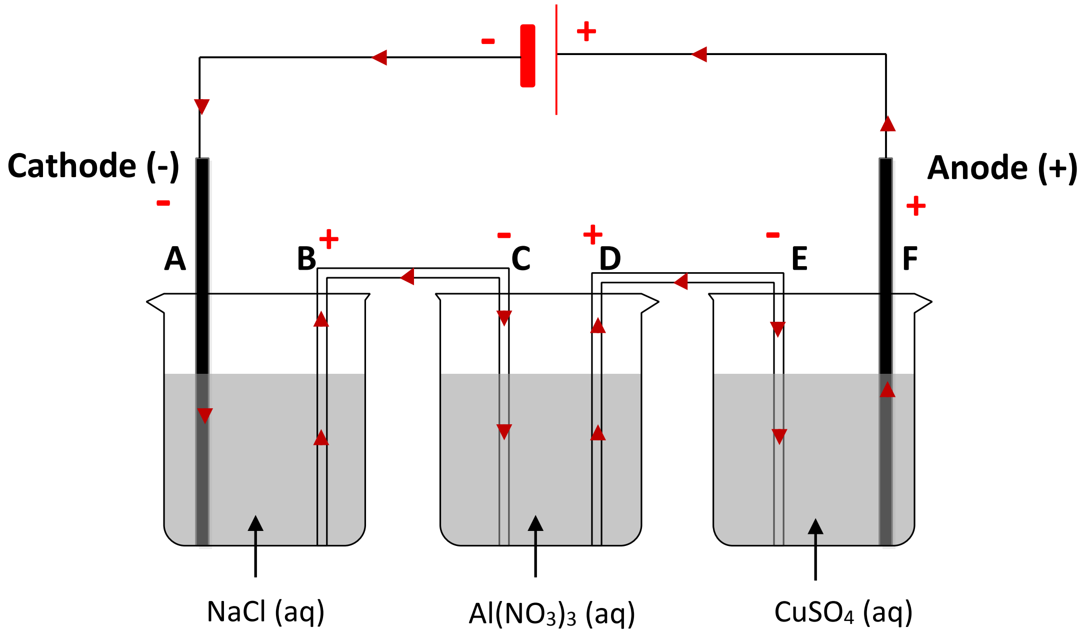
*This ratio was found by dividing the moles of M into itself and then into the moles of the electrons.*

*Now the half equation can be written as*

$M^{3+}(aq) + 3e^- \rightarrow M(s)$

## Electrolysis cells in series

The term **electrolysis cells in series,** refers to when 2 or more electrolysis cells are connected to the same power supply. Adjacent cells are also connected to each other. The set up below shows 3 electrolysis cells connected in series.



It appears as though 2 salt bridges are linking these beakers together. This is not the case as this is electrolysis. They are inert platinum wires. The parts of these wires immersed in the solutions are electrodes. All of the electrodes are made from platinimum and they have been labeled A to F. Each electrolyte has a temperature of 25 $^0$C and a concentration of 1.0 M

**Electrode A** is directly connected to the negative of the power supply and is therefore a cathode. The oxidants in the beaker are $Na^+$ and $H_2O$. $H_2O$ will be reduced on the surface of electrode A as it is the stronger oxidant.

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Since reduction is occurring at electrode A, **Electrode B** must be an anode as electrons are moving away from it. The strongest reductant $H_2O$ (l), is oxidised at this electrode. The electrons lost by the $H_2O$ molecules are pushed through the wire.

$2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$

The electrons move into **Electrode C** in the next beaker. These electrons are moving into the electrolyte so this electrode is a cathode and the strongest oxidant, $H_2O$ (l), will be reduced at its surface.

$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$

At **Electrode D**, electrons move out of the beaker so this electrode is an anode. The strongest reductant, $H_2O$ (l), will be oxidised at this electrode.

$2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$

The electrons given away by the oxidation of the water will now enter the last beaker through **Electrode E.** This electrode is a cathode and the strongest oxidant in this beaker, $Cu^{2+}$, will be reduced at this electrode.

$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$

At **Electrode F,** electrons will move back into the positive of the power supply so this electrode is an anode. The strongest reductant in this beaker is $H_2O$ (l) and it will be oxidised at this electrode.

$2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$

❖ It is very easy to work out which electrodes are cathodes and which are anodes when electrolysis cells are connected in series. When starting from the left, electrode A is directly attached to the negative of the power supply so it must be a cathode. So the next electrode B, must be an anode, C must be a cathode, D must be an anode, E must be a cathode and F must be an anode. The electrodes will always alternate from cathode to anode when moving through the cells. <u>Electrons will move out of a beaker through an anode and into a beaker through a cathode.</u>

# CHAPTER 12 REVIEW QUESTIONS

## Multiple Choice

**Question 1**
During the electrolysis of 100 mL of distilled water, the gases produced at the negative and positive electrodes are respectively

**A.** oxygen and hydrogen
**B.** hydrogen and oxygen
**C.** oxygen and oxygen
**D.** hydrogen and hydrogen

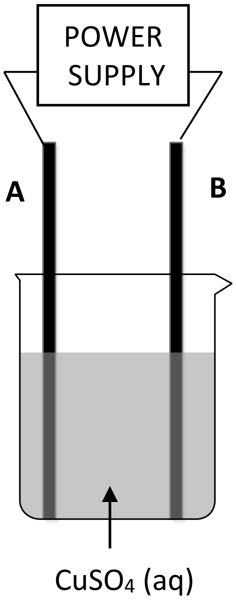
**Question 2**
When comparing electrolysis and galvanic cells it is correct to say that

**A.** oxidation occurs at the negative electrode in both types of cells.
**B.** oxidants migrate to the cathode in both types of cells.
**C.** oxidation occurs at the positive electrode only in galvanic cells.
**D.** in electrolysis cells reduction occurs at the anode.

**Question 3**
The electrolysis of a 1.0 M solution of NaCl will produce the same products at the anode and cathode as the electrolysis of

**A.** distilled water and 1.0 M $Fe(NO_3)_2$
**B.** 1.0 M $HNO_3$
**C.** 1.0 M $CuSO_4$
**D.** 1.0 M $Al(NO_3)_3$

**Question 4**
Consider the electrolysis cell below.

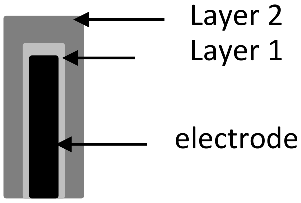


After this cell has been operating for about 30 minutes the mass of electrode B has increased and the concentration of the $CuSO_4$ in the electrolyte has decreased. Which of the statements regarding this cell is correct?

**A.** Electrode A is made from graphite and electrode B is connected to the negative terminal of the power supply.
**B.** Electrodes A and B are both made from copper.
**C.** Electrode B is connected to the positive terminal of the power supply and electrode A is made from platinum.
**D.** Electrode B is connected to the positive terminal of the power supply and electrode A is connected to the negative terminal of the power supply.

*Questions 5 and 6 refer to the following information.*

A solution containing 3 different ionic compounds is electrolysed at standard conditions. After several hours of electrolysis the cathode is removed and analysis shows that 2 different layers of material have deposited on the cathode during this time. The cathode is shown below.



**Question 5**
The solution that was electrolysed could have been a mixture of

**A.** $KNO_3$ , NaCl and $Pb(NO_3)_2$
**B.** $Al(NO_3)_3$ , $KNO_3$ and $NaNO_3$
**C.** $Ni(NO_3)_2$, $AgNO_3$ and $Ca(NO_3)_2$
**D.** NaCl, $Mn(NO_3)_2$ and $Al(NO_3)_3$

**Question 6**
The composition of layers 1 and 2 could not be

| | **Layer 1** | **Layer 2** |
|---|---|---|
| **A.** | Ag | Cu |
| **B.** | Zn | Ag |
| **C.** | Co | Ag |
| **D.** | Al | Li |

**Question 7**
An iron nail is to be coated with zinc metal in order to protect it from corrosion. The zinc metal can be coated onto the surface of the nail using electrolysis. During this process

**A.** the iron nail is connected to the negative of the power supply where it is oxidised.
**B.** $Zn^{2+}$ ions migrate to the nail where they are oxidised into Zn (s)
**C.** an electrode of Zn (s) is oxidised at the positive electrode in order to maintain a constant electrolyte concentration.
**D.** the iron nail is attached at the positive electrode where it will act as a cathode.

**Question 8**
During the electrolysis of a dilute $MgCl_2$ solution, the ions and molecules that will migrate towards the negative electrode are

**A.** $Mg^{2+}$
**B.** $H_2O$
**C.** $Mg^{2+}$ and $H_2O$
**D.** $Mg^{2+}$, $Cl^-$ and $H_2O$

**Question 9**
Which of the following metals cannot be produced from the electrolysis of an aqueous solution containing its cation?

**A.** Cu
**B.** Al
**C.** Ag
**D.** Zn

## Short Answers

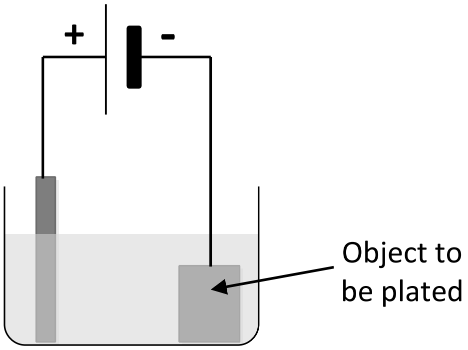
**Question 1**

Draw cells showing the electrolysis of the following solutions. Graphite electrodes are present in all cells. Your diagrams must be labelled and include the power supply, anode, cathode and the movement of electrons through the wires connecting the electrodes and power supply. You must include equations for the electrode reactions. States of matter must be shown.

**a.** distilled water
**b.** 1.0 M $KNO_3$
**c.** 1.0 M HBr

**Question 2**

The diagram below shows part of an electrolysis cell that is going to be used to plate copper onto the surface of an object. The object to be plated is connected at the negative electrode.



**a.** Give a suitable electrolyte for this cell.
**b.** From what material should the electrode connected to the positive terminal of the power supply be made from?
**c.** In reference to this cell, explain why electrolytic cells do not need a salt bridge.
**d.** In reference to this cell, explain why the concentration of the electrolyte remains constant during the operation of an electroplating cell.

**Question 3**

An electrolytic cell consists of a copper cathode and a platinum anode. The electrolyte is $Ni(NO_3)_2$ solution.

**a.** Give the electrode half equations for this cell.
**b.** If the electrolyte has a volume of 250.00 mL and a concentration of 1.00 M, calculate the concentration of the electrolyte after 2.00 A of electricity have passed through the cell for a time of 25.00 minutes.
**c.** Explain why the reaction occurring at the cathode may change after this cell has been operating for a long period of time.

**Question 4**

A cathode has 0.0962 mol of metal deposited onto its surface during the electrolysis of an aqueous solution of unknown identity. For a time of 25.0 minutes 12.36 A of electricity were passed through this cell.

**a.** Calculate the oxidation number of the cation dissolved in this electrolyte.
**b.** What is the identity of the metal deposited at the cathode if its mass increased by 5.0 g?

**Question 5**

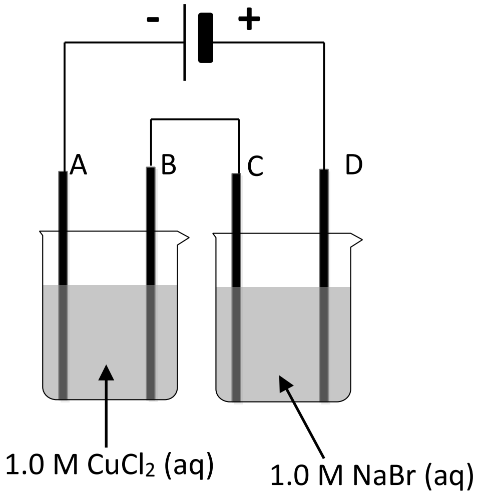
During an experiment to determine the value of Avogadro's number, 19,510.3 c of charge are passed through molten sodium chloride. The volume of $Cl_2$ gas collected at the anode at a temperature of 310 K and pressure of 1.5 atm is equal to 1.74 L.

**a.** Use the data provided to calculate Avogadro's number.

**b.** What error in the above experiment could cause a calculation of Avogadro's number to be higher than the true value? Explain your answer.

**Question 6**

The diagram below shows 2 electrolysis cells connected in series. All of the electrodes are made from platinum and the volume of each solution is 400.0 mL



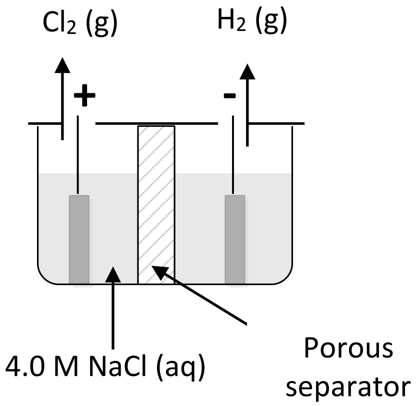
**a.** Give the half equations showing states, for the reactions occurring at electrodes A, B, C and D.

**b.** What mass of material will be deposited at electrode A if 0.025 mol of reductant has been oxidised at electrode D?

**c.** What current in amps, is needed in order to change the concentration of $Br^-$ ions to 0.75 M during a 2.0 hour period.

**Question 7**

Sodium hydroxide is produced industrially using the membrane cell which is shown below.



The electrode reactions are

**Anode**

$2Cl^- (aq) \rightarrow Cl_2 (g) + 2e^-$

**Cathode**

$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$

The electrolyte is first poured in at the positive electrode. Water and $Na^+$ ions are able to move through the separator and enter the negative electrode. $Cl^-$ ions are unable to pass through the separator.

**a.** Explain why the reaction at the anode is able to occur even though the electrochemical series table predicts that $H_2O$ should be oxidised in preference to $Cl^-$ ions.

**b.** Explain how sodium hydroxide is able to be produced at the negative electrode.

**c.** How does the porous separator help to ensure that the sodium hydroxide produced at the cathode is of high purity?

**d.** Why must the products at the 2 electrodes not be allowed to make contact with each other?

**e.** What current of electricity would be required to produce 2.0 tonnes of $Cl_2$ gas during a 24 hour period?

**f.** How many joules of electrical energy are required to produce 2.0 tonnes of sodium hydroxide? The voltage of the electricity is equal to 100.0 v.

# Appendix 1 – Significant Figures

Significant figures refer to the digits that make up a number. In chemistry, it is very important that we know the number of significant figures shown in numerical data. Numerical data refers to quantities that have been measured and expressed using specific units such as masses, volumes, temperatures etc. There are 4 major rules that will help you determine how many significant figures are present in a number:

**Rule 1 –** All non-zero digits such as 1, 2, 3 etc. in a number are significant.

*For example, the number 35 has 2 significant figures because the digits 3 and 5 are both non-zero digits.*

**Rule 2 –** Zeros between non-zero digits are significant.

*For example, 102 has 3 significant figures. The numbers 1 and 2 are significant as they are non-zero digits. The zero is a third significant figure as it is between the 2 non-zero digits, 1 and 2.*

**Rule 3 –** All zeros at the end of a number are significant.

*For example,*

*250 has 3 significant figures,*
*12.0 has 3 significant figures,*
*1000 has 4 significant figures.*

**Rule 4 –** Zeros at the start of a number are NOT SIGNIFICANT.

*For example,*

*0.025 has 2 significant figures,*
*0.10 has 2 significant figures,*
*0.002309 has 4 significant figures.*

- When a number is in scientific form the $10^{power}$ is not considered when determining the number of significant figures. This is because the $10^{power}$ part of the number just shows how many places the decimal point has moved either forwards or backwards when the number was converted into scientific form. For example, $2.1 \times 10^{-3}$ has 2 significant figures. Only the 2 and 1 are counted. So to convert $2.1 \times 10^{-3}$ back into a normal number, the decimal point is moved back 3 places to give a basic numeral of 0.0021 (2SF).

# Significant figures in chemistry calculations

When doing a calculation in chemistry involving either **MULTIPLICATION** or **DIVISION**, the final answer must be given the same number of significant figures as the piece of DATA containing the least number of significant figures. That is, the answer cannot be more precise than the least precise piece of data USED in the calculation. The more significant figures in a number the more precision the number has. For example 0.12 is a more precise number than 0.1.

0.1 shows 1/10
0.12 also shows 1/10 plus an extra 2/100. So 0.12 is a more precise/accurate number.

- **Data** refers to measurements such as masses, moles, volumes etc. that have been provided for a calculation. Only the data used in a calculation should be considered when deciding the number of significant figures in an answer. The numbers that our calculator crunches out when using the data are not considered. This will be explored further in a later example.

Here is an example of how significant figures are used when giving an answer to a calculation:

**Calculate the number of moles of atoms present in 1.8 g of iron. The temperature of the surrounding air is 25 $^{0}$C and the atmospheric pressure is 1 atm.**

m (Fe) = 1.8 g (2 SF)
Mr (Fe) = 55.8 (3 SF)

n (Fe) = $\frac{1.8}{55.8}$ = 0.032258065 mol = 0.032 mol

The mass of Fe, 1.8 g (2SF) is the piece of data used in the calculation containing the least number of significant figures. Therefore the answer should be rounded off to 2 significant figures, 0.032 mol.

- *Only data used in the calculation should be considered when deciding which piece of data contains the least number of significant figures. The temperature of 25 $^{0}$C and atmospheric pressure of 1 atm were not considered in the final rounding of the answer as these pieces of data <u>were not directly used in the calculation.</u> A common error with this type of question would be to round off the answer to 1 significant figure (0.03 g) due to the 1 significant figure present in the atmospheric pressure of 1 atm.*

If a calculation requires only **ADDITION** or **SUBTRACTION** the rules for rounding off are different to those involving multiplication and division. The final answer must have the same number of decimal places as the piece of data containing the least number of decimal places. Consider this example:

**Calculate the molar mass of $HNO_3$.**

M (H) = 1.0 gmol$^{-1}$
M (N) = 14.0 gmol$^{-1-}$
M (O) = 16.0 gmol$^{-1}$

**M ($HNO_3$) =** 1.0 + 14.0 + 16.0 x 3 = 63.0 gmol$^{-1}$

- *When molar masses are calculated for any question in the exam they should always be rounded off in the way just described.*

As the data was just added together, the final molar mass had to be expressed to one decimal place as all of the molar masses of the elements involved had one decimal place. So 63.0 has 1 decimal place but 3 significant figures. If this molar mass was to be used to calculate the moles of a mass of $HNO_3$, the 63.0 (3 SF) would be considered in the rounding off of the final answer, not the molar masses of the individual elements of H, N and O. Note that the "3" used to multiply the 16.0 was not considered at all in the rounding of the molar mass of $HNO_3$ as this number was not a piece of measured data as was the case with the molar masses.

Here is another example to consider:

**Calculate the moles of 25.0 g of $H_2CO_3$**

M (H) = 1.0 gmol$^{-1}$
M (C) = 12.0 gmol$^{-1}$
M (O) = 16.0 gmol$^{-1}$

M ($H_2CO_3$) = 2 x 1.0 + 12.0 + 16.0 x 3 = 62.0 gmol$^{-1}$

n ($H_2CO_3$) = $\frac{25.0}{62.0}$ = 0.40323 = 0.403 mol

The final molar mass of $H_2CO_3$ was given as 62.0 gmol$^{-1}$ as all the individual molar masses of the H, C and O contained 1 decimal place. This molar mass of 62.0 gmol$^{-1}$ contains 3 significant figures and is a piece of data that needs to be considered when calculating the moles of $H_2CO_3$. The 2 pieces of data used to calculate the moles of $H_2CO_3$, 62.0 gmol$^{-1}$ and 25.0 g, both contain 3 significant figures. Therefore the calculated moles must be rounded off to 3 significant figures, 0.403 mol.

- *A common error with this type of calculation is to use the molar mass of H, 1.0 gmol$^{-1}$, as the piece of data containing the least number of significant figures and rounding off the moles of $H_2CO_3$ to just 2 significant figures, 0.40. It is important to remember that it is the sum (added* *together) of the molar masses, not the individual molar masses of the elements that must be considered in the rounding off of the calculated moles of a compound.*

It is very common for exam questions to involve the use of 2 or more calculations in order to get to the final answer of the question. When doing these types of questions, it is important not to use a rounded answer from one calculation for subsequent calculations, otherwise the final answer may be slightly off the correct answer. This is known as a rounding error.

Consider the following example:

**57.0 g of hydrogen gas reacts completely with excess oxygen according to the following equation:**

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$

**a.** **Calculate the moles of hydrogen present.**
**b.** **Calculate the mass of oxygen that reacted.**
**c.** **Calculate the mass of water produced.**

**a.** $n\,(H_2) = \frac{57.0}{2.0} = 28.5 = 29$ mol

*This answer is rounded off to 2 significant figures as the Mr of $H_2$, 2.0, was the least precise piece of data with 2 significant figures.*

*This answer to part **a** will be required for the calculation in part **b.** The UNROUNDED ANSWER of 28.5 should be used for part **b**, not the rounded answer of 29 mol.*

**b.** $n\,(O_2) = ½ \times 28.5 = 14.25$ mol
$m\,(O_2) = 14.25 \times 32.0 = 456 = 4.6 \times 10^2$ g

*A point of confusion with part **b** is that the mass of $O_2$ was rounded to $4.6 \times 10^2$ g (2 SF) yet none of the numbers used in the calculation, 28.5 (3 SF), 14.25 (4 SF) and 32.0 (3 SF) contained 2 significant figures. Recall that it is only DATA that is considered in the final rounding of answers. 28.5 mol was not data but rather was the answer to part **a** that was obtained from data: mass of $H_2$ = 57.0 g and the Mr ( $H_2$) = 2.0. The moles of $O_2$ was obtained from 28.5 mol of $H_2$ which was derived from the Mr of $H_2$ (2.0), which with 2 significant figures was the least precise piece of data in the calculation. So the mass of $O_2$ was rounded off to 2 significant figures.*

❖ *A piece of data may not have been used directly in a calculation but if it was used to derive a value that took part in the calculation, then the number of significant figures in this piece of data must be considered in the rounding of the answer.*

**c.** $n(H_2O) = 28.5$ mol
$m(H_2O) = 28.5 \times 18.0 = 513 = 5.1 \times 10^2$ g

*The mass of $H_2O$ was rounded off to 2 significant figures for the same reasons why the answer to part **b** was rounded off to 2 significant figures.*

The calculations below show how the answers obtained for parts **b** and **c** from the above example are slightly off when using the answer to part **a** that was rounded to 2 significant figures (29 mol) and the calculated moles of $O_2$ that was rounded off to 2 significant figures (15 mol).

**a.** $n(H_2) = \frac{57.0}{2.0} = 28.5 = 29$ mol

**b.** $n(O_2) = \frac{1}{2} \times 29 = 14.5 = 15$ mol

$m(O_2) = 15 \times 32.0 = 480 = 4.8 \times 10^2$ g

**c.** $n(H_2O) = 29$ mol

$m(H_2O) = 29 \times 18.0 = 522 = 5.2 \times 10^2$ g

The values that have been rounded off to 2 significant figures have been highlighted in yellow. The answers to parts **b** and **c**, highlighted in blue, are slightly different and less accurate than the answers that were obtained previously using unrounded values.

- *With regards to significant figures in the end of year chemistry exam, the current policy is that errors in significant figures will only be penalised in one question. If a student makes an error in this question they lose 1 MARK. For example, if the answer to this question is 23.2 g (3 SF) and a student gives an answer of 23 g (2 SF) they will be penalised 1 mark. They can make significant figure errors in other questions in the exam but they will not be penalised. They will only be penalised for that one question that has been selected.*

  *It is not however, indicated in the exam paper which question has been selected for penalising errors in significant figures so it is important that students pay attention to correctly rounding off every question involving calculations in the exam.*

  *There is a possibility that a student may be penalised a mark in a question other than the one selected, if there has been a blatant disregard of the significant figures required for the answer. For example, if the answer to a question is 1.2 L (2 SF) and a student gives an answer of 1.199327 L (7 SF) they may lose a mark for blatantly disregarding the rules for rounding off answers to the correct number of significant figures.*

# Appendix 2 – Relative atomic masses

| Element | Atomic number | Relative atomic mass (Ar) |
|---|---|---|
| Hydrogen (H) | 1 | 1.0 |
| Helium (He) | 2 | 4.0 |
| Lithium (Li) | 3 | 6.9 |
| Beryllium (Be) | 4 | 9.0 |
| Boron (B) | 5 | 10.8 |
| Carbon (C) | 6 | 12.0 |
| Nitrogen (N) | 7 | 14.0 |
| Oxygen (O) | 8 | 16.0 |
| Fluorine (F) | 9 | 19.0 |
| Neon (Ne) | 10 | 20.1 |
| Sodium (Na) | 11 | 23.0 |
| Magnesium (Mg) | 12 | 24.3 |
| Aluminium (Al) | 13 | 27.0 |
| Silicon (Si) | 14 | 28.1 |
| Phosphorous (P) | 15 | 31.0 |
| Sulfur (S) | 16 | 32.1 |
| Chlorine (Cl) | 17 | 35.5 |
| Argon (Ar) | 18 | 39.9 |
| Potassium (K) | 19 | 39.1 |
| Calcium (Ca) | 20 | 40.1 |
| Scandium (Sc) | 21 | 44.9 |
| Titanium (Ti) | 22 | 47.9 |
| Vanadium (V) | 23 | 50.9 |
| Chromium (Cr) | 24 | 52.0 |
| Manganese (Mn) | 25 | 54.9 |
| Iron (Fe) | 26 | 55.8 |
| Cobalt (Co) | 27 | 58.9 |
| Nickel (Ni) | 28 | 58.7 |
| Copper (Cu) | 29 | 63.5 |
| Zinc (Zn) | 30 | 65.4 |
| Gallium (Ga) | 31 | 69.7 |
| Germanium (Ge) | 32 | 72.6 |
| Arsenic (As) | 33 | 74.9 |
| Selenium (Se) | 34 | 79.0 |
| Bromine (Br) | 35 | 79.9 |
| Krypton (Kr) | 36 | 83.8 |
| Rubidium (Rb) | 37 | 85.5 |
| Strontium (Sr) | 38 | 87.6 |
| Yttrium (Y) | 39 | 88.9 |

| | | |
|---|---|---|
| Zirconium (Zr) | 40 | 91.2 |
| Niobium (Nb) | 41 | 92.9 |
| Molybdenum (Mo) | 42 | 95.9 |
| Technetium (Tc) | 43 | 98.1 |
| Ruthenium (Ru) | 44 | 101.1 |
| Rhodium (Rh) | 45 | 102.9 |
| Palladium (Pd) | 46 | 106.4 |
| Silver (Ag) | 47 | 107.9 |
| Cadmium (Cd) | 48 | 112.4 |
| Indium (In) | 49 | 114.8 |
| Tin (Sn) | 50 | 118.7 |
| Antimony (Sb) | 51 | 121.8 |
| Tellerium (Te) | 52 | 127.6 |
| Iodine (I) | 53 | 126.9 |
| Xenon (Xe) | 54 | 131.3 |
| Caesium (Cs) | 55 | 132.9 |
| Barium (Ba) | 56 | 137.3 |
| Lanthanum (La) | 57 | 138.9 |
| Hafnium (Hf) | 72 | 178.5 |
| Tantalum (Ta) | 73 | 180.9 |
| Tungsten (W) | 74 | 183.8 |
| Rhenium (Re) | 75 | 186.2 |
| Osmium (Os) | 76 | 190.2 |
| Iridium (Ir) | 77 | 192.2 |
| Platinum (Pt) | 78 | 195.1 |
| Gold (Au) | 79 | 197.0 |
| Mercury (Hg) | 80 | 200.6 |
| Thallium (Tl) | 81 | 204.4 |
| Lead (Pb) | 82 | 207.2 |

# Appendix 3 – Valency table

| **Cations (+1)** | | **Cations (+2)** | | **Cations (+3)** | |
|---|---|---|---|---|---|
| **lithium** | $Li^{+}$ | **magnesium** | $Mg^{2+}$ | **aluminium** | $Al^{3+}$ |
| **sodium** | $Na^{+}$ | **calcium** | $Ca^{2+}$ | **chromium** | $Cr^{3+}$ |
| **potassium** | $K^{+}$ | **barium** | $Ba^{2+}$ | **iron (III)** | $Fe^{3+}$ |
| **caesium** | $Cs^{+}$ | **iron (II)** | $Fe^{2+}$ | | |
| **silver** | $Ag^{+}$ | **nickel** | $Ni^{2+}$ | | |
| **copper (I)** | $Cu^{+}$ | **copper (II)** | $Cu^{2+}$ | | |
| **ammonium** | $NH_4^{+}$ | **zinc** | $Zn^{2+}$ | | |
| **hydrogen** | $H^{+}$ | **tin (II)** | $Sn^{2+}$ | | |
| | | **lead (II)** | $Pb^{2+}$ | | |
| | | **manganese (II)** | $Mn^{2+}$ | | |
| | | **mercury (II)** | $Hg^{2+}$ | | |
| | | **strontium** | $Sr^{2+}$ | | |
| **Anions (-1)** | | **Anions (-2)** | | **Anions (-3)** | |
| **hydride** | $H^{-}$ | **oxide** | $O^{2-}$ | **nitride** | $N^{3-}$ |
| **fluoride** | $F^{-}$ | **peroxide** | $O_2^{2-}$ | **phosphide** | $P^{3-}$ |
| **chloride** | $Cl^{-}$ | **sulfide** | $S^{2-}$ | **phosphate** | $PO_4^{3-}$ |
| **bromide** | $Br^{-}$ | **sulfate** | $SO_4^{2-}$ | | |
| **iodide** | $I^{-}$ | **carbonate** | $CO_3^{2-}$ | | |
| **hydroxide** | $OH^{-}$ | **sulfite** | $SO_3^{2-}$ | | |
| **nitrate** | $NO_3^{-}$ | **dichromate** | $Cr_2O_7^{2-}$ | | |
| **hydrogen carbonate** | $HCO_3^{-}$ | **chromate** | $CrO_4^{2-}$ | | |
| **hydrogen sulfate** | $HSO_4^{-}$ | **thiosulfate** | $S_2O_3^{2-}$ | | |
| **chlorate** | $ClO_3^{-}$ | **hydrogen phosphate** | $HPO_4^{2-}$ | | |
| **hydrogen sulfite** | $HSO_3^{-}$ | | | | |
| **hydrogen sulfide** | $HS^{-}$ | | | | |
| **nitrite** | $NO_2^{-}$ | | | | |
| **permanganate** | $MnO_4^{-}$ | | | | |
| **hypochlorite** | $OCl^{-}$ | | | | |
| **dihydrogen phosphate** | $H_2PO_4^{-}$ | | | | |
| **cyanide** | $CN^{-}$ | | | | |

# Appendix 4 – Measurements, Errors and Personal mistakes

In chemistry, some of the measurements that can be taken during a practical activity include temperature, mass, pH etc.  The values of these measurements are referred to as data.  Most data has units.  For example, a mass of 25 g or a temperature of 25 $^{0}$C.  Some data has no units.  For example, pH measurements (eg. pH of 7) have a numerical value but no units.

The measurements or data that are obtained during practical activities can be described in many different ways which include – **accuracy, precision, repeatability, reproducibility and validity.**

## Accuracy

A measured quantity (piece of data) is considered to be accurate if it is judged to be close to the true value of the quantity being measured. The true value is the value that would be obtained if this quantity was measured perfectly. For example, if an experiment is performed and it is determined that a given substance had a mass of 2.70 g but the true value of the mass of this substance is really 3.20 g, then the measurement is not accurate since it is not close to the true value.  Accuracy is not a quantity so it cannot be measured numerically. The difference between a measured value and the true value is known as the **measurement error**.  Measurement error is used to quantify how accurate a piece of data is.  So for the example just given, the data is not very accurate and has a measurement error of: 3.20 – 2.70 = 0.50 g.

Not all measurements made in science can be judged as being accurate or inaccurate as not all measurements have a known true value. For example, a student may measure the phosphorous content of the water in the bowl of a bird bath they have at home.  The conditions of the water in this bird bath – temperature, microorganism count, pH etc. are unique so there would be no predetermined true value for its phosphorous content that can be compared to the measurements made by the student.

## Precision

Experimental precision refers to the closeness of 2 or more measured values. A set of precise measurements will have values that are very close to their mean. For example, if a given substance was weighed five times yielding mass values of

2.70 g, 2.69 g, 2.71 g, 2.71 g and 2.72 g.

$$\text{Mean of these values} = \frac{2.70 + 2.69 + 2.71 + 2.71 + 2.72}{5} = 2.706 = 2.71\text{ g}$$

Each of these 5 measured values of mass is very close to the mean value of 2.71 g so the values are said to be precise.  Even without calculating the mean it can be seen that the 5 values of mass are in close agreement with each other and can be described as precise.

**Precise** results are not necessarily **accurate** results. For example, the 5 precise results of mass shown above are not accurate results if the true value of the substance's mass is 3.20 g.

## Repeatability

**Repeatability** refers to the closeness of measured values that were obtained with the same method on identical test material, under the same conditions (same operator, same apparatus and/or same laboratory). So if the operator that obtained the 5 mass values shown on the previous page performs the same experiment again using the same equipment in the same laboratory and obtains a set of results that are very close in value to the 5 mass results obtained previously, then the experimental data and hence experimental procedure can be judged as repeatable.

## Reproducibility

**Reproducibility** refers to the closeness of measured values that were obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different day and/or different laboratories).

The main reason for trying to reproduce experimental results is to uncover any flaws in the procedure that was performed by the original practitioner. Testing the reproducibility of results is a good way of uncovering systematic errors, especially those due to faulty or incorrectly calibrated equipment such as thermometers and balances. Systematic errors and the calibration of equipment shall be discussed shortly.

## Validity

Before validity can be discussed, it is necessary to have an understanding of **independent, dependent** and **controlled** variables. A variable is a quantity that is able to change. For example, temperature, masses, pH etc. are all variables as they can have different values.

An **independent variable** – is a variable that is changed deliberately and by a controlled amount by the operator of an experiment.

A **dependent variable –** is a variable that changes as a result of the independent variable changing. It is the variable that is being measured during the experiment.

- The independent variable causes the dependent variable to change.

or

- The dependent variable is dependent upon the changes made to the independent variable.

**Controlled variables** are variables that can affect the measurement of the dependent variable but are kept constant in order to ensure that the measurements of the dependent variable are only influenced by the chosen independent variable.

The example below will help illustrate the difference between dependent variables, independent variables and controlled variables.

During an experiment in chemistry it is common to investigate how changing one variable affects another variable. For example, investigating the effect that increasing the mass of a limiting amount of magnesium has on the volume of hydrogen gas produced when magnesium is reacted with excess hydrochloric acid. Let us look at the reaction between different masses of magnesium (limiting reactant) with excess hydrochloric acid.

The equation for this reaction is shown below.

$Mg (s) + 2HCl (aq) \rightarrow MgCl_2 (aq) + H_2 (g)$

The table below shows the volume of hydrogen gas produced after the reaction of a given mass of Mg with 50 mL of excess 2 M hydrochloric acid.

| **Mass of Mg (g) reacting** | **Volume of $H_2$ gas (mL)** |
|---|---|
| 0.10 | 100 mL |
| 0.20 | 200 mL |
| 0.30 | 300 mL |
| 0.40 | 400 mL |
| 0.50 | 500 mL |

This table clearly shows that as one variable, the mass of Mg increases, the other variable, the volume of $H_2$ gas, increases.

The mass of Mg is the *independent variable* as it is changed by the practitioner performing the experiment. The volume of $H_2$ gas is the *dependent variable* because it is being measured during the experiment and is changing as the mass of Mg (independent variable) reacting changes.

There are variables other than the mass of Mg that can affect the volume of $H_2$ gas produced. Some of these variables include the concentration of HCl, the volume of the HCl used and the atmospheric pressure in the lab. All of these variables must be controlled (kept constant) so that they don't interfere with the measurement of the volume of $H_2$ gas produced due to the changing mass of Mg in the reaction with HCl. A likely list of controlled variable conditions for this experiment would be:

HCl concentration = 2 M
HCl volume = 50 mL
Atmospheric pressure = 0.987 atm

So when each mass of Mg reacts with HCl, the above conditions must always be adhered to so that the only variable that is changing is the mass of Mg reacting.

A measurement or piece of data is **valid** if it is caused by a single independent variable only. That is, it is caused by the chosen independent variable. If the experimental procedure is flawed by the failure to control variables, it is possible that a variable other than the independent variable being tested has influenced one or more of the measurements made. So the volumes of $H_2$ gas measured in the table on the previous page are only valid if all variables capable of changing the volume of $H_2$ gas other than the mass of Mg are controlled (kept constant)

Let's say that when the 0.40 g of Mg was used the volume of HCl was only 5.0 mL and its concentration was only 0.2 M. This would result in the HCl being the limiting reactant and the Mg the excess reactant. Now only some of the 0.40 g of Mg will react resulting in a lower than expected volume of $H_2$ gas. Now there are 3 variables influencing the volume of $H_2$ gas – mass of Mg, concentration of HCl and volume of HCl. This experiment is flawed as variables other than the chosen independent variable (mass of Mg) are affecting the volume of $H_2$ gas produced by the reaction.

So the volume of $H_2$ measured under these circumstances is **not valid** as variables (volume and concentration of HCl) other than the independent variable being tested (mass of Mg) have influenced the volume of $H_2$ gas produced.

## Uncertainties

The term uncertainty refers to the doubt associated with the accuracy of a measured piece of data. Uncertainties are factors that can affect the accuracy of a measured piece of data and are beyond the control of the person performing the experiment. Some sources of uncertainty are due to the calibration (ability of a piece of equipment to make accurate measurements) of equipment or the completeness of a chemical reaction (extent to which the reactants are converted to products for a non-equilibrium reaction). Experimental uncertainties are inherent in the experimental procedure and cannot be eliminated by repeating the experiment multiple times. There are two sources of experimental uncertainties: **systematic effects** and **random effects.**

A **systematic effect** is an uncertainty that has the potential to cause an error that is constantly repeated every time a measurement is made. Some examples of systematic effects are the doubt associated with the calibration of an instrument used for measuring such as an electronic balance, a burette, a pipette etc.

A **random effect** is an uncertainty that has the potential to cause an error that will affect only one measurement reading.

# ERRORS

Uncertainties are not errors. Uncertainties refer to errors that may occur before an experiment is performed. For example, when measuring the mass of a substance, it is uncertain if the balance is correctly calibrated. An error will occur if the balance is used and the mass of the substance is 0.20 g less than its true value due to the poor calibration of the balance. So an error will occur if an uncertainty actually happens during an experiment.

Errors can be divided into 2 types: **systematic errors** and **random errors**.

## Systematic errors

Systematic errors are errors that affect the accuracy of a measurement. Systematic errors cause readings to differ from the true value by a consistent amount each time a measurement is made, so that all the readings are shifted in one direction from the true value. The accuracy of measurements that are affected by systematic errors cannot be improved by performing multiple trials of the experiment and finding the average.

Common sources of systematic errors include: faulty calibration of measuring instruments (and uncalibrated instruments) that consistently give the same inaccurate reading for the same value being measured.

Systematic errors repeat themselves during an experiment. A poorly calibrated balance may consistently give mass readings that are 0.20 g higher than the true value. This is regarded as a systematic error because if the balance is used numerous times during the experiment, the error is repeated. The accuracy of the data obtained is affected as the mass readings are always 0.20 g higher than the true value. The precision of the data however, will not be affected as the readings from the balance may still be close together. For example, during an experiment, 3 masses with values of 1.76 g, 1.75 g and 1.76 g may be obtained. Assuming that no other errors have occurred, these errors will not be accurate as they are all 0.20 g higher than the true value. These masses however, have high precision as they are close in value. *Precise data is not necessarily accurate data.*

Systematic errors do not affect the repeatability of measured data. Data is repeatable if the same or very similar values are obtained when the experimental procedure is repeated by the same practitioner, in the same lab, using the same equipment, same method etc. Under these circumstances the error will be repeated each time the data is measured and the same results should be obtained after multiple trials. Systematic errors however, are very likely to produce data that is not reproducible. For data to be reproducible, the same values must be obtained by a different practitioner in a different lab using the same method but different equipment. It is likely that if the experiment is performed in another lab, equipment such as a balance will be calibrated differently and will give mass readings that are different to those obtained using an incorrectly calibrated balance.

## Random errors

Random errors unlike systematic errors do not affect measurements in the same direction and to the same extent. Random errors are unpredictable and can cause measurements to be either lower or higher than the true value. As a result random errors will affect the precision of measured data. For example, you may record the mass of a substance as 1.75 g but the reading on the balance may suddenly change to 1.74 g. It is unknown which is the more accurate value. This is a random error because each time you make a reading of the mass of a substance you may record a mass that is either too high or too low depending on when you decide to record the mass. It is not consistent (random) each time. So the operator may record a mass that is either higher or lower than the true value, depending on the effect of the fluctuation (lower or higher reading) of the balance when the mass was finally recorded. This can result in a large spread (low precision) between the mass values recorded for the same substance. For example a substance with a true value of 1.70 g may have balance readings of

1.69 g 1.75 g 1.72 g and 1.73 g

Some other common sources of random error are miss-judging when an indicator has undergone a permanent colour change during a titration, estimating a titre reading that is in between the calibration lines of a burette. For example, estimating a reading as either 28.60 mL or 28.61 mL etc. The same sort of random error can be made when making temperature readings from a thermometer.

*It is difficult to judge whether the bottom of the meniscus is lying at 28.60 mL or 28.61 mL.*

- The effect of random errors can be reduced by making many measurements and calculating the mean.
- Random errors can affect both the *precision and accuracy of data.*
- Random errors can affect both the repeatability and reproducibility of measurements.

## Personal mistakes

Personal errors or personal mistakes are different to the systematic and random errors that were just discussed.  Personal mistakes are not inherent in the equipment or procedure.  They are purely due to mistakes made by the person performing the experiment.  Personal mistakes include miscalculations of the concentration of a solution, reading the wrong scale on an ammeter or voltmeter, using 1.0 M HCl during a reaction instead of 2.0 M HCl, rinsing a burette out with water instead of 0.10 M NaOH solution, using a calorimeter without the insulating polystyrene jacket etc.

- *Personal mistakes are not errors.*

- *Some random errors can be confused with personal mistakes. Some might argue that a random error such as reading a titre value as 12.45 mL when it is really 12.43 mL is a personal mistake as it is caused by an error in judgement by the practitioner.  This is not the case however, as the distance between the calibration markings on a burette that show 0.10 mL are quite small and it is reasonable to expect that even when great care is taken, a reading could be miss-judged by 0.02 mL.  If however, the practitioner made a titre reading of 12 mL when it was actually 13 mL, this would be regarded as a personal mistake as the scale on the burette has been miss-read.  Differentiating between burette readings that are 1 mL apart should be very easy for most practitioners.*

## Outliers

Outliers are measurement readings that are either much greater or much lower than other measured results.  Outliers can be due to random errors but not systematic errors.  As systematic errors affect every reading in the same way, no reading will be much higher or much lower when compared to the other data.

# Chapter 1 Review Questions – Solutions

## Multiple Choice

### Question 1

Which of the following describes relative isotopic mass?

**A.** The mass of the carbon-12 isotope.
**B.** The mass of one mole of any substance.
**C.** The average mass of the isotopes that make up an element.
[✓ **D.**] None of the above.

### Question 2

The mass in gram of one molecule of $C_5H_{12}$ is

**A.** 72
[✓ **B.**] $\frac{72}{6.02 \times 10^{23}}$
**C.** $6.02 \times 10^{23} \times 72$
**D.** $\frac{6.02 \times 10^{23}}{72}$

m = n x M

$$n(C_5H_{12}) = \frac{\text{number of particles}}{6.02 \times 10^{23}} = \frac{1}{6.02 \times 10^{23}}$$

$$m(C_5H_{12}) = \frac{1}{6.02 \times 10^{23}} \times 72 = \frac{72}{6.02 \times 10^{23}}\ \text{g}$$

*B is the only common sense answer as all the other responses represent masses that are far too great for just one molecule.*

### Question 3

The greatest number of particles is found in

**A.** $7.5 \times 10^{23}$ $H_2O$ molecules
**B.** $1.5 \times 10^{23}$ Na atoms
**C.** 100 g of $C_6H_{12}O_6$
[✓ **D.**] 1.5 moles of $H_2$

*C and D need to be converted into the number of particles which is the number of molecules of each substance.*

$$N(C_6H_{12}O_6) = n \times 6.02 \times 10^{23} = \frac{100}{180.0} \times 6.02 \times 10^{23} = 3.34 \times 10^{23}$$

$$N(H_2) = 1.5 \times 6.02 \times 10^{23} = 9.03 \times 10^{23}$$

### Question 4

The greatest number of atoms are found in

**A.** $7.5 \times 10^{23}$ $H_2O$ molecules
**B.** $1.5 \times 10^{23}$ Na atoms
[✓ **C.**] 100 g of $C_6H_{12}O_6$
**D.** 1.5 moles of $H_2$

*In question 3 the number of particles was the number of molecules of each substance. The number of atoms is found by multiplying the number of molecules by the number of atoms in each molecule:*

A: $7.5 \times 10^{23} \times 3 = 2.25 \times 10^{24}$
B: $1.5 \times 10^{23} \times 1 = 1.5 \times 10^{23}$
C: $3.34 \times 10^{23} \times 24 = 8.016 \times 10^{24}$
D: $9.03 \times 10^{23} \times 2 = 1.806 \times 10^{24}$

**Question 5**
The value of Avogadro's constant is equivalent to

**A.** the number of atoms present in 18 g of $H_2O$.
[✓ **B.**] the number of atoms present in 1.0 g of $H_2$ gas.
**C.** the number of atoms in 2.0 g of $H_2$ gas.
**D.** the number of atoms of Na in 1.0 mole of $Na_2CO_3$.

*Avogadro's constant is $6.02 \times 10^{23}$ so the correct response is the one that shows $6.02 \times 10^{23}$ atoms or molecules.*

A: n ($H_2O$) = $\frac{18}{18.0}$ = 1.0 mol, n (atoms) = 3 x 1.0 = 3.0 mol, N (atoms) = 3.0 x $6.02 \times 10^{23}$ = $1.806 \times 10^{24}$

B: n ($H_2$) = $\frac{1.0}{2.0}$ = 0.50 mol, n (atoms) = 2 x 0.50 = 1.0 mol, N (atoms) = 1.0 x $6.02 \times 10^{23}$ = $6.02 \times 10^{23}$

C: n ($H_2$) = $\frac{2.0}{2.0}$ = 1.0 mol, n (atoms) = 2 x 1.0 = 2.0 mol, N (atoms) = 2.0 x $6.02 \times 10^{23}$ = $1.204 \times 10^{24}$

D: n (Na) = 2 x 1.0 = 2.0 mol, N (Na) = 2.0 x $6.02 \times 10^{23}$ = $1.204 \times 10^{24}$

**Question 6**
The mass of sodium atoms in $\frac{1}{3}$ of a mole of $Na_3PO_4$ is the same as

[✓ **A.**] the molar mass of sodium.
**B.** the mass of $\frac{1}{3}$ of a mole of sodium.
**C.** the mass of 3 moles of sodium.
**D.** 41 % of the molar mass of $Na_3PO_4$.

*n (Na) = $\frac{1}{3}$ x 3 = 1 mol*

*m (Na) = 1 x 23.0 = 23.0 g. Therefore the correct answer is A as the molar mass of Na is 23.0 $gmol^{-1}$*

**Question 7**
The number of atoms in 1.5 moles of $(NH_2)_2CO$ is equivalent to

**A.** the number of atoms in 6.0 moles of $CO_2$.
[✓ **B.**] the number of chlorine atoms in 6.0 moles of $Cl_2$.
**C.** the number of molecules in 3.0 moles of $Cl_2$.
**D.** the number of ions in 3.0 moles of $Na_2O$.

n (atoms) = 1.5 x 8 = 12 mol

N (atoms) = 12 x $6.02 \times 10^{23}$
= $7.224 \times 10^{24}$

*A: n (atoms) = 6.0 x 3 = 18 mol, N (atoms) = 18 x $6.02 \times 10^{23}$ = $1.0836 \times 10^{25}$ atoms*
*B: n (Cl atoms) = 6.0 x 2 = 12 mol, N (Cl atoms) = 12 x $6.02 \times 10^{23}$ = $7.224 \times 10^{24}$*
*C: N ($Cl_2$) molecules = 3.0 x $6.02 \times 10^{23}$ = $1.806 \times 10^{24}$*
*D: n (ions) 3.0 x 3 = 9.0 mol N (ions) = 9.0 x $6.02 \times 10^{23}$ = $5.418 \times 10^{24}$*

**Question 8**

The percentage by mass of nitrogen in $(NH_4)_2SO_4$ is

[✓ **A.**] 21.2 %
**B.** 10.6 %
**C.** 13.3 %
**D.** 25%

*% N =* $\frac{14.0 \times 2}{132.1}$ *x 100 = 21.196 = 21.2 %*

**Question 9**

A rock contains 30.0 % $CaCO_3$ and 70.0% $SiO_2$ by mass. What is the percentage of carbon in the rock?

**A.** 30 %
[✓ **B.**] 3.60 %
**C.** 12 %
**D.** 36 %

*% C in* $CaCO_3$ *=* $\frac{12.0}{100.1}$ *x 100 =11.988 %*

*All of the C in the rock comes from* $CaCO_3$*. So if 30.0 % of the rock is* $CaCO_3$ *then 11.988 % of that 30 % is carbon. So the % of C in the rock*

*=* $\frac{11.988}{100}$ *x 30 = 3.60 %*

**Question 10**

Analysis of a sample of fertilizer shows that it contains 58.8 % potassium nitrate. The remaining mass of the fertilizer is due to potassium chloride. What mass of nitrogen is present in 0.500 Kg of fertilizer?

**A.** 0.294 Kg
**B.** 0.06925 Kg
[✓ **C.**] 0.041 Kg
**D.** 0.206 Kg

*% N in* $KNO_3$ *=* $\frac{14.0}{101.1}$ *x 100 = 13.8477 %*

*So 13.8477 % of potassium nitrate is N. If 58.8 % the mass of the fertiliser is potassium nitrate, then 13.8477 % of 58.8 % will give the % of N in the fertiliser.*

$\frac{13.8477}{100}$ *x 58.8 = 8.142 % of the fertilizer contains N.*

$\frac{8.142}{100}$ *x 0.500 = 0.04071 Kg*

*The information about the KCl is irrelevant as it contains no N.*

## Short Answers

**Question 1**
What is the mass of $5.50 \times 10^{25}$ molecules of glucose ($C_6H_{12}O_6$)?

$n\ (C_6H_{12}O_6) = \frac{5.50 \times 10^{25}}{6.02 \times 10^{23}} = 91.362\ mol$

$m\ (C_6H_{12}O_6) = 91.362 \times 180.0 = 16{,}445.18 = 1.64 \times 10^{4}\ g$

*A common error with this question is to give the answer to 2 significant figures, 1.6 x 10*$^{4}$*g based on the molar mass of H being 1.0. <u>This is not correct because it is the sum of the molar masses, not the molar masses of individual elements that is considered when determining the significant figures in the final answer.</u>*

$M\ (C) = 12.0\ g\ mol^{-1}$ $M\ (H) = 1.0\ g\ mol^{-1}$ $M\ (O) = 16.0\ g\ mol^{-1}$

$M\ (C_6H_{12}O_6) = 6 \times 12.0 + 12 \times 1.0 + 6 \times 16.0 = 180.0\ g\ mol$

*The sum of the molar masses of the elements in* $C_6H_{12}O_6$ *is equal to 180. As this calculation is based purely on the addition of the raw data, the answer must contain the same number of decimal places as the piece of data containing the least number of decimal places. The molar masses of the C, H and O all contained one decimal place so the molar mass of* $C_6H_{12}O_6$ *must contain one decimal place, 180.0. The rest of the calculation includes multiplication and division so the final answer to the question must be rounded off to 3 significant figures as the least precise piece of data,* $5.50 \times 10^{25}$ *contained 3 significant figures. REFER TO APPENDIX ONE.*

**Question 2**
What is the mass of 10.0 moles of $KNO_3$?

$m\ (KNO_3) = 10.0 \times 101.1 = 1{,}011 = 1.01 \times 10^{3}\ g$

**Question 3**
How many molecules are present in 42 g of $SO_2$?

$n\ (SO_2) = \frac{42}{64.1} = 0.655226\ mol$

$N\ (SO_2) = 0.655226 \times 6.02 \times 10^{23} = 3.94446 \times 10^{23} = 3.9 \times 10^{23}$

**Question 4**
How many moles of $O^{2-}$ ions are present in 2.65 g of MgO?

$n\ (MgO) = \frac{2.65}{40.3} = 0.0657568$

n ($O^{2-}$) = 0.0657568 = 0.0658 mol

**Question 5**
What is the mass of oxygen in 5.0 moles of $H_2SO_4$?

n (O) = 5.0 x 4 = 20 mol
m (O) = 20 x 16.0 = 320 = 3.2 x $10^2$ g

**Question 6**
What is the amount of carbon in **mmole,** present in 2.5 mg of $C_8H_{10}N_4O_2$?

*n ($C_8H_{10}N_4O_2$) = $\frac{0.0025}{194.0}$ = 1.28866 x $10^{-5}$ mol*

*n (C) = 1.28866 x $10^{-5}$ x 8 = 0.0001030928 mol = 0.0001030928 x $10^3$ = 0.1030928 = 0.10 mol*

**Question 7**
What is the total number of atoms present in 1.0 Kg of $Fe(NO_3)_2$?

*1.0 Kg = 1,000 g*

*n ($Fe(NO_3)_2$) = $\frac{1{,}000}{179.8}$ = 5.56174 mol*

*n (atoms) = 5.56174 x 9 = 50.05566 mol*
*N (atoms) = 50.05566 x 6.02 x $10^{23}$ = 3.013351 x $10^{25}$ = 3.0 x $10^{25}$*

**Question 8**
How much does one atom of oxygen weigh?

*n (O) = $\frac{1}{6.02 \text{ x } 10^{23}}$ = 1.66113 x $10^{-24}$ mol*

*m (O) = 1.66113 x $10^{-24}$ x 16.0 = 2.657808 x $10^{-23}$ = 2.66 x $10^{-23}$ g.*

*The "1" used in the calculation was not a measured piece of data so it is not considered in the final rounding on the answer.*

**Question 9**
How much does one atom of oxygen weigh in a molecule of $CO_2$?

n (O) = $\frac{1}{6.02 \text{ x } 10^{23}}$ = 1.66113 x $10^{-24}$ = 1.66 x $10^{-24}$ g

*As the question asked for the mass of one oxygen atom, the fact that there are 2 O atoms in $CO_2$ is irrelevant. One oxygen atom weighs the same whether it is on its own or in a molecule.*

# Chapter 2 Review Questions – Solutions

## Multiple Choice

**Question 1**

A solution containing 0.25 g of NaCl in 50 mL of deionised water will also contain 0.25 mg of NaCl in

**A.** 0.50 mL of deionised water.
**B.** 5.0 mL of deionised water.
[✓ **C.**] 0.050 mL of deionised water.
**D.** 0.0005 L of deionised water.

*The key to this question is to find the response that has the same solute to solvent ratio as 0.25 g of NaCl in 50 mL of water.*

*Convert 0.25 mg into grams:* $0.25 \times 10^{-3} = 2.5 \times 10^{-4}$ *g*

*Now we can cross multiply.*

*50 mL deionised water →* $0.25$ *g*
*x mL deionised water →* $2.5 \times 10^{-4}$*g*

So 0.25 g NaCl in 50 mL of water has the same ratio as $2.5 \times 10^{-4}$ g NaCl in 0.050 mL of water

$$\mathbf{X} \times 0.25 = 50 \times 2.5 \times 10^{-4}$$

$$x = \frac{50 \times 2.5 \times 10^{-4}}{0.25} = 0.050 \text{ mL}$$

**Question 2**

The concentration that is equivalent to 1.0 M $KNO_3$ is

**A.** $1.0 \times 10^{2}$ mg mL$^{-1}$ $KNO_3$
[✓ **B.**] $1.0 \times 10^{-7}$ $\mu$g mL$^{-1}$ $KNO_3$
**C.** 101.1 % w/v $KNO_3$
**D.** $1.0 \times 10^{2}$ Kg/L

*As was the case for question 1, the key to this question is to find the response that has the same ratio of solute to solvent as 1.0 M* $KNO_3$.

*1.0 M* $KNO_3$ *means that 1.0 L of solution has 1.0 mole of* $KNO_3$.

*Mass of* $KNO_3$ *in 1.0 L of solution:* $m(KNO_3) = n \times M = 1.0 \times 101.1 = 101.1$ *g*

$101.1 \times 10^{-3} = 0.1011$ *mg*

*Now we can cross multiply to see if response A is correct.*

*1,000 mL (1.0 L) solution → 0.1011 mg* $KNO_3$
*1.0 mL solution → x mg* $KNO_3$

$$\boldsymbol{X} \times 1{,}000 = 1.0 \times 0.1011$$

$$\boldsymbol{X} = \frac{1.0 \times 0.1011}{1{,}000} = 1.011 \times 10^{-4} \text{mg mL}^{-1}$$ *so A is incorrect.*

*1.011 x 10$^{-4}$ x 10$^{-3}$= 1.011 x 10$^{-7}$µg mL$^{-1}$ so B is correct. (just convert 1.011 mg into µg)*

**Question 3**

When 2.5 x 10$^{24}$ molecules of $NH_3$ are dissolved in 1.0 L of distilled water, the resultant solution will have a molar concentration of

[✓ **A.**] 4.2 M
**B.** 2.5 x 10$^{24}$ mol L$^{-1}$
**C.** 71 mol/L
**D.** 71 g L$^{-1}$

*n ($NH_3$) =* $\frac{2.5 \text{ x } 10^{24}}{6.02 \text{ x } 10^{23}}$ *= 4.1528 mol in 1.0 L*

*Therefore molar concentration = 4.2 M*

**Question 4**

When a solution is diluted,

[✓ **A.**] the moles of solute are unchanged.
**B.** the mass of solute and solution both increase.
**C.** the concentration of the solution will increase but the moles of solute remain unchanged.
**D.** All of the above are correct.

*When a solution is diluted, the moles and mass of solute are not affected by the water. The concentration of the solution will always decrease after a dilution.*

**Question 5**

On average, an adult has a concentration of creatine in their urine that is equal to 0.10 %w/v. Creatine is also found in the blood where its concentration is 100 times less than in the urine. On average, what mass of creatine would be present in 1.0 L of blood from an adult?

[✓ **A.**] 0.010 g
**B.** 0.00010 g
**C.** 0.10 g
**D.** 1.0 g

*Concentration of creatine in blood = 0.10 ÷ 100 = 1.0 x 10$^{-3}$ %w/v*

*100 mL blood → 1.0 x 10$^{-3}$ g creatine*
*1,000 mL blood →**X** g creatine*

***X*** x 100 = 1,000 x *1.0 x 10$^{-3}$*

$$X = \frac{1{,}000 \text{ x } 1 \text{ x } 10^{-3}}{100} = 1.0 \text{ x } 10^{-2} \text{ g}$$

**Question 6**

25 mL of a 0.12 M $HNO_3$ solution is poured into 100 mL of distilled water. The concentration of the resultant solution is

**A.** 0.48 M
**B.** 0.030 M
[✓ **C.**] 0.024 M
**D.** 0.60 M

$C_1V_1 = C_2V_2$
$C_1 = 0.12\ M$ $C_2 = ?$
$V_1 = 25\ mL$ $V_2 = 125\ mL\ (100 + 25)$

$$C_2 = \frac{C_1 \times V_1}{V_2} = \frac{0.12 \times 25}{125} = 0.024\ M$$

## Short Answers

**Question 1**

How many carbon atoms are present in 100.0 mL of a 10.0 ppm solution of $C_6H_{12}O_6$?

*10.0 ppm means $10^6$ mL of the solution contains 10.0 g of $C_6H_{12}O_6$.*

$10^6$ mL → 10.0 g $C_6H_{12}O_6$
100.0 mL → $\boldsymbol{X}$ g $C_6H_{12}O_6$

$\boldsymbol{X} \times 10^6 = 100.0 \times 10.0$

$\boldsymbol{X} = \frac{100.0 \times 10.0}{10^6} = 10^{-3}$ g of $C_6H_{12}O_6$

$n\ (C_6H_{12}O_6) = \frac{0.0010}{180.0} = 5.5556 \times 10^{-6}$ mol

$N\ (C_6H_{12}O_6) = 5.5556 \times 10^{-6} \times 6.02 \times 10^{23} = 3.344712 \times 10^{18}$

$N$ (C atoms) $= 3.344712 \times 10^{18} \times 6 = 2.00668 \times 10^{19} = 2.01 \times 10^{19}$

**Question 2**

How many nanograms of $Fe^{2+}$ ions are contained in 50.0 mL of a 0.026 M $Fe^{2+}$ solution?

$n\ (Fe^{2+}) = C \times V = 0.026 \times 0.050 = 1.3 \times 10^{-3}$ mol

$m\ (Fe^{2+}) = 1.3 \times 10^{-3} \times 55.8 = 0.07254$ g

$0.07254 \text{ g} \times 10^{-9} = 7.254 \times 10^{-11} = 7.3 \times 10^{-11}$ ng

**Question 3**

Express 25 mL of 2.0 M $Al(NO_3)_3$ solution as % m/v.

$n\ (Al(NO_3)_3) = C \times V = 0.025 \times 2.0 = 0.05$ mol

$m\ (Al(NO_3)_3) = 0.05 \times 213 = 10.65$ g

10.65 g → 25 mL
$\boldsymbol{X}$ g → 100 mL

$\boldsymbol{X} \times 25 = 10.65 \times 100$

$\boldsymbol{X} = \frac{10.65 \times 100}{25} = 42.6 = 43$ %m/m

*Alternatively, ignore the volume of 25 mL and just work with the concentration of 2.0 M.*

$n\ (Al(NO_3)_3)$ in 1.0 L = 2.0 mol
$m\ (Al(NO_3)_3)$ in 1.0 L = $2.0 \times 213 = 426$ g

426 g → 1000 mL
$\boldsymbol{X}$ g → 100 mL

$\boldsymbol{X} \times 1000 = 426 \times 100$

$\boldsymbol{X} = \frac{426 \times 100}{1000} = 42.6 = 43$ %mv

**Question 4**

Convert a solution with a concentration of 23 %w/v into mg L$^{-1}$.

*100 mL → 23 g*
*1,000 mL → x g*

$\boldsymbol{X} \text{ x } 100 = 23 \text{ x } 1{,}000$

$$\boldsymbol{X} = \frac{23 \text{ x } 1{,}000}{100} = 230 \text{ g}$$

$230 \text{ x } 10^{3} = 2.3 \text{ x } 10^{5} \text{ mg L}^{-1}$

**Question 5**

A batch of oysters is suspected of being contaminated with mercury (Hg). Analysis of one of the oysters reveals a concentration of Hg that is equal to 200.0 ppb. Express the level of Hg in the oyster as mg/Kg.

*200.0 ppb means that* $10^{9}$ *g of the oysters contains 200 g of Hg.*

*mg/Kg means the mg of Hg present in 1 Kg of oysters.*

*The first thing to do is change the* $10^{9}$*g of oysters into Kg:*

$10^{9} \text{ x } 10^{-3} = 10^{6}$ *kg of oysters.*

*Now change 200 g of Hg into mg:*

$200 \text{ x } 10^{3} = 2.00 \text{ x } 10^{5} \text{ mg}$

$10^{6}$ *Kg oysters → 2.00 x* $10^{5}$ *mg Hg*
*1.0 Kg oysters →* ***X****mg Hg*

$\boldsymbol{X} \text{ x } 10^{6} = 1.0 \text{ x } 2.00 \text{ x } 10^{5}$

$$\boldsymbol{X} = \frac{1.0 \text{ x } 2.00 \text{ x } 10^{5}}{10^{6}} = 0.2000 \text{ mg/Kg}$$

**Question 6**

2,500 gigalitres of water pass through a dam each day. Discharge from a nearby steel works plant has contaminated the water passing through the dam with highly toxic metals such as lead. The concentration of lead in a sample of water taken near the dam was 2.88 ppm during each day of testing during a 5 day period. How many micrograms of lead passed through the dam during this 5 day testing period?

*2.88 ppm means that $10^6$ mL of water contains 2.88 g of lead.*

*Change $10^6$ mL into GL:*

$10^6 \times 10^{-12} = 10^{-6}$ GL

*Change 2.88 g of lead into micrograms:*

$2.88 \times 10^6 = 2.88 \times 10^6$ µg

$10^{-6}$ GL → $2.88 \times 10^6$ µg lead
2,500 GL → **X** µg lead

$X \times 10^{-6} = 2{,}500 \times 2.88 \times 10^6$

$$X = \frac{2{,}500 \times 2.88 \times 10^6}{10^{-6}} = 7.20 \times 10^{15} \text{ µg in one day.}$$

*During the 5 day testing period:*

$7.20 \times 10^{15} \times 5 = 3.6 \times 10^{16}$ µg

**Question 7**

What volume of water, in mL, is required to produce a 1.0 L bottle of 3.0 M NaOH solution. The stock solution used for this dilution has a concentration of 10.0 M.

$C_1V_1 = C_2V_2$

$C_1 = 3.0$ M $\quad C_2 = 10.0$ M
$V_1 = 1.0$ L $\quad V_2 = ?$

$$V_2 = \frac{C_1V_1}{C_2} = \frac{3.0 \times 1.0}{10.0} = 0.30 \text{ L}$$

*So 0.30 L of the 10 M stock solution must be diluted to a volume of 1.0 L in order to produce a solution with a 3.0 M concentration. The volume of water added to produce the diluted solution = 1.0 – 0.30 = 0.70 L*

**Question 8**

10.0 g of $Na_2CO_3$ is dissolved in 250 mL of water. A 100.0 mL sample of this $Na_2CO_3$ solution is transferred to an empty beaker.

**a.** What is the number of moles of $Na_2CO_3$ dissolved in the 250 mL of water.

$$n\ (Na_2CO_3) = \frac{10.0}{106.0} = 0.09434 = 0.0943\ mol$$

**b.** What is the molarity of the original 250 mL solution of $Na_2CO_3$?

$$C\ (Na_2CO_3) = \frac{0.09434}{0.250} = 0.37736 = 0.377\ M$$

**c.** What is the molarity of the 100.0 mL sample of $Na_2CO_3$ .

*The 100 mL sample is taken directly from the original 250 mL solution. As no water was added the concentration must also be 0.377 M.*

**d.** How many moles of $Na_2CO_3$ are present in the 100.0 mL sample?

$n = C \times V$

$n = 0.37736 \times 0.100 = 0.037736 = 0.0377\ mol$

**e.** The beaker containing the 100.0 mL solution of $Na_2CO_3$ is diluted with 100.0 mL of water. How many moles of $Na_2CO_3$ are present after the dilution with 100.0 mL of water?

*Adding water will decrease the concentration but the number of mole of dissolved $Na_2CO_3$ will not be changed.*

*Therefore the number of moles = 0.377 mol*

**f.** What is the molarity of the 100.0 mL $Na_2CO_3$ solution after dilution with 100 mL of water?

$C_1V_1 = C_2V_2$

$C_1 = 0.37736\ M$ $\quad$ $C_2 = ?$

$V_1 = 100\ mL$ $\quad$ $V_2 = 100 + 100 = 200\ mL$

$$C_2 = \frac{C_1V_1}{V_2} = \frac{0.37736 \times 100}{200} = 0.18868 = 0.189\ M$$

**g.** How many $Na^+$ ions are present in 1.0 µL of the diluted $Na_2CO_3$ solution from part f?

*1.0 µL =* $1.0 \text{ x } 10^{-3}$ *mL*

*n* ($Na_2CO_3$) *in 1.0 µL = C x V =* $0.18868 \text{ x } 1.0 \text{ x } 10^{-3} = 1.8868 \text{ x } 10^{-4}$ *mol*
*n* ($Na^+$) = $1.8868 \text{ x } 10^{-4} \text{ x } 2 = 3.7736 \text{ x } 10^{-4}$ *mol*

*N* ($Na^+$) = $3.7736 \text{ x } 10^{-4} \text{ x } 6.02 \text{ x } 10^{23} = 2.2717 \text{ x } 10^{20} = 2.3 \text{ x } 10^{20}$ $Na^+$*ions.*

# Chapter 3 Review Questions – Solutions

**Question 1**
If a gas is at a pressure of 200 KPa, the equivalent pressure in mmHg is

- **A.** 760
- **B.** 1.97
- **C.** 2.0 x $10^5$
- [✓ **D.**] 1.5 x $10^3$

*200 ÷ 101.3 x 760 = 1,500 = 1.5 x* $10^3$ *Kpa*

*Use the following information to answer questions 2 and 3.*

Some important information about 2 gases, A and B is shown below.

| Gas A | Gas B |
|---|---|
| 2.0 atm pressure | 4.0 atm pressure |
| 5 $^0$C temperature | 10 $^0$C temperature |
| 5.0 L of volume | 2.5 L of volume |

**Question 2**
The greater pressure of Gas B is mainly due to

- **A.** its greater temperature.
- [✓ **B.**] its lower volume.
- **C.** its lower volume and greater temperature to an equal extent.
- **D.** Unable to be determined unless the identity of Gases A and B is known.

*According to the ideal gas equation (Pv=nRT), the pressure of a gas can be calculated by*

$$P = \frac{nRT}{V}$$

*So moles (n), temperature (T) and volume (V) will affect the pressure of a gas.*

*When expressed in Kelvin, gas A and B have very similar temperatures, 278 K and 283 K respectively. Only a doubling in Kelvin temperature can cause a doubling in pressure so clearly temperature cannot be the main factor here. The only factor left that can cause the doubling of the pressure in gas B is that the volume of gas B is half that of gas A. The question did not mention anything about the moles of each gas. However, since the pressure of each gas is shown to be directly related to the volume, it can be assumed that <u>the moles of gas A and B must be very similar.</u>*

**Question 3**
The moles of gas A is closest to

[✓ **A.**] 0.44 mol
**B.** 0.219 mol
**C.** 0.877 mol
**D.** Unable to be determined unless the identity of Gases A and B is known.

*Pressure of gas A in KPa = 2.0 x 101.3 = 202.6 KPa*

n (gas A) = $\frac{PV}{RT}$

$$= \frac{202.6 \text{ x } 5.0}{8.31 \text{ x } 278} = 0.4385 \text{ mol}$$

**Question 4**
Which of the following gases has a density of 1.78 g $L^{-1}$ at SLC conditions?

**A.** $O_2$
**B.** $N_2$
**C.** $CH_4$
[✓ **D.**] $CO_2$

*A gas with a density of 1.78 g $L^{-1}$ means that 1.0 L of the gas has a mass of 1.78 g. At SLC conditions 1.0 mole of any gas occupies a volume of 24.8 L. So if we can find the mass of 24.8 L of this gas, then we also have the mass of 1.0 mol of this gas.*

$$Density = \frac{mass}{volume}$$

$$1.78 = \frac{mass}{24.8}$$

*mass = 1.78 x 24.8 = 44.144g*

*Therefore 1.0 mol of this gas has a mass of 44.144 g.*

*Now we have to find which gas has a molar mass (mass of 1.0 mole) that is closest to 44.144 g $mol^{-1}$.*
*M ($CO_2$) = 12.0 + 2 x 16.0 = 44.0 g $mol^{-1}$*

**Question 5**

20 grams of He gas is blown into a rubber balloon. If the same mass of Ar gas is blown into another balloon at the same temperature and pressure, it is correct to say that the balloon containing Ar will be

**A.** at a volume equal to the balloon containing He.
**B.** at a volume greater than the balloon containing He.
**C.** at a pressure that is greater than the balloon containing He.
[✓ **D.**] at a volume that is less than the balloon containing He.

*The volume of each gas can be calculated using the ideal gas equation. The question stated that the temperature and pressure of each gas are the same. Therefore any values for temperature and pressure can be used as long as they are the same for each gas. In this case a pressure of 101.3 KPa and temperature of 278 K are used for both He and Ar.*

$n\ (He) = \frac{20}{4.0} = 5.0\ mol$ $\qquad$ $n\ (Ar) = \frac{20}{39.9} = 0.50\ mol$

$V\ (He) = \frac{nRT}{P}$ $\qquad$ $V\ (Ar) = \frac{nRT}{P}$

$V = \frac{5.0 \text{ x } 8.31 \text{ x } 278}{101.3}$ $\qquad$ $V = \frac{0.50 \text{ x } 8.31 \text{ x } 278}{101.3}$

$V = 114.03\ L$ $\qquad$ $V = 11.403\ L$

*It is useful to picture these 2 gases in a gas syringe. The gas with the smaller number of moles (Ar), will occupy a smaller volume in order to have the same pressure as He which has the greater number of moles. Since temperature and pressure are the same for these 2 gases, the gas with the greater number of moles will cause the plunger of a gas syringe to push out to a larger volume .*

**Question 6**

A gas syringe contains 100 mL of Ne gas at a pressure of 1.0 atm and temperature of 25 $^{0}$C.
If the temperature of the gas is raised to 50 $^{0}$C then

[✓ **A.**] the volume of the gas will increase.
**B.** the volume of the gas will decrease.
**C.** the volume and pressure of the gas will decrease.
**D.** the volume and pressure will both increase. *The pressure will not increase because the gas syringe will increase in volume and keep the pressure within the syringe constant.*

$\frac{P_1V_1}{T_1n_1} = \frac{P_2V_2}{T_2n_2}$ *Make $V_2$ the unknown in the equation*

*The pressure of the gas will be the same after the temperature is increased because the gas is in a gas syringe so its volume will change as the temperature changes. This will keep the pressure at 1.0* *atm as the increase in kinetic energy of the gas molecules is counteracted by the increase in volume of the gas syringe. The moles of the gas will not change as there is no mention of any gas being added or removed from the syringe. So the constant variables, P and n can be removed from the equation.*

$$\frac{\cancel{P_1}V_1}{T_1\cancel{n_1}} = \frac{\cancel{P_2}V_2}{T_2\cancel{n_2}}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 \text{ x } T_2}{T_1} = \frac{100 \text{ x } 323}{298} = 108.4 \text{ mL}$$

**Question 7**

Two bottles of gas, bottle Y and bottle Z are at the same temperature and volume.

Bottle Y contains 20 g of $O_2$
Bottle Z contains 20 g of $N_2$

When comparing the moles and pressure of each gas it is correct to say that

**A.** Bottle Y has more moles and a lower pressure.
[✓ **B.**] Bottle Z has more moles and a greater pressure.
**C.** Bottle Y has less moles and a greater pressure.
**D.** Bottles Y and Z have the same pressure but Z has the greater number of moles.

*Bottle Y:* $n(O_2) = \frac{20}{32.0} = 0.625$ mol

*Bottle Z:* $n(N_2) = \frac{20}{28.0} = 0.714$ mol

*Since the volume and temperature are the same, the only variable that will affect the pressure is the moles of each gas. As a result bottle Z will have the greater pressure due to the greater number of moles of gas present. This is illustrated by the general gas equation, PV=nRT. Any volumes and temperatures can be used as long as they are the same for each gas: 2 L and 25 $^0$C.*

*Bottle Y*

$$P = \frac{0.625 \text{ x } 8.31 \text{ x } 298}{2} = 774 \text{ KPa}$$

*Bottle Z*

$$P = \frac{0.714 \text{ x } 8.31 \text{ x } 298}{2} = 884 \text{ KPa}$$

**Question 8**
If 5.0 g of ethene gas ($C_2H_4$) has a pressure of 200 KPa, then the pressure of the same mass of butene gas ($C_4H_8$) at the same conditions of volume and temperature would be

**A.** 400 KPa
**B.** 200 KPa
[✓ **C.**] 100 KPa
**D.** 300 KPa

$n(C_2H_4) = \frac{5.0}{28.0} = 0.17857\ mol$

$n(C_4H_8) = \frac{5.0}{56} = 0.089286\ \text{mol}$

*Since the volume and temperature of each gas are the same, the only variable that will make the pressure of each gas different is the moles. The moles of the butene gas is half that of the ethene, therefore the pressure will also be half, 100 KPa.*

*This is illustrated by the general gas equation.*

$$P = \frac{n\ \cancel{R}\ \cancel{T}}{\cancel{V}}$$

*If R, T and V are the same for both butene and ethene, the only thing left in the equation that will affect the pressure is moles (n). So if the n for butene is half that of ethene, the pressure of butene will also be half that of ethene.*

**Question 9**
The molar volume of a gas in mL, that is at a temperature of 50 $^0$C and a pressure of 2.0 atm is

[✓ **A.**] $1.32 \times 10^4$
**B.** $6.1 \times 10^3$
**C.** $5.9 \times 10^4$
**D.** $2.45 \times 10^4$

*The term molar volume refers to the volume of one mole of a gas at a particular temperature and pressure. The volume of one mole of this gas can be calculated using PV=nRT.*

$$V = \frac{nRT}{P}$$

$$V = \frac{1.0 \times 8.31 \times 323}{202.6} = 13.2\ L = 1.32 \times 10^4\ mL$$

**Question 10**

What is the pressure exerted by 24.5 g of argon gas that has been placed in a 2.0 Litre container at a temperature of 125 $^0$C ?

**A.** 1.0 atm
**B.** 2.0 atm
[✓ **C.**] 10 atm
**D.** 20 atm

$n\ (Ar) = \frac{24.5}{39.9} = 0.61404\ mol$

$PV=nRT$

$P = \frac{nRT}{V}$

$P = \frac{0.61404 \text{ x } 8.31 \text{ x } 398}{2.0}$ =1,015 KPa divided by 101.3 = 10.02 atm

## Short Answer Questions

### Question 1

Calculate the mass of 10.0 L of $O_2$ gas at SLC conditions.

*At SLC conditions* $V = n \times 24.8$

$$n = \frac{V}{24.8} = \frac{10.0}{24.8} = 0.40323 \text{ mol}$$

$$m(O_2) = 0.40323 \times 32.0 = 12.903 = 12.9 \text{ g}$$

### Question 2

How many Litres of argon gas will fill up a gas syringe at SLC conditions if the mass of the gas is equal to 20.0 g?

$$n(Ar) = \frac{20.0}{39.9} = 0.50125 \text{ mol}$$

*at SLC conditions* $V = n \times 24.8$

$$V = 0.50125 \times 24.8 = 12.431 = 12.4 \text{ L}$$

### Question 3

An incandescent light globe of 50.0 mL volume operates at a temperature of 3,300 K. How many moles of inert gas will such a light bulb contain if the pressure within the bulb is to be maintained at 80.0 % of atmospheric pressure?

*80.0% of atmospheric pressure* $= 0.800 \times 101.3 = 81.04$ *KPa.*

$PV=nRT$

$$n = \frac{PV}{RT} = \frac{81.04 \times 0.050}{8.31 \times 3{,}300} = 1.45862962 \times 10^{-4} = 1.48 \times 10^{-4} \text{mol}$$

**Question 4**

A glass flask contains 16.0 g of oxygen gas at 30.0 $^0$C temperature and 2.00 atm pressure. What would be the molar mass of 15.0 g of a gas in a second identical flask that was at the same conditions of temperature and pressure?

*If the 15.0 g of a gas is at the same conditions of volume (the 2 flask are identical), temperature and pressure as the 16.0 g of oxygen, then according to PV=nRT the moles of both gases will be the same.*

$n = \frac{\cancel{P}\cancel{V}}{\cancel{R}\cancel{T}}$

$n\ (O_2) = \frac{16.0}{32.0}$ *= 0.500 mol. Therefore n (unknown gas) = 0.500 mol*

*Molar mass of unknown gas* $= \frac{mass}{moles} = \frac{15.0}{0.500} = 30.0\ gmol^{-1}$

# Chapter 4 Review Questions – Solutions

## Multiple Choice

**Question 1**
Magnesium metal will react to produce a salt only when it reacts with

[✓ **A.**] hydrochloric acid.
**B.** sodium hydroxide.
**C.** sodium carbonate
**D.** All of the above are correct.

**Question 2**
A solid substance is placed into a beaker containing sulfuric acid. A gas produced from this reaction is bubbled into a flask containing distilled water. The pH of the water is tested afterwards and is found to be below 7. This solid substance is

**A.** sodium hydroxide.
**B.** magnesium metal.
**C.** zinc metal.
[✓ **D.**] sodium carbonate powder.

*When a metal carbonate is added to an acid, salt, water and carbon dioxide gas are produced. The $CO_2$ reacts with water to produce carbonic acid ($H_2CO_3$):*
$H_2O + CO_2 \rightarrow H_2CO_3$
*The carbonic acid causes the pH of the water to drop below 7.*

**Question 3**
A post graduate chemistry student places a small solid pellet into a flask containing hydrochloric acid. A gaseous product of this reaction is allowed to pass into a gas syringe through a rubber hose connected to the flask. The syringe collects 11.2 mL of gas at SLC conditions. The mass of this gas is found to be 0.0010 g. The solid pellet that the student placed into the hydrochloric acid was

**A.** gold metal
[✓ **B.**] zinc metal
**C.** sodium hydrogen carbonate
**D.** potassium carbonate

*First of all find the moles of the gas:*

$V = n \times 24.8$

$$n = \frac{V}{24.8} = \frac{0.0112}{24.8} = 4.51613 \times 10^{-4} \text{ mol}$$

*Now find the molar mass of the gas:*

$$n = \frac{m}{M} \qquad M = \frac{m}{n} = \frac{0.0010}{0.000451613} = 2.21 \text{ gmol}^{-1}$$

*A and B are metals and would produce $H_2$ gas when placed in HCl. C and D are metal hydrogen carbonates and metal carbonates respectively and produce $CO_2$ when placed in HCl. As the molar mass of the gas is 2.21 gmol$^{-1}$. The answer must be either A or B as $H_2$ gas has a molar mass of 2.0 g mol$^{-1}$. It can't be A because gold is not a reactive metal and will not produce $H_2$ gas when mixed with HCl. Therefore the metal must Zn as it is a reactive metal.*

## Short Answers

### Question 1

Write out balanced equations for the following. States of matter must be shown.

**a.** Ethanoic acid is mixed with sodium hydroxide.

$CH_3COOH\ (aq)\ +\ NaOH\ (aq) \rightarrow CH_3COONa\ (aq)\ +\ H_2O\ (l)$

**b.** Sodium hydroxide pellets are placed in a beaker containing phosphoric acid.

$3NaOH\ (s)\ +\ H_3PO_4\ (aq) \rightarrow Na_3PO_4\ (aq)\ +\ 3H_2O\ (l)$

**c.** Sodium carbonate solution is mixed with sulfuric acid.

$Na_2CO_3\ (aq)\ +\ H_2SO_4\ (aq) \rightarrow Na_2SO_4\ (aq)\ +\ H_2O\ (l)\ +\ CO_2\ (g)$

**d.** Solid calcium hydroxide is placed in hydrochloric acid.

$Ca(OH)_2\ (s)\ +\ 2HCl\ (aq) \rightarrow CaCl_2\ (aq)\ +\ 2H_2O\ (l)$

**e.** Vinegar ($CH_3COOH$) is poured over marble chips (solid calcium carbonate).

$2CH_3COOH\ (aq)\ +\ CaCO_3\ (s) \rightarrow (CH_3COO)_2Ca\ (aq)\ +\ H_2O\ (l)\ +\ CO_2\ (g)$

### Question 2

Write out balanced equations for the following. States of matter must be shown.

**a.** $H_2SO_4\ (aq)\ +\ MgCO_3\ (s) \rightarrow$

$H_2SO_4\ (aq)\ +\ MgCO_3\ (s) \rightarrow MgSO_4\ (aq)\ +\ H_2O\ (l)\ +\ CO_2\ (g)$

**b.** $Fe_2O_3\ (s)\ +\ HNO_3\ (aq) \rightarrow$

$Fe_2O_3\ (s)\ +\ 6HNO_3\ (aq) \rightarrow 2Fe(NO_3)_3\ (aq)\ +\ 3H_2O\ (l)$

**c.** $NaOH\ (aq)\ +\ H_2SO_4\ (aq) \rightarrow$

$2NaOH\ (aq)\ +\ H_2SO_4\ (aq) \rightarrow Na_2SO_4\ (aq)\ +\ 2H_2O\ (l)$

# Chapter 5 Review Questions – Solutions

**Question 1**
During a chemical reaction 2 moles of A completely reacts with 3 moles of B to produce 1.5 moles of C. This reaction is represented by which equation?

**A.** $A + B \rightarrow C$
**B.** $2A + 3B \rightarrow C$
**C.** $4A + 6B \rightarrow 2C$
[✓ **D.**] $4A + 6B \rightarrow 3C$

*Find the ratio of the moles of A : B: C*

*A : B : C*
*2 : 3 : 1.5 (x2)*
*4 : 6 : 3 The coefficients in response D show this ratio.*

**Question 2**
Hydrogen gas reacts explosively with oxygen to produce water and a large amount of heat. The equation for this reaction is given below.

$2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$

A chemist mixes some hydrogen and oxygen gas together in a gas bottle and ignites the mixture with a spark. When the reaction is complete 5.0 mol of hydrogen gas remains unreacted and 10 mol of water are produced. Select the statement below which is consistent with the above information.

**A.** The hydrogen is the limiting reactant and the oxygen is in excess.
**B.** 5.0 mole of hydrogen has completely reacted.
**C.** 15 mol of hydrogen has completely reacted with 5.0 mole of oxygen.
[✓ **D**] 15 mol of hydrogen is mixed with 5.0 mole of oxygen.

*Since 5.0 mol of $H_2$ remains unreacted, $H_2$ must be the excess reactant. This eliminates response A. If 10 mol of water are produced, then 10 mol of $H_2$ and 5.0 mol of $O_2$ must have completely reacted eliminating responses B and C. Therefore response D is correct. Of the 15 mol present, 5.0 mol is in excess leaving 15 – 5 = 10 mol that reacted.*

**Question 3**
The dissociation of $KNO_3$ in water is described by the following equation.

$KNO_3\ (s) \rightarrow K^+\ (aq) + NO_3^-\ (aq)$

What is the concentration of $K^+$ ions when 1.0 g of $KNO_3$ dissociates on 2.0 L of water?

**A.** $1.0 \times 10^{-3}$ M
**B.** $1.0\ g\ L^{-1}$
[✓ **C.**] $4.9 \times 10^{-3}$ M
**D.** $39.1\ g\ L^{-1}$

$n\ (KNO_3) = \frac{1.0}{101.1} = 9.8912 \times 10^{-3} mol$

$n\ (K^+) = 9.8912 \times 10^{-3} mol$ $\qquad C\ K^+) = \frac{0.009812}{2.0} = 4.9 \times 10^{-3} M$

**Question 4**
What is the concentration of hydroxide ions remaining in solution when 25.0 mL of 0.30 M $Ba(OH)_2$ is mixed with 25 mL of 0.10 M $HNO_3$?

**A.** 0.050 M
**B.** 0.075 M
[✓ **C.**] 0.250 M
**D.** 0.125 M

| | *$Ba(OH)_2$ (aq)* | + | *$2HNO_3$ (aq)* | → | *$Ba(NO_3)_2$ (aq) + $2H_2O$ (l)* |
|---|---|---|---|---|---|
| *n (supplied)* | *n = 0.30 x 0.025<br>= 0.0075 mol* | | *n = 0.10 x 0.025<br>= 0.0025 mol* | | |
| *n (required) using ratio* | *0.0025 x ½<br>= 0.00125 mol* | | *0.0075 x 2<br>= 0.0150 mol* | | |

*n ($Ba(OH)_2$) unreacted = 0.0075 – 0.00125 = 0.00625 mol*

*When the 2 solutions are mixed together the final volume = 25.0 + 25.0 = 50.0 ml. Therefore the 0.00625 mol of unreacted $Ba(OH)_2$ is dissolved in 50 ml of solution.*

$C\ (Ba(OH)_2) = \frac{0.00625}{0.0500} = 0.125\ M$

$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

$C(OH^-)$ *unreacted = 2 x 0.125 = 0.250 M*

**Question 5**
28 g of calcium carbonate are reacted in a solution containing excess sulfuric acid. What volume of carbon dioxide gas will be collected at SLC conditions after the reaction has reached completion.

**A.** 0.24 L
**B.** 6.3 L
**C.** 2.7 L
[✓ **D.**] 6.9 L

$\underline{CaCO_3\ (s)} + H_2SO_4\ (aq) \rightarrow CaSO_4\ (aq) + H_2O\ (l) + \underline{CO_2\ (g)}$
*28 g* *x L*

$n\ (CaCO_3) = \frac{28}{100.1} = 0.27972\ mol$

$n\ (CO_2) = 0.27972\ mol$

*V = n x 24.8 = 0.27972 x 24.8 = 6.9371 = 6.9 L*

**Question 6**
Sulfur dioxide and oxygen react according to the following equation.

$2SO_2$ (g) + $O_2$ (g) → $2SO_3$ (g)

If 1.0 mole of $O_2$ and 0.50 mole of $SO_2$ are mixed together and allowed to react completely there will be

**A.** no reactants remaining.
**B.** no $O_2$ remaining and 1.0 mole of $SO_3$.
[✓ **C.**] 0.75 mole of $O_2$ and 0.50 mole of $SO_3$.
**D.** 0.75 mole of $O_2$ and 1.0 mole of $SO_3$.

| | *$2SO_2$ (g)* | + | *$O_2$ (g)* | → | *$2SO_3$ (g)* |
|---|---|---|---|---|---|
| *n (supplied)* | *0.50 mol* | | *1.0 mol* | | |
| *n (required) using ratio* | *1.0 x 2 = 2.0 mol* | | *0.50 x ½ = 0.25 mol* | | |

*Limiting reactant = $SO_2$*
*n ($O_2$) unreacted = 1.0 – 0.25 = 0.75 mol*
*n ($SO_3$) produced = n ($SO_2$) = 0.50 mol*

**Question 7**
When 5.0 L of $H_2$ gas is allowed to react with 5.0 L of $O_2$ gas, $H_2O$ gas is produced according to the following equation.

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (g)$

If the conditions of the reaction are kept at a constant 25 $^{0}$C and 760 mm Hg pressure, the resultant gaseous mixture will contain

**A.** 5.0 L of $H_2O$ and 2.5 L of $H_2$.
[✓ **B.**] 2.5 L of $O_2$ and 5.0 L of $H_2O$.
**C.** 2.5 L of $H_2O$ only.
**D.** 5.0 L of $H_2$, 5.0 L of $O_2$ and 5.0 L of $H_2O$.

*As the temperature and pressure of the gases remain constant during the reaction, the mole ratio in the balanced equation can be applied to the volumes of the gases.*

| | $2H_2 (g)$ | + | $O_2 (g)$ | → | $2H_2O (g)$ |
|---|---|---|---|---|---|
| *v (supplied)* | *5.0 L* | | *5.0 L* | | |
| *v (required) using ratio* | *5.0 x 2 = 10 mol* | | *5.0 x ½ = 2.5 mol* | | |

*Limiting reactant =* $H_2$
*v* $(H_2O)$ *= v* $(H_2)$ *= 5.0 L*
*Excess reactant =* $O_2$
*v* $(O_2)$ *remaining =5.0 – 2.5 = 2.5 L*

# Short Answers

**Question 1**

When exposed to heat calcium carbonate will decompose into calcium oxide and carbon dioxide gas.

$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$

**a.** What mass of CaO will be produced from the decomposition of 3.4 g of $CaCO_3$?

$\underline{CaCO_3\ (s)} \rightarrow \underline{CaO\ (s)} + CO_2\ (g)$

*3.4 g* *x g*

$n\ (CaCO_3) = \frac{3.4}{100.1} = 0.033967\ mol$

$n\ (CaO) = 0.033967\ mol$

$m\ (CaO) = 0.033967 \times 56.1 = 1.90555 = 1.9\ g$

**b.** What mass of $CaCO_3$ would have been decomposed if 25 mL of $CO_2$ was collected in a balloon with a pressure of 760 mm Hg at a temperature of 35 $^0$C?

$\underline{CaCO_3\ (s)} \rightarrow CaO\ (s) + \underline{CO_2\ (g)}$

*x g*

*25 mL = 0.025 L*

*760 mm Hg = 101.3 KPa*

$35\ ^0C + 273 = 308\ K$

$PV=nRT$

$n\ (CO_2) = \frac{PV}{RT} = \frac{101.3 \text{ x } 0.025}{8.31 \text{ x } 308} = 9.89459 \times 10^{-4}\ mol$

$n\ (CaO) = 9.89459 \times 10^{-4}\ mol$

$m\ (CaCO_3) = 9.89459 \times 10^{-4} \times 100.1 = \ = 0.0990448 = 0.099\ g$

**Question 2**

5.0 g of Al metal is placed in a 2.0 L flask containing $Cl_2$ gas at a pressure of 2.0 atm and temperature of 25 $^0$C. The product of the reaction is aluminium chloride.

**a.** Which reactant is in excess?

$2Al\ (s) + 3Cl_2\ (g) \rightarrow 2AlCl_3\ (s)$

| | 2 Al (s) | + | 3 $Cl_2$ (g) | → | 2 $AlCl_3$ |
|---|---|---|---|---|---|
| *n (supplied)* | $n = \frac{5.0}{27.0} = 0.1852$ mol | | $n = \frac{PV}{RT} = \frac{202.6 \text{ x } 2.0}{8.31 \text{ x } 298}$<br>$= 0.16363$ mol | | |
| *n (required) using ratio* | $\frac{2}{3}$ x 0.16363 =<br>0.109087 mol | | $\frac{3}{2}$ x 0.1852 = 0.2778 mol | | |

*Al is in excess.*

**b.** How many grams of the excess reactant will remain after the reaction?

*n (Al) in excess = 0.1852 – 0.109087 = 0.076113 mol*

*m (Al) = 0.076113 x 27.0 = 2.05505 = 2.1 g*

**c.** What mass, in grams, of $AlCl_3$ will be produced?

$n\ (AlCl_3) = n\ (Cl_2) \text{ x } \frac{2}{3}$

$= 0.16363 \text{ x } \frac{2}{3} = 0.10909$ mol

$m\ (AlCl_3) = 0.10909 \text{ x } 133.5 = 14.5635 = 15$ g

**Question 3**

What volume of 1.0 M NaOH in mL, would be required to completely react with a 50.0 mL solution containing $1.31 \times 10^{23}$ molecules of HCl?

$\underline{NaOH\,(aq)} + \underline{HCl\,(aq)} \rightarrow NaCl\,(aq) + H_2O\,(l)$
*1.0 M* *50.0 mL*
*x mL* $1.31 \times 10^{23}$ *molecules*

$n\,(HCl) = \frac{1.31 \times 10^{23}}{6.02 \times 10^{23}} = 0.21761$ *mol*

$n\,(NaOH) = 0.21761$ *mol*

$V = \frac{n}{c}$

$v\,(NaOH) = \frac{0.21761}{1.0} = 0.21761 = 0.21761 \times 1{,}000 = 217.61\ mL = 2.2 \times 10^2\ mL$

**Question 4**

$Cl_2$ gas was used as a chemical weapon during World War 1. Soldiers protected themselves from this poisonous gas by breathing through handkerchiefs that were soaked in urine. It is believed that the $NH_3$ in the urine reacted with the $Cl_2$ according to the equation:

$4NH_3 + 3Cl_2 \rightarrow NCl_3 + 3NH_4Cl$

If 5.0 L of $Cl_2$ is passed through a solution containing excess $NH_3$, what would be the change in pressure, in atm, of the 5.0 L of $Cl_2$ gas if the temperature throughout the reaction remained at 27 $^0$C ? The initial pressure of the $Cl_2$ gas was 2.0 atm.

*Since the 5.0 L of* $Cl_2$ *gas was passed though excess* $NH_3$*, all of the* $Cl_2$ *gas will react. If there is no* $Cl_2$ *gas left then the final pressure of the gas has to be 0 atm. The change in pressure is equal to:*

*Initial pressure – final pressure = 2.0 – 0 = 2.0 atm*

# Chapter 6 Review Questions – Solutions

## Multiple Choice

**Question 1**
Which of the following reactions is exothermic?

[✓ **A.**] $2CO \rightarrow CO_2 + C$ $\Delta H = -161\ KJ\ mol^{-1}$
**B.** $2H_2O \rightarrow 2H_2 + O_2$ $\Delta H = +570\ KJ\ mol^{-1}$
**C.** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ $\Delta H = +2800\ KJ\ mol$
**D.** $FeCl_2 \rightarrow Fe + Cl_2$ $\Delta H = +341.8\ KJ\ mol$

*All exothermic reactions have a negative* ΔH value.

**Question 2**
One mole of benzoic acid can be combusted to produce 1600 KJ of heat energy. What is the ΔH for this reaction if the balanced equation is

$2C_6H_5COOH + 15O_2 \rightarrow 14CO_2 + 6H_2O$

**A.** -1600 KJ/mol
**B.** - 3200 KJ/ mol$^{-1}$
**C.** 3200 KJ mol$^{-1}$
[✓ **D.**] -3200 KJ/mol

*The ΔH is the KJ of heat energy released by 2 mol of benzoic acid as the coefficient of $C_6H_5COOH$ is 2. Calculate by cross multiplying:*

*1 mol benzoic acid → 1600 KJ*
*2 mol benzoic acid* ***X***

***X*** *= 1600 x 2 = - 3200 KJ mol$^{-1}$. The negative sign is required since this is an exothermic reaction (all combustion reactions are exothermic.).*

**Question 3**
When 1.0 mol of methane gas undergoes complete combustion it releases 889 KJ of heat energy. At SLC conditions, what volume of methane gas would release twice this amount of heat energy?

[✓ **A.**] 49.6 L
**B.** 2.0 L
**C.** 44.8 L
**D.** 24.8 ?

*Twice the amount of heat energy = 889 x 2 = 1,778 KJ*

*1.0 mol methane → 889 KJ*
***X*** *mol methane → 1,778 KJ*

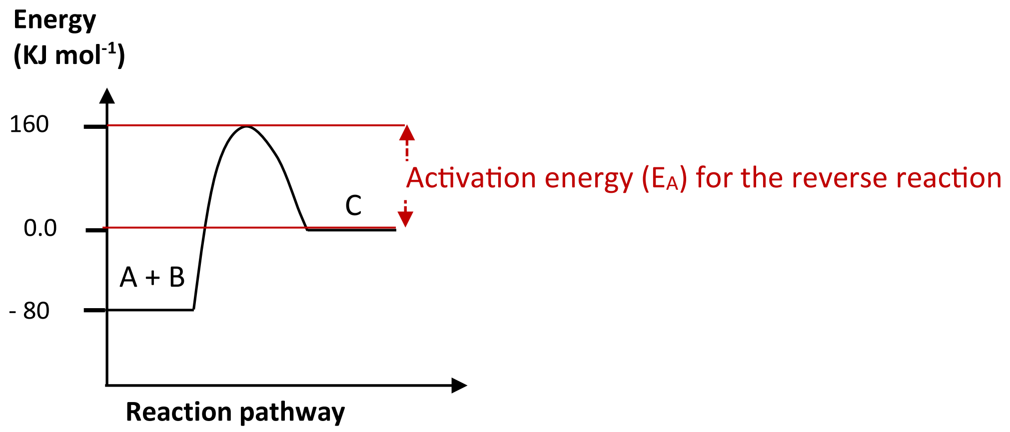
*at SLC: V = n x 24.8*
*V = 2.0 x 24.8 = 49.6 L*

***X*** *x 889 = 1.0 x 1,778*

$$X = \frac{1.0 \text{ x } 1{,}778}{889} = 2.0 \text{ mol}$$

**Question 4**

This energy profile shows the changes in energy that occur when the reactants A and B are converted into the product C.



If C is converted into A and B, the activation energy required for this reaction is equal to

[✓ **A.**] +160 KJ mol$^{-1}$
**B.** +80 KJ mol$^{-1}$
**C.** -80 KJ mol$^{-1}$
**D.** +240 KJ mol$^{-1}$

*C converted into A and B is the reverse of the reaction shown. Therefore the energy profile diagram will be the reverse of the one shown. The activation energy for the reverse reaction is shown on the graph and is equal to 160 – 0.0 = 160 KJ mol$^{-1}$. Activation energy is always a positive value.*

**Question 5**

When bonds are formed in the products of a chemical reaction, energy is released

**A.** during exothermic reactions only.
[✓ **B.**] during exothermic and endothermic reactions.
**C.** during endothermic reactions only.
**D.** only if the activation energy of the reaction is less than the difference in enthalpy between the reactants and products.

*When looking at the energy profile diagram of an endothermic or exothermic reaction from left to right, the line going down from the top of the hill to the enthalpy of the products always represents the energy released when bonds in the products form.*

## Short Answers

**Question 1**

Water can be produced from an explosive reaction between hydrogen gas and oxygen gas. The thermochemical equation for this reaction is shown below.

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g) \qquad \Delta H = -572\ \text{KJ mol}^{-1}$

**a.** How many Kilojoules of heat energy would be released if 25.0 g of oxygen gas completely reacted?

$$n\,(O_2) = \frac{25.0}{32.0} = 0.78125\ mol$$

$1.00\ mol\ O_2 \rightarrow 572\ KJ$
$0.78125\ mol\ O_2 \rightarrow \mathbf{X}\ KJ$

$$\mathbf{X} \times 1.00 = 0.78125 \times 572$$
$$\mathbf{X} = \frac{0.78125 \times 572}{1.00} = 446.875 = 447\ KJ$$

**b.** How many Kilojoules of heat energy would be released if 1.0 Kg of water was produced?

$$n\,(H_2O) = \frac{1 \times 10^3}{18.0} = 55.5556\ mol$$

$2.00\ mol\ H_2O \rightarrow 572\ KJ$
$55.5556\ mol\ H_2O \rightarrow \mathbf{X}\ KJ$

$$\mathbf{X} \times 2.00 = 55.5556 \times 572$$

$$\mathbf{X} = \frac{55.5556 \times 572}{2.00} = 15{,}888.9 = 1.6 \times 10^4\ KJ$$

**c.** How many kilojoules of heat energy would be released if 50.0 mL of $H_2$ gas was mixed with 100.0 mL of $O_2$ gas at SLC conditions?

- *Since the reaction is involving gases at constant temperature and pressure, the mole ratio given by the balanced equation can be applied to the volumes of the gases. The first thing that needs to be done is to calculate which reactant, $H_2$ or $O_2$ is the limiting reactant.*

| | **$2H_2$ (g)** | **+** | **$O_2$ (g)** | **→** | **$2H_2O$ (g)** |
|---|---|---|---|---|---|
| *v (supplied)* | 50.0 mL | | 100.0 mL | | |
| *v (required) using ratio* | 100.0 x 2<br>= 200.0 mL | | 50.0 x ½ = 25.0 mL | | |

- *The limiting reactant is $H_2$ since the volume supplied, 50.0 mL, is less than the volume required of 200.0 mL. Therefore 50.0 mL of $H_2$ fully reacts.*

$$n(H_2) = \frac{v}{24.8} = \frac{0.050}{24.8} = 2.01613 \times 10^{-3} \text{ mol}$$

$2.00$ mol $H_2 \rightarrow 572$ KJ
$2.01613 \times 10^{-3}$ mol $H_2 \rightarrow \mathbf{X}$ KJ

$$\mathbf{X} \times 2.00 = 2.01613 \times 10^{-3} \times 572$$

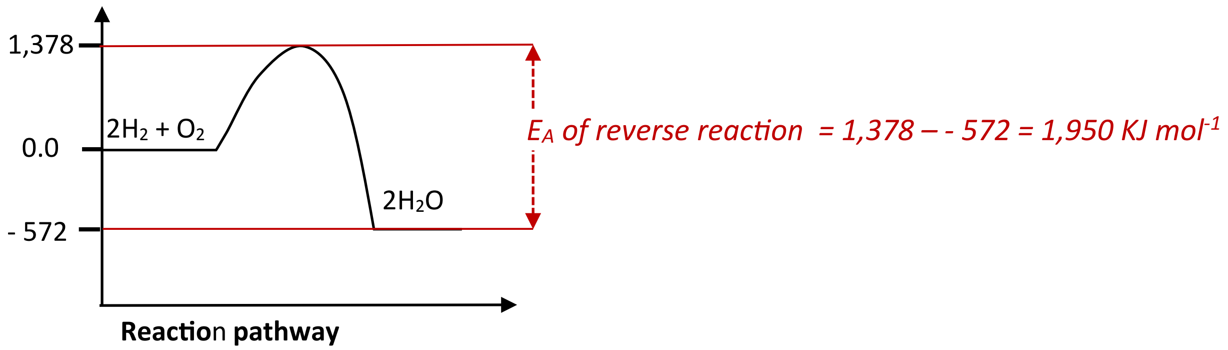
$$\mathbf{X} = \frac{0.0021613 \times 572}{2.00} = 0.61813 = 0.618 \text{ KJ}$$

**d.** Rewrite the above thermochemical equation if the heat of reaction was +286 KJ $mol^{-1}$.

- *As the heat of reaction is now a positive number, the original equation must be reversed. The value of the new heat of reaction, 286 KJ is half that of the original one, 572 KJ. Therefore the coefficients must be halved. Hence the thermochemical equation is*

$$H_2O(g) \rightarrow H_2(g) + \tfrac{1}{2} O_2(g) \qquad \Delta H = +286 \text{ KJ mol}^{-1}$$

**e.** Draw the energy profile diagram for the reaction described by the original equation if the activation energy of the reverse reaction is 1,950 KJ mol$^{-1}$. You must show and label the enthalpy of the reactants and products, the ΔH and the activation energy.



**f.** How would the ΔH of the reaction,

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

compare with the ΔH for the above (original) equation? You must explain your answer by referring to the equation showing the condensation of steam into liquid water:

$H_2O (g) \rightarrow H_2O (l)$ ΔH = -

*The ΔH for this reaction:*

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

*would be greater (more negative). The equation showing the condensation of steam into liquid water is an exothermic process as it has a negative* ΔH value. *Therefore when* $H_2O (g)$ *changes into* $H_2O (l)$ *some heat energy is given off which will make the overall heat energy released by the reaction*

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

*greater than the original reaction where the* $H_2O$ *produced is in gas form:*

$2H_2 (g) + O_2 (g) \rightarrow 2H_2O (g)$

**Question 2**

When Mg is dissolved into excess hydrochloric acid, the change in enthalpy is equal to 58.8 KJ $mol^{-1}$. How many mL of hydrogen gas would be produced at 405 $^0$C and pressure 2.0 atm if the reaction produced 215 KJ of heat energy?

$Mg\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + \underline{H_2\ (g)}$ $\quad \Delta H = -\ 58.8\ KJ\ mol^{-1}$

$2.0\ atm \times 101.3 = 202.6\ KPa$

$405 + 273 = 678\ K$

$V = ?\ mL$

*Calculate the moles of $H_2$ produced when 215 KJ of heat energy is produced by the reaction:*

$1.0\ mole\ H_2 \rightarrow 58.8\ KJ$

$\mathbf{X}\ mol\ H_2 \rightarrow 215\ KJ$

$\mathbf{X} \times 58.8 = 1.0 \times 215$

$$\mathbf{X} = \frac{1.0 \times 215}{58.8} = 3.65646\ \text{mol}$$

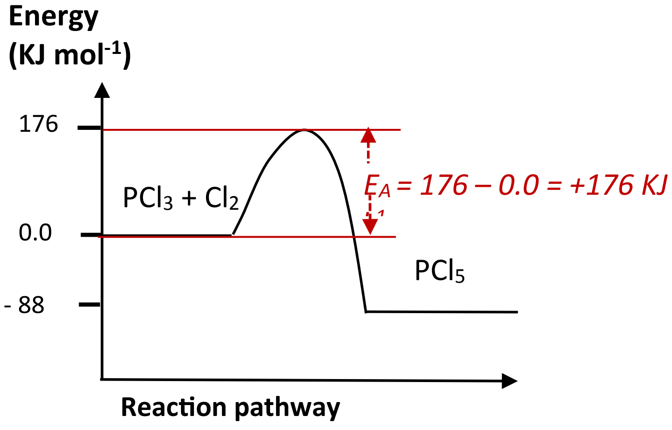
$PV = nRT$

$$V = \frac{nRT}{P}$$

$$V = \frac{3.65646 \times 8.31 \times 678}{202.6} = 101.6839\ L = 101{,}683.9\ mL = 1.0 \times 10^5 mL$$

**Question 3**

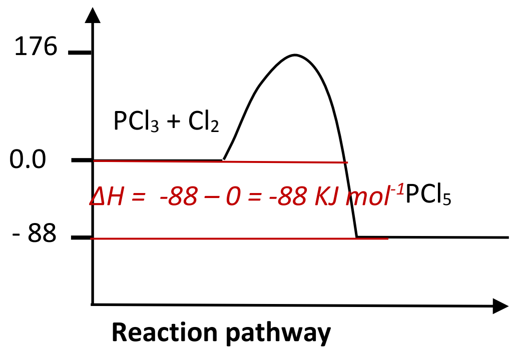
The energy profile shown below is for the formation of $PCl_5$ from $PCl_3$ and $Cl_2$.



**a.** What is the activation energy for the formation of $PCl_5$?

*Activation energy = 176 KJ $mol^{-1}$*

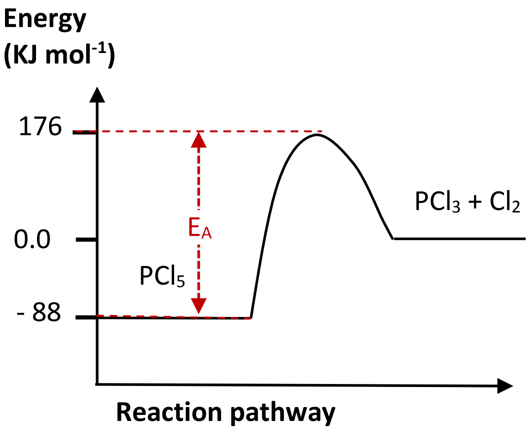
**b.** What is the ΔH for the formation of $PCl_5$?



*ΔH = -88 – 0.0 = -88 KJ mol$^{-1}$*

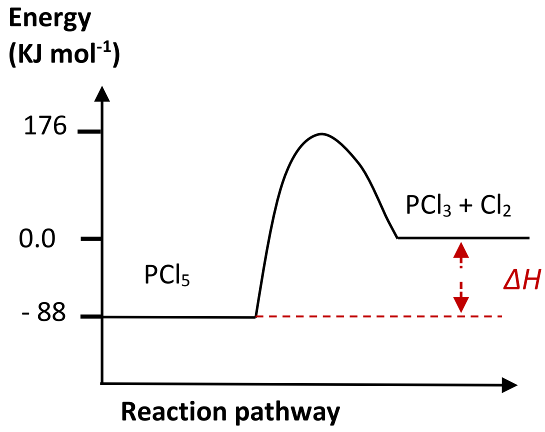
**c.** What is the activation energy for the formation of $PCl_3$ and $Cl_2$?

*This is referring to the reverse reaction so the energy profile diagram should be flipped around.*



*$E_A$ = 176 – -88 = 176 + 88 = +264 KJ mol$^{-1}$*

**d.** What is the ΔH for the decomposition of $PCl_5$?



*$\Delta H = 0 - -88 = 0 + 88$*
*$= 0 + 88 = +88$ KJ mol$^{-1}$*

- *The decomposition of $PCl_5$ just refers to the reverse of the original reaction given. So the decomposition of $PCl_5$ is the same equation for the formation of $PCl_3$ and $PCl_2$:*

$PCl_5 \rightarrow PCl_3 + Cl_2$

**e.** Are the covalent bonds stronger in 1 mol of $PCl_5$ or 1 mol of $PCl_3$ and 1 mol of $Cl_2$? Discuss.

*The activation energy for the reaction between $PCl_3$ and $Cl_2$ is 176 KJ mol$^{-1}$. This means that 176 KJ of energy are required to break the covalent bonds in 1 mole of $PCl_3$ and 1 mole of $Cl_2$.*

*The activation energy for the decomposition of $PCl_5$ is 264 KJ mol$^{-1}$. This means that 264 KJ of energy are required to break the covalent bonds in 1 mole of $PCl_5$.*

*Therefore the strength of the covalent bonds in 1 mol of $PCl_5$ are greater than the strength of the covalent bonds in 1 mol of $Cl_2$ and 1 mol of $PCl_3$ as more energy (activation energy) is required to break the bonds in 1 mol of $PCl_5$.*

**Question 4**

The gas used in stoves is mainly comprised of methane gas. A spark or flame is used to provide the activation energy for the combustion of methane gas to produce the heat that is needed for cooking food. The thermochemical equation for the combustion of methane gas is shown below.

$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \qquad \Delta H = -803\ KJ\ mol^{-1}$

Use this thermochemical equation to explain why the methane gas keeps burning even after the ignition source, the flame or spark, is taken away from the gas.

*The reaction between methane gas and oxygen releases heat energy as all combustion reactions are exothermic. The heat energy produced by the initially reacting* $CH_4$ *and* $O_2$ *molecules provides the activation energy required for other surrounding molecules to react. Therefore the heat energy from the flame or spark that initiated the reaction is no longer required to keep it going as the heat energy released by the reacting molecules provides the activation energy for the subsequently (later on) reacting particles.*

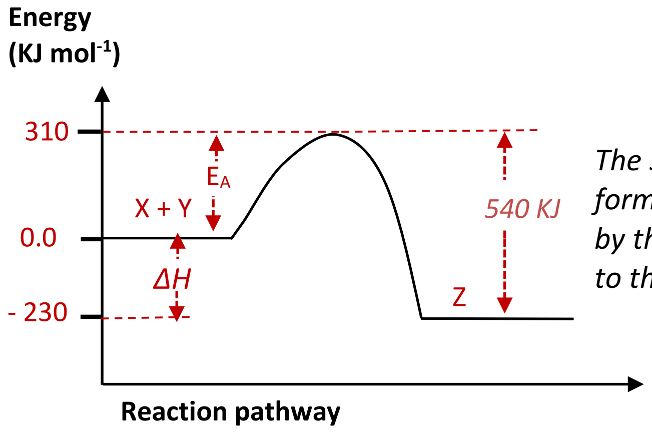
**Question 5**

When X and Y react to produce Z,

$X + Y \rightarrow Z$,

the energy produced during the formation of bonds in Z is equal to 540 KJ mol$^{-1}$ and the energy absorbed to break the bonds in X and Y is equal to 310 KJ mol$^{-1}$.

**a.** Draw the energy profile for this reaction. You must show the enthalpy of the reactants and products (give values) and the activation energy for the reaction. The **ΔH** and **activation energy** must be clearly labeled on your diagram.



*The 540 KJ of energy released during the formation of bonds in Z is shown on the graph by the line going down from the top of the hill to the enthalpy of Z.*

**b.** Write out the thermochemical equation for this reaction.

$X + Y \rightarrow Z \quad \Delta H = -230\ KJ\ mol^{-1}$

**Question 6**
Give the thermochemical equation for the combustion of butane if one mole of butane produces 2874 KJ of heat energy when completely combusted in oxygen.

*The thermochemical equation for the combustion of butane shows the balanced chemical equation and the ΔH for the reaction. The ΔH for this reaction will show the KJ of heat energy released by a number of moles of butane that is equivalent to its coefficient in the balanced equation.*

$C_4H_{10}\ (g) + 6.5\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 5\ H_2O\ (g) \qquad \Delta H = -2874\ KJ\ mol^{-1}$

*With the above equation there is no coefficient for* $C_4H_{10}$ *so the ΔH will show the KJ of heat energy released by 1 mole of butane.*

*If the coefficients are doubled, the thermochemical equation will be:*

$2\ C_4H_{10}\ (g) + 13\ O_2\ (g) \rightarrow 8\ CO_2\ (g) + 10\ H_2O\ (g) \qquad \Delta H = -5748\ KJ\ mol^{-1}$

*As the coefficient of* $C_4H_{10}$ *is 2, the ΔH must show the KJ of heat energy released by 2 moles of butane: 2 x 2874 = 5748 KJ.*

**Question 7**
How does the activation energy for the reaction,

$N_2 + 3H_2 \rightarrow 2NH_3$

compare with the activation energy for the reaction

$\frac{1}{2}\ N_2 + 1.5\ H_2 \rightarrow NH_3$.

Discuss your answer.

*The coefficients of the reactants and products in the first equation are double those in the second equation. Therefore the activation energy for the first equation will be double that of the second equation as twice as many moles of reactants are reacting. The bonds in 1 mol of* $N_2$ *and 3 mol of* $H_2$ *require twice as much energy to break as the bonds in ½ mol of* $N_2$ *and 1.5 mol of* $H_2$*.*

**Question 8**
Write out equations, including states, for the following:

**a.** the complete combustion of $C_7H_{16}$ (l)

$C_7H_{16}\ (l) + 11O_2\ (g) \rightarrow 7CO_2\ (g) + 8H_2O\ (g)$

**b.** The incomplete combustion of $C_5H_{12}$ (l) producing carbon monoxide.

$C_5H_{12}\,(l) + 5.5O_2\,(g) \rightarrow 5CO\,(g) + 6H_2O\,(g)$

*OR*

$2C_5H_{12}\,(l) + 11O_2\,(g) \rightarrow 10CO\,(g) + 12H_2O\,(g)$

**c.** The incomplete combustion of $C_4H_9OH$ (l) producing soot (C).

$C_4H_9OH\,(l) + 2O_2\,(g) \rightarrow 4C\,(s) + 5H_2O\,(g)$

# Chapter 7 Review Questions – Solutions

## Multiple Choice

**Question 1**
Which of the following fuels produces the largest quantity of greenhouse gases ($CO_2$)?

**A.** petrodiesel
[✓ **B.**] coal
**C.** natural gas
**D.** octane

**Question 2**
An environmental problem associated with the extraction of coal seam gas is

[✓ **A.**] the release of heavy metals into the water table
**B.** the clearing of large amounts of forests.
**C.** the production of acid rain.
**D.** the release of $CO_2$ into the atmosphere.

**Question 3**
Which fuel releases the most energy per gram of fuel combusted?

[✓ **A.**] natural gas
**B.** coal
**C.** petrodiesel
**D.** LPG

**Question 4**
Biofuels are less polluting than fossil fuels because they

**A.** are renewable.
**B.** are made from biomass.
**C.** don't produce $CO_2$ gas when combusted.
[✓ **D.**] are made either directly or indirectly from photosynthesis.

**Question 5**

A similarity between biodiesel and petrodiesel is that

**A.** they are both made from fats and oils.
**B.** they are both derived from crude oil.
**C.** they are both highly hydroscopic.
[✓ **D.**] they both have dispersion forces acting between adjacent molecules.

**Question 6**

Most of the electricity produced in Australia is from the conversion of the enthalpy in coal into electricity. During this conversion

**A.** chemical energy (enthalpy) is converted directly into electrical energy.
**B.** approximately 70% of the heat produced from the combustion in coal is converted directly into electricity.
**C.** about 30% of the chemical energy in coal is converted into heat.
[✓ **D.**] None of the above are correct.

**Question 7**

The COMPLETE combustion of all fossil fuels and biofuels produces

**A.** significant amounts of $CO_2$ and CO.
**B.** significant amounts of sulfur dioxide.
[✓ **C.**] NO and $NO_2$
**D.** CO.

## Short Answers

**Question 1**

Compare coal seam gas and biogas in terms of renewability, energy content and impact on the environment.

*Coal seam gas is mainly composed of* $CH_4$ *which has formed from the slow decomposition of organisms. That is, coal seam gas is non-renewable as it is a fossil fuel and therefore takes millions of years to be replaced.* $CH_4$ *from biogas is produced from the action of bacteria on animal and plant waste. Both the bacteria and animal/plant waste are constantly replenished by nature so methane sourced in this way is renewable.*

*The energy content coal seam gas is higher as it has a higher content of* $CH_4$*. Biogas is a mixture of* $CH_4$ *and* $CO_2$*. The proportion of* $CO_2$ *in a mixture of biogas is quite high which means that biogas will release less energy than an equivalent mass of coal seam gas which contains a higher proportion of* $CH_4$*.*

*The sourcing of coal seam gas through fracking has the potential to pollute drinking water, rivers and streams with toxic chemicals such as hydrocarbons and heavy metals. These chemicals can get transported by rain and the water table into the soil of farms. This contamination of soil and water poses a health risk to humans, other animals and plants. Land needs to be cleared in order to produce the animal and plant waste required for biogas production. This clearing of land can cause soil erosion which renders land infertile. The clearing of land also destroys the habitats of many plants and animals.*

**Question 2**

Butane ($C_4H_{10}$) has a heat combustion of 2874 KJ mol$^{-1}$. That is, the combustion of 1 mole of butane produces 2874 KJ of heat energy. Using this information calculate

**a.** the heat of reaction (ΔH) of butane.

$C_4H_{10}\,(g) + 6.5O_2\,(g) \rightarrow 4CO_2\,(g) + 5H_2O\,(g) \quad \Delta H = -2874\ KJ\ mol^{-1}$

*OR*

$2C_4H_{10}\,(g) + 13O_2\,(g) \rightarrow 8CO_2\,(g) + 10H_2O\,(g) \quad \Delta H = -5748\ KJ\ mol^{-1}$

**b.** the heat of combustion of butane in KJ/g.

The mass of 1.0 mol of $C_4H_{10}$ = 58.0 g (its molar mass)

*58.0 g* $C_4H_{10} \rightarrow$ 2874 KJ
*1.0 g* $C_4H_{10} \rightarrow$ ***X*** *KJ*

**X** *x 58.0 = 1.0 x 2874*

$$\boldsymbol{X} = \frac{1 \text{ x } 2874}{58.0} = 49.5517 = 49.6 \text{ KJ/g}$$

**c.** the energy content of butane in KJ $L^{-1}$ at SLC conditions.

*At SLC conditions 1 mole of $C_4H_{10}$ occupies 24.8 L.*

*Therefore 24.8 L of $C_4H_{10}$ releases 2874 KJ of heat energy.*

*24.8 L $C_4H_{10}$* → 2874 KJ
*1 L $C_4H_{10}$* → ***X*** *KJ*

**X** *x 24.8 = 1.0 x 2874*

$$\boldsymbol{X} = \frac{1 \text{ x } 2874}{24.8} = 115.887 = 116 \text{ KJ } L^{-1}$$

**Question 3**
Calculate the % of carbon present in a 50.0 g sample of brown coal if it produces 90.0 g of $CO_2$ when completely combusted.

*All of the $CO_2$ is produced from the combustion of carbon in the brown coal.*

$C\ (s) + O_2 \rightarrow \underline{CO_2\ (g)}$
*90.0 g*

$$n\ (CO_2) = \frac{90.0}{44.0} = 2.04545 \text{ mol}$$

*n (C) = 2.04545 mol*

*m (C) = 2.04545 x 12.0 = 24.5454 g*

*Therefore mass of C in 50.0 g of brown coal = 24.5454 g*

$$\%\ C \text{ in brown coal} = \frac{24.5454}{50.0} \text{ x } 100 = 49.0908 = 49.1\ \%$$

**Question 4**
The energy content of ethane ($C_2H_6$) is 51.9 KJ $g^{-1}$. Express this as

**a.** KJ $mol^{-1}$

$$\text{mole of 1 g of } C_2H_6 = \frac{1}{30.0} = 0.03333 \text{ mol}$$

*0.03333 mol $C_2H_6$ → 51.9 KJ*
*1 mol $C_4H_{10}$* → ***X*** *KJ*

**X** *x 0.03333 = 1.0 x 51.9*

$\mathbf{X} = \frac{1.0 \text{ x } 51.9}{0.03333}$ *= 1,557.1557 KJ = 1.56 x* $10^3$ *KJ* $mol^{-1}$

**b.** J $g^{-1}$

*1 g* $C_2H_6$ *releases 51.9 KJ*
*Therefore 1 g releases 51.9 x 1000 = 51,900 J = 5.19 x* $10^4$ *J* $g^{-1}$

**c.** MJ $Kg^{-1}$

*1 g* $C_2H_6 \rightarrow$ *51.9 KJ*
*1000 g (1 Kg)* $C_4H_{10} \rightarrow$ **X** *KJ*

**X** *x 1 = 1000 x 51.9*

$\mathbf{X} = \frac{1000 \text{ x } 51.9}{1}$ *= 51,900 KJ ÷ 1000 = 51.9 MJ = 51.9 MJ* $Kg^{-1}$

**Question 5**

Why are the combustion engines of motor vehicles so inefficient at converting chemical energy into kinetic energy?

*The chemical energy of the fuel in a combustion engine is firstly converted into heat energy. Heat energy is easily lost from the engine and escapes into the surrounding environment. As a consequence only a fraction of the heat energy released is available to be converted into kinetic energy.*

**Question 6**

When the $CO_2$ emissions of fuels are compared, it is usually done by comparing the mass of $CO_2$ produced per unit amount of energy produced. For example the grams of $CO_2$ produced per MJ of energy produced. Why is this better than comparing the mass of $CO_2$ produced per gram of fuel combusted? You should support your answer with calculations by referring to the following data:
*Heat of combustion of* $C_4H_{10}$ *= 49.6 KJ* $g^{-1}$
*Heat of combustion of* $C_{12}H_{22}O_{11}$ *= 16.5 KJ* $g^{-1}$

*Mass of* $CO_2$ *produced from the combustion of 1 gram of butane (*$C_4H_{10}$*):*

$\underline{C_4H_{10}} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$
*1 g*

$n(C_4H_{10}) = \frac{1}{58.0} = 0.0172414 \text{ mol}$

$n(CO_2) = 0.0172414 \times 4 = 0.0689656 \text{ mol}$

$m(CO_2) = 0.0689656 \times 44.0 = 3.0344 = 3.03\ g$

*Mass of $CO_2$ produced from the combustion of 1 gram of sucrose ($C_{12}H_{22}O_{11}$):*

$\underline{C_{12}H_{22}O_{11}}\ +\ 12O_2 \rightarrow 12CO_2\ +\ 11H_2O$
1 g

$n(C_{12}H_{22}O_{11}) = \frac{1}{342.0} = 0.00292398\ mol$

$n(CO_2) = 0.00292398 \times 12 = 0.0350878\ mol$

$m(CO_2) = 0.0350878 \times 44.0 = 1.5438632 = 1.54\ g$

*According to these calculations it appears as though sucrose is a much better fuel in regards to $CO_2$ emissions as it produces 1.54 g of $CO_2$ per gram of fuel combusted which is less than the 3.03 g of $CO_2$ released by the combustion of 1 gram of butane.*

*This is not a fair comparison however because the combustion of 1 gram of sucrose releases much less energy than the combustion of 1 gram of butane. So more sucrose needs to be combusted in order to obtain the same amount of energy as that produced from the combustion of butane. If more sucrose is combusted then of course a greater mass of $CO_2$ will be produced. It would be better to compare the grams of $CO_2$ produced for each MJ of energy released from the combustion of each fuel.*

*Mass (g) of $CO_2$ produced from each MJ produced from the combustion of $C_4H_{10}$:*

$\underline{C_4H_{10}}\ +\ 6.5O_2 \rightarrow 4CO_2\ +\ 5H_2O$ Heat of combustion = 49.6 KJ $g^{-1}$

Moles of 1 g of butane: $n(C_4H_{10}) = \frac{1}{58.0} = 0.0172414\ mol$

Heat energy produced from 0.0172414 mol of butane= 49.6 KJ

$n(CO_2) = 0.0172414 \times 4 = 0.0689656\ mol$

$0.0689656\ mol\ CO_2 \rightarrow 49.6\ KJ$
$\mathbf{X}\ mol\ CO_2 \rightarrow 1000\ KJ\ (1\ MJ)$

$\mathbf{X} \times 49.6 = 0.0689656 \times 1000$

$\mathbf{X} = \frac{0.0689656\ \times 1000}{49.6} = 1.390435\ mol$

$m(CO_2) = 1.390435 \times 44.0 = 61.179\ g$

*Therefore 61.179 g of $CO_2$ produced for each MJ of energy released.*

*61.2 g $CO_2$ / MJ*
*Mass (g) of $CO_2$ produced from each MJ produced from the combustion of $C_{12}H_{22}O_{11}$:*

$\underline{C_{12}H_{22}O_{11}}$ + $12O_2 \rightarrow 12CO_2 + 12H_2O$ *Heat of combustion = 16.5 KJ $g^{-1}$*

*Moles of 1 g of $C_{12}H_{22}O_{11}$:* $n\ (C_{12}H_{22}O_{11}) = \frac{1}{342.0} = 0.00292398$ *mol*

*Heat energy produced from 0.00292398 mol of $C_{12}H_{22}O_{11}$= 16.5 KJ*

$n\ (CO_2) = 0.00292398 \times 12 = 0.0350878$ *mol*

*0.0350878 mol $CO_2$ → 16.5 KJ*
***X** mol $CO_2$ → 1000 KJ (1 MJ)*

$\mathbf{X} \times 16.5 = 0.0350878 \times 1000$

$\mathbf{X} = \frac{0.0350878\ \ \text{x}\ 1000}{16.5} = 2.12653$ *mol*

$m\ (CO_2) = 2.12653 \times 44.0 = 93.5673$ *g*

*Therefore 93.5673 g of $CO_2$ produced for each MJ of energy released.*

*93.6 g $CO_2$ / MJ*

*So $C_{12}H_{22}O_{11}$ releases a lower mass of $CO_2$ for each gram of fuel produced, however, since $C_{12}H_{22}O_{11}$ releases less energy per gram than $C_4H_{10}$, a greater mass of $C_{12}H_{22}O_{11}$ must be combusted resulting in a greater mass of $CO_2$ produced for each MJ of energy produced.*

**Question 7**
Express the greenhouse gas emissions of propanol as Kg $CO_2$ / MJ if the combustion of 1 mole of propanol produces 2016 KJ of heat energy.

$C_3H_7OH + 4.5O_2 \rightarrow 3CO_2 + 4H_2O$

*$n\ (CO_2)$ produced from 1 mol of $C_3H_7OH$ = 3 x 1 = 3 mol*

*3 mol $CO_2$ → 2016 KJ*
$m\ (CO_2) = 3 \times 44.0 = 132$ *g*

*132 g $CO_2$ → 2016 KJ*
***X** g $CO_2$ → 1000 KJ (1 MJ)*

$\mathbf{X} \times 2016 = 132 \times 1000$

$$\mathbf{X} = \frac{132 \times 1000}{2016} = 65.4762\text{g } CO_2 = 0.0654762 \text{ Kg} = 0.0655 \text{ Kg } CO_2 / MJ$$

**Question 8**
The molecular formulae shown below are of fuels that can be used to power buses.

$C_{14}H_{30}$
$C_{17}H_{35}COOCH_2CH_3$

These buses are going to transport tourists to the snow fields in Victoria's alpine region during winter. Give the formula of the fuel which is best suited for the transportation needs described in this question. Discuss why this fuel is best suited.

*The formula of the best suited fuel is $C_{14}H_{30}$. This fuel has weaker intermolecular bonding than $C_{17}H_{35}COOCH_2CH_3$ since it has a lower mass and will form weaker dispersion forces. It also lacks the ester group (COO) which enables the other fuel to form stronger dipole-dipole bonds. The weaker intermolecular bonding and smaller molecular size of $C_{14}H_{30}$ makes it less viscous and better at flowing through fuel lines. This is particular important since the low temperature of Victoria's snow fields will increase the viscosity of all liquid fuels.*

**Question 9**
Compare petrodiesel and biodiesel in terms of

**a.** the impact their sourcing and combustion has on the environment.

*Petrodiesel is sourced from crude oil. It is possible for the crude oil to spill into the ocean while it is being extracted from under the ground through pipes and while it is transported by ships. Crude oil can destroy marine life and life on land if the oil spill reaches the shore. Petrodiesel is extracted from crude oil during fractional distillation. During this process the highly flammable components of crude oil can burn or explode. Fire and explosions can kill plants and animals in the immediate vicinity and the $CO_2$ released contributes to the longer term problem of global warming which is gradually destroying the habitats of many organisms on Earth. The combustion of petrodiesel also releases $CO_2$ which contributes to global warming. The sulfur present in petrodiesel can react with $O_2$ to produce $SO_2$. $SO_2$ is a respiratory irritant and can contribute to the production of acid rain which can destroy buildings and plants. The combustion of petrodiesel produces $NO_x$ which is a respiratory irritant and can contribute to acid rain. Another product of the combustion of petrodiesel is CO which is a highly toxic gas to most organisms.*

*Biodiesel is sourced from plants and animals which require land which needs to be cleared of trees and other vegetation resulting in the destruction of the habitat of plants and animals. The clearing of land can cause soil erosion which renders land infertile, sometimes for decades. Biodiesel is derived from photosynthesis so when it is combusted the $CO_2$ produced is just replacing the $CO_2$ that was removed from the air when the fuel was made during* *photosynthesis. As a consequence the combustion of biodiesel causes a very low increase in atmospheric $CO_2$ levels. As most biodiesel production involves energy derived from fossil fuels, there is a small increase in the level of $CO_2$ due to its use. Biodiesel has a low sulfur content so the emissions of $SO_2$ due to its combustion are very low. The combustion of biodiesel does produce $NO_x$. . Another product of the combustion of biodiesel is CO which is a highly toxic gas to most organisms.*

**b.** long term storage.

*Petrodiesel is made from non-polar hydrocarbon molecules which are not attracted to water. As a consequence petrodiesel has low hydroscopy and will not absorb significant amounts of water from the atmosphere while it is stored. Biodiesel however, has a polar ester group (COO) which is able to form hydrogen bonds with water. As a consequence biodiesel has high hydroscopy and can absorb water from the air while it is being stored. The water content of the biodiesel makes it harder to combust. The water in biodiesel can also produce mould which further diminishes its performance as a fuel. The mould can also damage the tanks used to store biodiesel. The water present in the biodiesel fuel can cause rust to form in storage tanks.*

**c.** the ease of movement of the fuels through fuel lines.

Petrodiesel is generally made from smaller molecules than biodiesel. It is also a fully non-polar substance so it only has weak dispersion forces as its intermolecular bonding. So petrodiesel has a lower viscosity than biodiesel. The viscosity of biodiesel is greater because its molecules are generally larger and can form stronger dispersion forces. The COO group in biodiesel further strengthens the intermolecular forces as it allows adjacent molecules to form dipole-dipole bonds which are stronger than dispersion forces. The greater viscosity of biodiesel means that it will not flow through fuel lines as easily as the less viscous petrodiesel.

**Question 10**

Explain why the combustion of all fuels produces nitrous oxides such as NO and $NO_2$.

*When all fuels are combusted, the heat produced provides the activation energy for the reaction between $N_2$ and $O_2$ which are naturally found in the air. So the products of this reaction, NO and $NO_2$ ($NO_x$) will always be produced when fuels are combusted.*

**Question 11**

A 2.5 gram sample of glucose ($C_6H_{12}O_6$) is completely combusted. The heat released from the reaction causes the temperature of 100 mL of water to increase from 10 $^0$C to 80 $^0$C. Calculate the energy content of the glucose in KJ g$^{-1}$

$m\ (H_2O) = d \times v = 0.997 \times 100 = 99.7$ g

$E = m\ (H_2O) \times 4.18 \times \Delta T$

*= 99.7 x 4.18 x 70 (80 – 10)*
*= 29,172.22 J = 29.17222 KJ*

*Therefore it can be concluded that when the 2.5 g of glucose was combusted 29.17222 KJ of heat was released.*

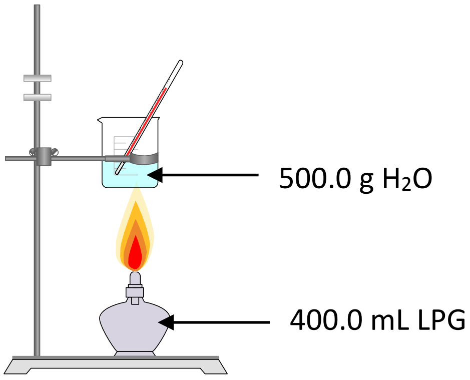
*2.5 g glucose → 29.17222 KJ*
*1 g → **X** KJ*

$\mathbf{X} \text{ x } 2.5 = 29.17222 \text{ x } 1$

$$\mathbf{X} = \frac{29.17222 \text{ x } 1}{2.5} = 11.6689\ KJ = 12\ KJ\ g^{-1}$$

**Question 12**

LPG is a mixture of propane and butane gas. 400.0 mL of LPG is combusted and the heat released by this reaction made the temperature of 500.0 g of water rise by 17.9 $^0$C. The apparatus used is shown below.



**a.** Calculate the number of KJ of heat absorbed by the 500.0 g of water.

*E = m ($H_2O$) x 4.18 x ΔT*
*= 500.0 x 4.18 x 17.9*
*= 37,411 J = 37.411 KJ*

**b.** Most of the heat energy released by the LPG does not get absorbed by the water. Where does this heat go to?

*This heat is lost to the surrounding air.*

**c.** If 35.0 % of the heat released is absorbed by the water, calculate the heat of combustion of the LPG in KJ/L.

*The 37.411 KJ of heat absorbed by the water represents 35.0 % of the total heat energy released by the LPG. Cross multiplication can be used to find the total amount of heat energy released (100 %) by the 400.0 mL of LPG.*

*37.411 KJ → 35.0 %*
***X** KJ → 100 %*

$\mathbf{X} \times 35.0 = 37.411 \times 100$

$\mathbf{X} = \frac{37.411 \text{ x } 100}{35.0} = 106.88857 \text{ KJ}$

*106.88857 KJ → 400.0 mL LPG*
***X** KJ → 1000 mL (1 L) LPG*

**X** x 400.0 = 106.88857 x 1000

$\mathbf{X} = \frac{106.88857 \text{ x } 1000}{400.0} = 267.2214 = 267 \text{ KJ/L}$

**d.** If 90.0 % of the volume of the LPG is propane, calculate the heat of combustion of the LPG in KJ/g if the 400.0 mL of LPG gas was at standard laboratory conditions before it was combusted.

*V (propane) in LPG =* $\frac{90.0}{100}$ *x 400.0 = 360 mL*

*n (propane) at SLC =* $\frac{V}{24.8} = \frac{0.360}{24.8}$ *= 0.0145161 mol*

*m (propane) = 0.0145161 x 44.0 = 0.6387084 g*

*V (butane) in LPG =* $\frac{10}{100}$ *x 400.0 = 40 mL*

*n (butane) at SLC =* $\frac{V}{24.8} = \frac{0.040}{24.8}$ *= 0.0016129 mol*

*m (butane) = 0.0016129 x 58.0 = 0.0935482 g*

*total mass of LPG = 0.6387084 g + 0.0935482 g = 0.7322566 g*

*0.7322566 g → 106.88857 KJ*
*1 g → **X** KJ*

**X** x 0.7322566 g = 106.88857 x 1

$\mathbf{X} = \frac{106.88857 \text{ x } 1}{0.7322566} = 145.97\text{J} = 146 \text{ KJ g}^{-1}$

**e.** Calculate the Kg of $CO_2$ produced per KJ of heat released (Kg $CO_2$ / KJ) from the combustion of the 400.0 mL of LPG.

$\underline{C_3H_8} + 5O_2 \rightarrow 3CO_2 + 4H_2O$

*n* $(C_3H_8)$ *in 360 mL = 0.0145161 mol*
*n* $(CO_2)$ *= 3 x 0.0145161 = 0.0435483 mol*
*m* $(CO_2)$ *= 0.0435483 x 44.0 = 1.91613 g*

$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$

*n* $(C_4H_{10})$ *in 40.0 mL = 0.0016129 mol*
*n* $(CO_2)$ *= 4 x 0.0016129 = 0.0064516 mol*
*m* $(CO_2)$ *= 0.0064516 x 44.0 = 0.2838704 g*

*Total mass of* $CO_2$ *formed from the combustion of 400.0 mL of LPG =*
*1.91613 g + 0.2838704 g = 2.2000 g*

*So the combustion of 400.0 mL of LPG produces 106.88857 KJ of energy and 2.2000 g of* $CO_2$*.*

*2.2000 g of* $CO_2$*.* → *106.88857 KJ*
***X g*** → *1 KJ*

**X** x 106.88857 KJ = 2.2000 x 1

$$\boldsymbol{X} = \frac{2.2000 \times 1}{106.88857} = 0.020582\ g = 2.05822 \times 10^{-5}\ Kg$$

*2.06 x* $10^{-5}$ *Kg* $CO_2$ */ KJ*

**Question 13**
Bioethanol is produced from the fermentation of the glucose that is produced by plants during photosynthesis. The equations showing the formation of bioethanol are shown below.

<u>photosynthesis</u>
$6CO_2\ (g) + 6H_2O\ (l) \rightarrow C_6H_{12}O_6\ (aq) + 6O_2\ (g)$

<u>Fermentation</u>
$C_6H_{12}O_6\ (aq) \rightarrow 2CO_2\ (g) + 2C_2H_5OH\ (aq)$

When the bioethanol is used as a fuel it is combusted in oxygen:

$C_2H_5OH\ (l) + 3O_2\ (g) \rightarrow 2CO_2\ (g)\ 3H_2O\ (g)$

**a.** Use the stoichiometry shown in these equations to show that the combustion of bioethanol is a **carbon neutral process.** That is, show that the combustion of bioethanol does not increase the levels of $CO_2$ in the Earth's atmosphere.

*From the photosynthesis equation,* ***6 moles of $CO_2$ are absorbed*** *from the atmosphere in order to produce* ***1 mole of glucose.*** *During fermentation* ***1 mole*** *of glucose* ***releases 2 moles of $CO_2$*** *into the atmosphere and* ***2 moles of $C_2H_5OH$*** *are also made. According to the ratio given by the balanced combustion equation, the combustion of* ***2 moles of $C_2H_5OH$ releases 4 moles of $CO_2$.***
*So the* ***6 moles of $CO_2$ removed*** *from the atmosphere during photosynthesis has been put back into the atmosphere –* ***2 moles of $CO_2$ produced during fermentation and 4 moles of $CO_2$ produced*** *during the combustion of ethanol.*

**b.** Explain why in practice, using bioethanol as a fuel does slightly increase the level of $CO_2$ in the atmosphere.

*During the production of bioethanol the combustion of fossil fuels such as coal are used to provide energy for the process. The combustion of fossil fuels raises the level of $CO_2$ in the atmosphere.*

**Question 14**
Discuss the impact that the activation energy of the combustion of a fuel has on the net (overall) amount of energy it can release.

*The higher the activation energy of a fuel the greater the amount of energy required to start the reaction. So when reactants are converted into products, a greater proportion of the heat energy released will need to be absorbed to provide the activation energy for subsequently reacting particles. This reduces the overall release of energy that can be used for the intended purpose such providing kinetic energy for a car.*

**Question 15**

Write out the thermochemical equation for the complete combustion of hydrogen gas.

*First of all write out the combustion equation for hydrogen gas.*

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$

*Now calculate the ΔH (molar enthalpy of combustion). From page 10 of the end of year data book, the molar heat of combustion of hydrogen is 282 KJ mol*$^{-1}$*. That is the combustion of 1 mole of hydrogen gas releases 282 KJ. Now find the heat energy released by 2 moles of* $H_2$ *as the coefficient of* $H_2$ *is 2 in the balanced equation.*

$1\ mol\ H_2 \rightarrow 282\ KJ$
$2\ mol\ H_2 \rightarrow \mathbf{X\ KJ}$

$\mathbf{X} \times 1 = 2 \times 282$

$$\mathbf{X} = \frac{2 \times 282}{1} = 564\ KJ\ mol^{-1}$$

*Now add the ΔH value to the equation in order to get the thermochemical equation.*

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g) \qquad \Delta H = -564\ KJ\ mol^{-1}$

*If the combustion equation used is:*

$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g)$

*The thermochemical equation is*

$H_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g) \qquad \Delta H = -282\ KJ\ mol^{-1}$

# Chapter 8 Review Questions – Solutions

## Multiple Choice

**Question 1**
Which of the following actions will not increase the number of times in a 1 second time interval that reactant molecules will collide with each other?

**A.** Increasing temperature and adding a catalyst.
**B.** Adding a catalyst and increasing concentration.
**C.** Increasing surface area.
[✓ **D.**] Adding a catalyst to gaseous mixture.

*A catalyst will lower the activation energy required for a reaction to occur. This will increase the number of collisions per second that will result in a chemical reaction but it will not increase the total number of collisions occurring each second as the catalyst does not make reactant particles move more quickly nor does it increase the amount of reactant particles. So a catalyst will increase the proportion of the particles present that are able to react but it doesn't change the original or total number of particles that are present.*

**Question 2**
When a mixture containing gaseous reactants is transferred to a container of smaller volume,

**A.** the number of particles present increases.
**B.** the total number of collisions remains the same but the frequency of successful collisions increases. *As the volume of the container is smaller the gas particles are more concentrated which increases the likelihood of all collisions – successful and unsuccessful.*
[✓ **C.**] the number of all collisions increases.
**D.** the energy of the particles increases. *Only heat will increase the energy of the particles.*

**Question 3**
When zinc granules are placed in 1.0 M $H_2SO_4$ solution, which of the following is not likely to increase the rate of the reaction?

**A.** Adding a catalyst.
[✓ **B.**] Capturing the gaseous product in a gas syringe at very high pressure. *This is irrelevant to the rate of the reaction as the reaction has already occurred when the gaseous product is captured in a gas syringe.*
**C.** Increasing the temperature of the $H_2SO_4$.
**D.** Grinding the zinc granules into smaller sized particles.

**Question 4**
Sulfur trioxide can be produced by the oxidation of $SO_2$. The equation for this reaction is shown below.

$2SO_2\ (g)\ +\ O_2\ (g)\ \rightarrow\ 2SO_3\ (g)$

If the temperature of the reaction mixture is increased from 300 $^{0}$C to 500 $^{0}$C, 2 major things will happen:

1. The number of collisions between particles each second increases.
2. The fraction of collisions with kinetic energy above the activation energy increases.

Of these 2 factors,

**A.** 2 is the only one that will increase the rate of the reaction.
**B.** 1 and 2 will increase the rate of reaction to an equal extent.
**C.** Both factors will cause an increase in the rate of the reaction but factor 1 has a greater impact on the increase in the reaction rate than factor 2.
[✓ **D.**] Both factors will cause an increase in the rate of the reaction but factor 1 has less of an impact on the increase in the reaction rate than factor 2.

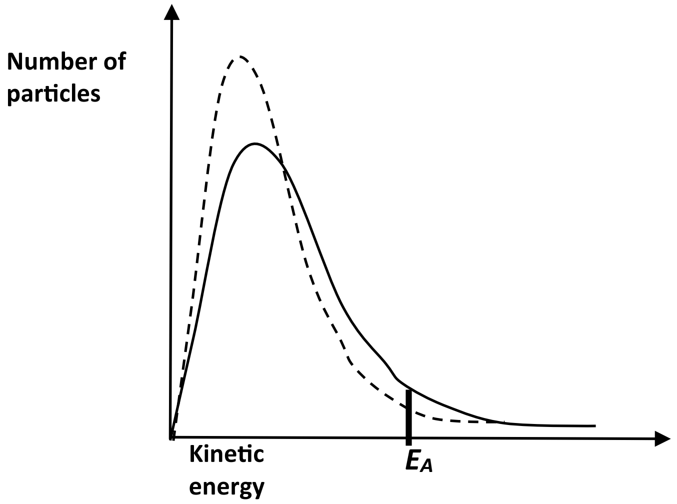
**Question 5**
The statement explaining the action of a catalyst that is incorrect is

**A.** Catalysts do not change the kinetic energy of particles.
**B.** Catalysts increase the proportion of fruitful collisions.
**C.** Catalysts can make reactant particles collide at angles that are more favourable for a chemical reaction.
[✓ **D.**] Catalysts increase the number of collisions per unit time.

*A catalyst will weaken the bonds in the reactant particles. This will not increase the number of collisions between particles (response D) but it will increase the number of or the proportion of the collisions which are able to result in a chemical reaction in a given amount of time.*

Refer to the information below when answering questions 6 and 7.

Each line on this graph shows the distribution of reactant particles with different kinetic energies at a particular temperature



**Question 6**

If the temperature of the particles shown by the broken line is 100 $^0$C, then the temperature of the particles shown by the solid line is

**A.** 50 $^0$C
[✓ **B.**] 150 $^0$C.
**C.** 100 $^0$C
**D.** could be 100 $^0$C or 50 $^0$C.

*The solid line shows a lower number of particles with low energy but a greater number of particles with higher energy. Therefore it must represent those particles at a higher temperature.*

**Question 7**

If a catalyst is added to the reaction mixture shown by the solid line,

**A.** the area under this line would increase. *The area under the line shows the number of particles present at a given temperature. A catalyst will not change the number of reactant particles present.*
**B.** the number of particles with higher kinetic energy would increase. *A catalyst does not give particles kinetic energy. Only an increase in temperature can do that.*
[✓ **C.**] the number of particles with sufficient kinetic energy to cause a reaction will increase. *The catalyst lowers the activation energy which means there will be a greater proportion of reactant particles present with sufficient kinetic energy to cause a reaction.*
**D.** the shape of the line would start to resemble the shape of the broken line.

## Short Answers

**Question 1**

Use collision theory to explain the following:

**a.** Wood chips will burn more quickly than a log of wood of the same mass.

*The woodchips represent the same mass as the log of wood but in a much greater surface area. In other words, if the log of wood was broken up into little wood chips a much greater area of its surface would be exposed to oxygen molecules during the combustion reaction. As a consequence the number of total collisions and hence successful collisions between oxygen and the wood chips is greater than those occurring between the oxygen and the log of wood.*

**b.** The decomposition of hydrogen peroxide,

$2H_2O_2 \rightarrow 2H_2O + O_2$

will only occur in the presence of an $MnO_2$ catalyst at room temperature.

*At room temperature (25 $^{0}$C) the collisions between $H_2O_2$ molecules are not strong enough to break covalent bonds and cause the decomposition reaction. The $MnO_2$ catalyst will weaken the bonds in the $H_2O_2$ resulting in fruitful collisions that lead to the decomposition of the $H_2O_2$ molecules.*

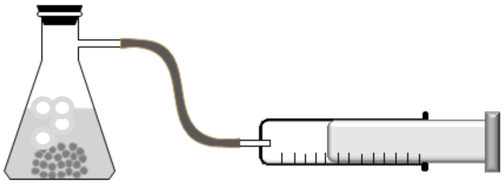
**c.** The souring of milk is much slower inside a fridge.

*The low temperatures inside a fridge will cause all particles to have low kinetic energy. This will result in a decrease in the frequency of successful collisions and a lower proportion of successful collisions between the reactant molecules that are causing the souring of the milk.*

**Question 2**

The apparatus shown below is used to measure the rate of the reaction between marble chips ($CaCO_3$) and 20.0 mL of 0.20 M HCl. The equation for this reaction is shown below.

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$



The $CO_2$ gas produced by the reaction is collected in a gas syringe at SLC conditions over a 5 minute period. The volume of $CO_2$ gas produced each minute during this time period is shown in the table below.

| Time (minutes) | Volume $CO_2$ (mL) |
|---|---|
| 0.0 | 0.0 |
| 1.0 | 5.0 |
| 2.0 | 9.0 |
| 3.0 | 12.0 |
| 4.0 | 14.1 |
| 5.0 | 14.1 |

**a.** Calculate the mass of $CaCO_3$ originally added to the flask. Assume that marble chips are pure $CaCO_3$ and that the HCl was in excess.

*After 4.0 minutes the maximum volume of $CO_2$ gas was produced. If this is converted into moles, stoichiometry can be used to calculate the moles of $CaCO_3$ that reacted. As the HCl was in excess, all of the $CaCO_3$ that was present in the flask reacted. Therefore the moles and mass of $CaCO_3$ that reacted is equal to the moles and mass of $CaCO_3$ that was present in the flask.*

*At SLC conditions V = n x 24.8*

$$n\ (CO_2) = \frac{V}{24.8} = \frac{0.0141}{24.8} = 5.68548 \times 10^{-4}\ mol$$

$$n\ (CaCO_3) = 5.68548 \times 10^{-4}\ mol$$

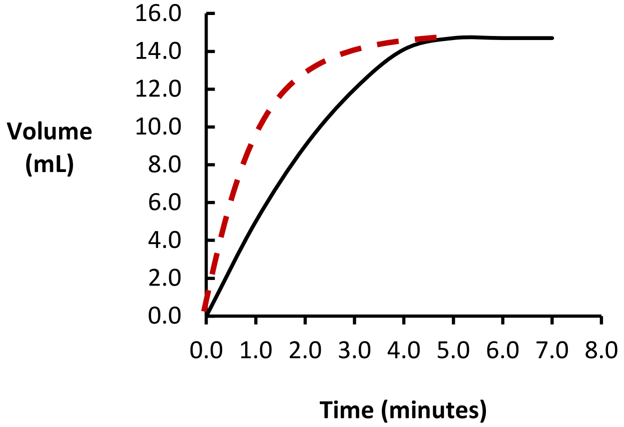
$$m\ (CaCO_3) = 5.68548 \times 10^{-4} \times 100.1 = 0.0569117 = 0.0569\ g$$

**b.** How did the rate of the reaction change during the 5 minute period of this reaction. Use collision theory to explain why the rate of the reaction changed in this way.

*The table shows that during the 5 minute time period of the reaction, the volume of $CO_2$ produced decreased with each passing minute. For example, after 1.0 minute 5.0 mL of $CO_2$ was produced, after 2.0 minutes an extra 4.0 mL of $CO_2$ was produced, after 3 minutes an extra 3.0 mL of $CO_2$ was produced etc. This shows that <u>the rate of $CO_2$ production and hence rate of reaction decreased during the 5 minute period of the reaction.</u>*

*This decrease in reaction rate was due to the fact that during the course of any reaction, the number of reactant particles decreases as they are converted into products. So during this reaction the number of $CaCO_3$ particles and concentration of HCl decreased resulting in a lowering in the frequency of successful collisions as the reaction progressed.*

**c.** The graph of the time versus volume of $CO_2$ for this reaction is shown below.



*The change in the graph is shown with a red dotted line. As the HCl is twice as concentrated (0.40 M) the rate of the reaction should be twice as fast. So the maximum volume of $CO_2$ should be produced in approximately half the amount of time as when 0.20 M HCl was used.*

The concentration of the HCl has been increased to 0.40 M. Draw a rough sketch of the graph using the axes above to show how the volume of $CO_2$ will change over time at this higher concentration.

**d.** Would the change in the rate of the reaction during the 5 minute period be the same if 40.0 mL 0.20 M HCl was used instead of 20.0 mL of 0.20 M HCl? You must support your answer with calculations.

*Initially the rate of both reactions would be the same as the concentrations are the same. As time goes by however, the concentration of the remaining HCl in the solution with the larger volume (40.0 mL) will be higher due to the fact that the initial moles were higher resulting in a higher concentration after the same number of moles have reacted. Therefore the reaction with the 40.0 mL of 0.20 M HCl will show a slower decrease in rate than the reaction with 20.0 mL of 0.20 M HCl.*

- ❖ *This is supported by the calculations below which show how the concentration of HCl decreases over time in both solutions. Let's assume that after 1.0 minute 0.0010 mol of HCl in both solutions has reacted. The calculations below show the concentrations of the HCl remaining in the 2 solutions after this time.*

| *20.0 mL of 0.20 M HCl* | *40.0 mL of 0.20 M HCl* |
|---|---|
| *n (HCl) initially present = C x V*<br>*= 0.20 x 0.020*<br>*= 0.0040 mol* | *n (HCl) initially present = C x V*<br>*= 0.20 x 0.040*<br>*= 0.0080 mol* |
| *n (HCl) reacted = 0.0010 mol* | *n (HCl) reacted = 0.0010 mol* |
| *n (HCl) remaining = 0.0040 – 0.0010*<br>*= 0.0030 mol* | *n (HCl) remaining = 0.0080 – 0.0010*<br>*= 0.0070 mol* |

*C (HCl) remaining* = $\frac{0.0030}{0.020}$ = *0.15 M*    *C (HCl) remaining* = $\frac{0.0070}{0.040}$ = *0.175 M*

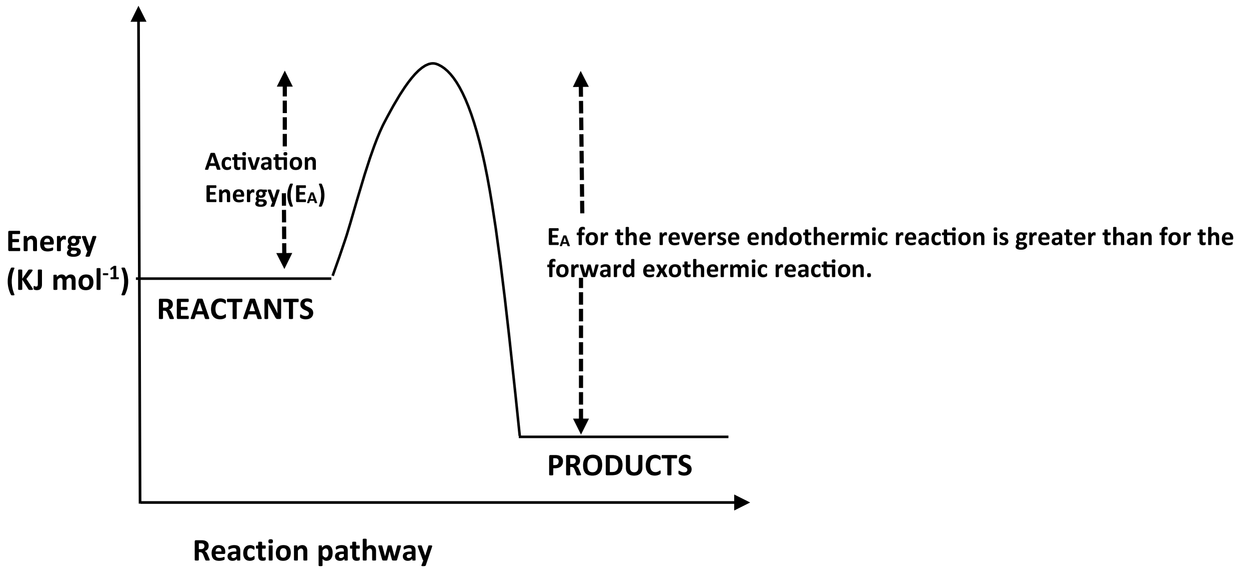
- *These calculations show that after 1.0 minute the concentration of the 20.0 mL solution has decreased from 0.20 M to 0.15 M and the concentration of the 40.0 mL solution has decreased from 0.20 M to 0.175 M. The concentration of the 40.0 mL solution is higher because the initial number of moles present was higher. Now the rate of the reaction of the 40.0 mL solution will be faster due to the higher concentration. The decrease in concentration of the 40.0 mL solution (0.20 to 0.175 M) is lower than for the 20.0 mL solution (0.20 to 0.15 M), therefore its rate of reaction with the* $CaCO_3$ *will decrease at a lower rate than for the 20.0 mL solution.*

**e.** Briefly describe another procedure that could be used to measure the rate of this reaction over a 5 minute period.

*Have the reaction between the* $CaCO_3$ *and the HCl occur in a flask that has been placed on an electronic balance. As the reaction proceeds the mass of the flask will decrease due to the loss of* $CO_2$ *gas. Now the rate of the reaction can be analysed in terms of the loss of mass due to the loss of* $CO_2$ *over time.*

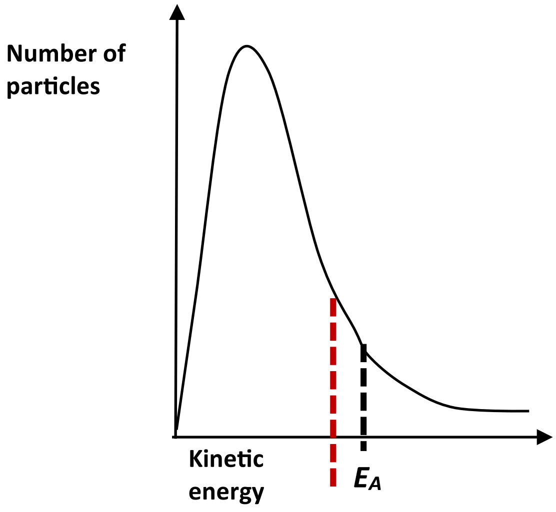
**f.** The activation energy of this reaction is less than the activation energy for the reverse reaction. Explain how this information can be used to justify that the temperature of this reaction mixture will increase during the 5 minute period.

*This shows that the reaction is exothermic. When viewing an energy profile diagram of an exothermic reaction (shown below), the activation energy for the forward exothermic reaction will always be lower than the activation energy for the endothermic reverse reaction. If the reaction is exothermic, heat energy will be released and the temperature of the reaction mixture will increase.*



**Question 3.**

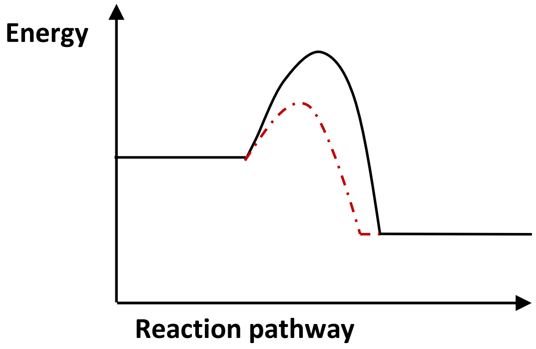
The distribution of the kinetic energy of particles of a reaction mixture at 120 $^0$C is shown below.



**a.** Make changes to this graph that would be consistent with the addition of a catalyst to the reaction mixture. Use the graph and the changes you made to explain the effect that the catalyst will have on the rate of the reaction.

*The changes to the graph have been shown with a red dotted line. When a catalyst is added the activation energy required to start the reaction will decrease. Therefore molecules with lower kinetic energy are now able to react. As a consequence a greater number of reactant particles within the reaction mixture have the necessary kinetic energy to cause fruitful collisions. Now the rate of reaction will increase due to an increase in the proportion of collisions that have sufficient kinetic energy to break bonds and cause a reaction.*

**b.** The energy profile diagram for this reaction in the ABSENCE of a catalyst is shown below.



Make the necessary changes to this diagram to show the effect of a catalyst on the energy profile of the reaction.

*Changes are shown with the red dotted line.*

**g.** A year 12 chemistry student looking over the results of this experiment stated that the volumes of $CO_2$ gas obtained at 4.0 minutes and 5.0 minutes were precise as they were both 14.1 mL. Do you agree with this student? Discuss. *You may need to refer to appendix 4.*

*No. Even though the 2 volumes are both 14.1 mL they are not precise results because they are different measurements. One value is for the volume of $CO_2$ gas at 4.0 minutes and the other is for the volume of $CO_2$ gas at 5.0 minutes. For results to be precise they must be close in value and for the same measurement. So if this experiment was repeated a second time using identical conditions and a volume 14.1 mL (or close to 14.1 mL) of $CO_2$ gas was obtained for a second time after 4.0 minutes, then the 2 pieces could be classified as precise.*

**h.** Give the dependent and independent variables for this experiment.

*Independent variable = time (minutes)*
*Dependent variable = volume of $CO_2$ (mL)*

**i.** What is meant by the term, **valid results.** Give 3 variables that would need to be controlled in order to ensure the validity of the results if the procedure was performed multiple times.

*Results are valid if they are caused by a single independent variable that was chosen prior to the experiment.*

*Any 3 controlled variables include – temperature of HCl solutions, surface area of marble chips, volume of HCl, concentration of HCl, pressure of the atmosphere in the lab and volume of the flask.*

**j.** Before this experiment was performed it was hypothesised that the volume of $CO_2$ gas produced over time would increase due to the increase in frequency of collisions between $CaCO_3$ and HCl particles. Comment on the accuracy of this hypothesis by referring to **collision theory.**

*This hypothesis is not very accurate. The increase in the volume of $CO_2$ over time is due to the fact that more $CaCO_3$ had reacted with increasing time. Over time the increase in collisions between $CaCO_3$ and HCl particles is actually getting lower. As the reaction between $CaCO_3$ and HCl proceeds, the number of $CaCO_3$ particles decreases and the concentration of HCl particles decreases resulting in a decrease in the frequency of total collisions and successful collisions over time.*

# Chapter 9 Review Questions – Solutions

## Multiple Choice

**Question 1**
This equilibrium expression,

$$K = \frac{[A] \times [B]^3}{[C]^2}$$

belongs to the equation

**A.** $A + 3B \rightleftharpoons 2C$
[✓ **B.**] $2C \rightleftharpoons A + 3B$
**C.** $\frac{1}{2}A + 1\frac{1}{2}B \rightleftharpoons C$
**D.** A and C are both correct.

**Question 2**
Consider the equation,

$$a\,Y \rightleftharpoons b\,X + c\,Z$$

If the value of K is 125 M, the values of *a, b and c* are respectively

**A.** 1,2 and 3
**B.** 2, 1 and 1
[✓ **C.**] 2, 1 and 2
**D.** 2, 2 and 2.

*There are no concentrations of Y, X or Z given so it is impossible to calculate the K value of 125. All that can be done is to find the combination of coefficients (a, b and c) that will give the units of "M" for K. The only combination that works is C:*

$$2Y \rightleftharpoons X + 2Z$$

$$\frac{[X] \times [Z]^2}{[Y]^2} = \frac{M \times M^2}{M^2} = \frac{M^3}{M^2} = M^{3-2} = M$$

**Question 3**

2.0 mol of hydrogen iodide decomposes in a 1.0 L vessel according to the equation:

$2HI \rightleftharpoons H_2 + I_2$

What is the equilibrium constant for this reaction if 0.50 mol of $I_2$ is present at equilibrium?

**A.** 4
[✓ **B.**] 0.25
**C.** 2.0
**D.** 0.17

| | $2HI \quad \rightleftharpoons$ | $H_2 \quad +$ | $I_2$ |
|---|---|---|---|
| *n (initial)* | *2.0 mol* | *0* | *0* |
| *n (reacted/produced)*<br>(↓) (↑) | *0.50 x 2 = 1.0 mol* ↓ | *0.50* ↑ | *0.50* ↑ |
| *n (equilibrium)* | *2.0 – 1.0 = 1.0 mol* | *0 + 0.50 = 0.50 mol* | *0 + 0.50 = 0.50 mol* |
| *[equilibrium]* $C = \frac{n}{V}$ | $\frac{1.0}{1.0} = 1.0\ M$ | $\frac{0.50}{1.0} = 0.50\ M$ | $\frac{0.50}{1.0} = 0.50\ M$ |

$$K = \frac{[H_2] \times [I_2]}{[HI]^2}$$

$$K = \frac{0.50 \times 0.50}{1.0^2} = 0.25$$

*Questions 4, 5 and 6 refer to the following equilibrium reaction.*

$4HCl\ (g) + O_2\ (g) \rightleftharpoons 2H_2O\ (g) + 2Cl_2\ (g)$

$K = 1.98 \times 10^3$ *at 105* $^0$*C*

**Question 4**
The equilibrium expression for this reaction is

[✓ **A.**] $$\frac{[H_2O]^2 \times [Cl_2]^2}{[HCl]^4 \times [O_2]}$$

**B.** $$\frac{HCl]^4 \times [O_2]}{[H_2O]^2 \times [Cl_2]^2}$$

**C.** $$\frac{H_2O] \times [Cl_2]}{[HCl] \times [O_2]}$$

**D.** $$\frac{2[H_2O] \times 2[Cl_2]}{4[HCl] \times [O_2]}$$

**Question 5**
A mixture of these gases at equilibrium is immersed into a container holding 100 mL of hot water. As a result the temperature of the mixture of gases increases from 20 $^0$C to 90 $^0$C. When the system regains equilibrium at the new temperature, the number of molecules in the mixture has *decreased.* It can be concluded that

**A.** the reaction is exothermic.
**B.** the reduction in the number of molecules caused a net forward reaction to occur.
**C.** the reaction opposed the increase in temperature by shifting towards the reactants.
[✓ **D.**] the reverse reaction produces heat.

*The decrease in the number of molecules indicates that a net forward reaction has occurred in response to the increase in temperature. A net forward reaction will turn 5 molecules of gas (4HCl and* $O_2$*) into 4 molecules (*$2H_2O + 2Cl_2$*). The reaction has opposed the increase in temperature by shifting forwards, therefore the forward reaction absorbs heat and is endothermic. Therefore the reverse reaction will release heat as it is exothermic.*

**Question 6**

At 105 $^0$C, the equilibrium constant for the reaction,

$4H_2O\ (g) + 4Cl_2\ (g) \rightleftharpoons 8HCl\ (g) + 2O_2\ (g)$

is

**A.** 0.000505
[✓ **B.**] $2.6 \times 10^{-7}$
**C.** $3.9 \times 10^{6}$
**D.** 0.00101

*This equation was produced by reversing the original equation and multiplying the coefficients by 2. Therefore the equilibrium constant for this equation will be the reciprocal (caused by reversing the original equation) and the square (caused by multiplying the coefficients by 2) of the original equilibrium constant.*

$$K = \left(\frac{1}{1.98 \times 10^3}\right)^2 = 2.6 \times 10^{-7}$$

**Question 7**

An empty gas jar is filled with 2.0 mol of $H_2$ and 2.0 mol of $Cl_2$ gas. The 2 gases are allowed to form an equilibrium mixture according to the following equation.

$H_2\ (g) + Cl_2\ (g) \rightleftharpoons 2HCl\ (g)\ \ \Delta H < 0$

As the reaction approaches equilibrium

**A.** the moles of HCl produced will always be double the moles of $Cl_2$ remaining.
**B.** the pressure in the gas jar will be increased.
[✓ **C.**] the moles of $Cl_2$ remaining will equal the moles of $H_2$ remaining.
**D.** the concentration fraction will always be greater than the K value for the reaction.

*The $H_2$ and $Cl_2$ react in a 1 to 1 ratio, so the moles of $H_2$ and $Cl_2$ that react as the system approaches equilibrium will always be the same. The moles of each gas remaining is calculated by subtracting the moles reacted from 2.0 moles (initial moles of each gas), therefore the moles of each gas remaining as the system approaches equilibrium will be the same.*

*Response D is incorrect because as the system approaches equilibrium, the concentration fraction will always be increasing because as reactants are converted into products, the concentration of products will always increase and the concentration of reactants will always decrease until the K value is eventually reached. So the concentration fraction will never equal K.*

**Question 8**
When the temperature of the equilibrium system,

$2NO\,(g) + Cl_2\,(g) \rightleftharpoons 2NOCl\,(g)\ \ \Delta H = -39\ KJ\ mol^{-1}$

is increased,

[✓ **A.**] the rate of the forward reaction increases.
**B.** the rate of the forward reaction decreases.
**C.** the proportion of reactants to products decreases.
**D.** the pressure decreases.

*When the temperature of any equilibrium reaction is increased, the rate of both the forward and reverse reaction will increase. Response B may initially seem like the correct answer because the increase in temperature will cause a net back reaction as the reaction is exothermic. That doesn't mean that the forward reaction has slowed down. Both reactions have increased in rate but the rate of the reverse reaction has increased by a greater amount which causes the net back reaction.*

**Question 9**
Unsaturated hydrocarbon molecules are produced by a process known as *cracking.* This process involves the thermal decomposition of saturated molecules. An example of a cracking reaction is shown below.

$C_5H_{12}\,(g) \rightleftharpoons C_5H_{10}\,(g) + H_2\,(g)\ \ \Delta H = +\text{ value}$

The conditions that would not favour a high yield of $C_5H_{10}$ include

**A.** using a catalyst, low pressure and high temperature.
[✓ **B.**] cooling the product mixture.
**C.** using a catalyst and low pressure.
**D.** increasing the volume of the reaction mixture.

*As $C_5H_{10}$ is a product, the conditions that will favour a high yield of $C_5H_{10}$ are those that will cause the reaction to shift in the forward direction. This reaction is endothermic so cooling the product mixture will result in a back reaction as this will oppose the decrease in temperature by producing heat. All of the other changes will increase the yield of $C_5H_{10}$ as they will cause a net forward reaction.*

**Question 10**
An equilibrium reaction is represented by the equation

$A(g) + 2B(g) \rightleftharpoons A_2B(g) \qquad K = 10^{-7}\ M^{-2}$

When 1.0 mol of A is allowed to react with 3.0 mol of B, the moles of $A_2B$ produced would be expected to be

**A.** 2.0 mol
**B.** 1.0 mol
[✓ **C.**] Less than 1.0 mol
**D.** 4.0 mol

*If this reaction was a complete reaction where all of the limiting reactant is converted into products, 1.0 mol of $A_2B$ would be produced. The 1.0 mol of A is the limiting reactant so 1.0 mol of $A_2B$ will be produced as the mole ratio of A : $A_2B$ is 1 : 1.*

*As this is an equilibrium reaction however, not all of the 1.0 mol of A will be converted into products so the mole of $A_2B$ produced at equilibrium will be less than 1.0 mol.*

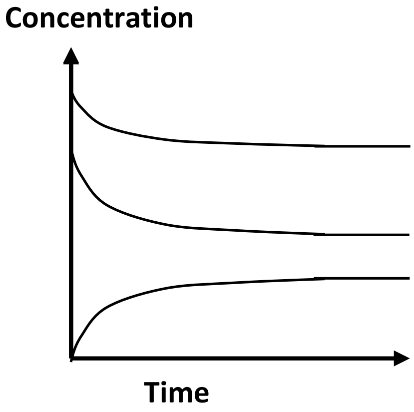
**Question 11**
The rate of an exothermic reaction will ALWAYS increase when

**A.** the temperature is decreased and a catalyst is employed.
**B.** When the pressure is increased and the temperature decreased.
**C.** the pressure is decreased and heat allowed to escape from the system.
[✓ **D.**] the pressure is increased and the temperature increased.

*A common error with this type of question is to confuse increasing the rate of a reaction with increasing the yield of products (causing a net forward reaction to occur). Increasing the temperature of an exothermic reaction will cause a net back reaction to occur but the rate of the forward reaction will be faster than before the temperature was increased. The net back reaction occurs due to the fact that the increase in the rate of the reverse reaction is greater as the system is favouring the back reaction as it is endothermic and will absorb some of the extra heat. So when the temperature of an exothermic reaction is increased, the rate of both the forward and reverse reactions will increase, but the increase in the reverse reaction will be greater.*

**Question 12**

Consider the graph below which shows how the concentration of reactants and products change when a reaction approaches equilibrium.



The reaction represented by this graph is

[✓ **A.**] $N_2 + 3H_2 \rightleftharpoons 2NH_3$
**B.** $S + O_2 \rightleftharpoons SO_2$
**C.** $H_2 + O_2 \rightleftharpoons 2H_2O$
**D.** $2HI \rightleftharpoons H_2 + I_2$

*The graph shows that the reaction has either 2 reactants or 2 products. This is evident by the fact that the 2 lines on the top of the graph show 2 chemical species that are both decreasing in concentration, so they must be on the same side of the equation. The lower of these 2 lines is decreasing at approximately 3 times the rate of the higher line. The bottom line which shows a chemical species increasing in concentration which indicates that there is only one chemical species on the opposite side of the equation. The rate at which the concentration of this chemical species is increasing is in between the rate of decrease of the chemical species on the opposite side of the equation. Response A shows the most suitable equation.*

**Question 13**

In which one of the following equations would the position of equilibrium be affected by an increase in volume?

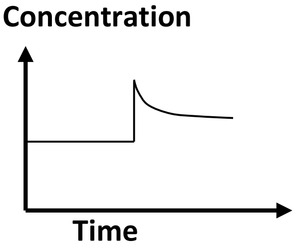
**A.** $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$ *Same number of gas particles on both sides of the equation.*
**B.** $CO (g) + H_2O (g) \rightleftharpoons CO_2 (g) + H_2 (g)$ *Same number of gas particles on both sides of the equation.*
[✓ **C.**] $N_2 (g) + 2O_2 (g) \rightleftharpoons N_2O_4 (g)$ *Has different numbers of gas particles on both sides of the equation.*
**D.** $KNO_3 (aq) \rightleftharpoons K^+ (aq) + NO_3^- (aq)$ *Not a gaseous system. If the question mentioned that the increase in volume was due to a dilution however, response D would be correct.*

**Question 14**

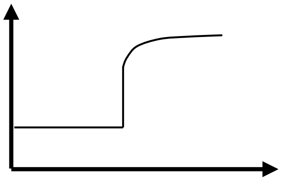
Which of the following graphs correctly shows the change in the concentration of $SO_2$ gas when the following equilibrium system is compressed at constant temperature? This reaction is represented by the following equation.

$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$

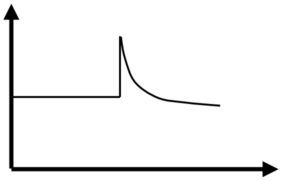
**[✓ A.]**



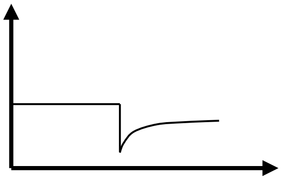
**B.**



**C.**



**D.**



*When the system is compressed (volume decreased and pressure increased) the concentration of $SO_2$ will instantaneously increase. The reaction will oppose the increase in pressure by shifting in the forwards direction where less particles of gas are produced resulting in a decrease in the pressure of the system and a decrease in $SO_2$ concentration. The change in pressure is only a partial one so the line showing the equilibrium concentration of the $SO_2$ at the new equilibrium must be above the line showing the initial $SO_2$ concentration (before the compression).*

## Short Answers

**Question 1**

Give the expression for the equilibrium constant for the following equations. You must include the units.

**a.** $H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2HCl\,(g)$
**b.** $4HCl\,(g) + O_2\,(g) \rightleftharpoons 2H_2O\,(g) + 2Cl_2\,(g)$
**c.** $2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$

**a.** $K = \dfrac{[HCl]^2}{[H_2] \times [Cl_2]}$ *no units for K*

**b.** $K = \dfrac{[H_2O]^2 \times [Cl_2]^2}{[HCl]^4 \times [O_2]}$ $M^{-1}$

*c.* $K = \dfrac{[N_2O_4]}{[NO_2]^2}$ $M^{-1}$

**Question 2**

A gaseous equilibrium mixture consisting of 0.251 mol of CO, 0.5001 mol of $O_2$ and 2.5 mol of $CO_2$ is held in a 3.0 L sealed flask at $250^0$C.

**a.** Calculate the equilibrium constant if the equation for the reaction is

$2CO\,(g) + O_2 \rightleftharpoons 2CO_2\,(g)$

$$[CO] = \frac{0.251}{3.0} = 0.083667\ M$$

$$[O_2] = \frac{0.5001}{3.0} = 0.1667\ M$$

$$[CO_2] = \frac{2.5}{3.0} = 0.8333\ M$$

$$K = \frac{[CO_2]^2}{[CO]^2 \times [O_2]}$$

$$K = \frac{0.8333^2}{0.083667^2 \times 0.1667} = 595.057 = 6.0 \times 10^2\ M^{-1}$$

**b.** Another mixture of these gases held at 100 $^0$C in a sealed 3.0 L flask has the following composition, 0.171 mol of CO, 0.4601 mol of $O_2$ and 2.58 mol of $CO_2$. Calculate the K value at this temperature.

$$[CO] = \frac{0.171}{3.0} = 0.057\ M$$

$$[O_2] = \frac{0.4601}{3.0} = 0.15337\ M$$

$$[CO_2] = \frac{2.58}{3.0} = 0.86\ M$$

$$K = \frac{[CO_2]^2}{[CO]^2 x\ [O_2]}$$

$$K = \frac{0.86^2}{0.057^2 x\ 0.15337} = 1{,}484.249 = 1.5 \times 10^3\ M^{-1}$$

**c.** Using your answers to **a** and **b,** determine if the reaction described by the equation,

$2CO\ (g) + O_2 \rightleftharpoons 2CO_2\ (g)$

is exothermic or endothermic.

*At 250 $^0$C, the K value for this reaction is $6.0 \times 10^2\ M^{-1}$. When the temperature was lowered to 100 $^0$C the K value increased to $1.5 \times 10^3\ M^{-1}$. This shows that a decrease has temperature has caused a net forward reaction to occur. Therefore the forward reaction is opposing the decrease in temperature by producing heat energy. As a consequence the reaction must be exothermic.*

- *Recall that when a change in temperature causes a net forward reaction, the concentration of the products increases and the concentration of the reactants decreases. As a consequence the fraction [products]/[reactants] gets higher resulting in a higher K value.*

**Question 3**

An equilibrium mixture is made by allowing 5.98 mol of $CO$ to react with 2.73 mol of $H_2$ in a 2.0 L vessel. When equilibrium is reached the moles of $CH_3OH$ in the mixture are equal to 1.21 mol. Calculate the equilibrium constant for this reaction. The equation is shown below.

$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

| | $CO$ + | $2H_2$ ⇌ | $CH_3OH$ |
|---|---|---|---|
| *n (initial)* | *5.98 mol* | *2.73 mol* | *0* |
| *n (reacted/produced)*<br>(↓) (↑) | *1.21 mol* ↓ | *1.21 x 2 = 2.42 mol* ↓ | *1.21 mol* ↑ |
| *n (equilibrium)* | *5.98 – 1.21 = 4.77 mol* | *2.73 – 2.42 = 0.31 mol* | *1.21 mol* |
| *[equilibrium]* $C = \frac{n}{V}$ | $\frac{4.77}{2.0}$ = 2.385 M | $\frac{0.31}{2.0}$ = 0.155 M | $\frac{1.21}{2.0}$ = 0.605 M |

$$K = \frac{[CH_3OH]}{[CO] \times [H_2]^2}$$

$$= \frac{0.605}{2.385 \times 0.155^2} = 10.559 = 11\ M^{-1}$$

**Question 4**

Nitrogen dioxide can be produced by the following equation.

$2NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g)$

**a.** A 1.0 L vessel is filled with 0.645 mol of NO, 2.18 mol of $O_2$ and 0.76 mol of $NO_2$. After some time analysis of the mixture revealed that the amount of the $O_2$ increased by 0.24 mol. Calculate the equilibrium constant for this reaction at 25 $^0$C**.**

| | *2NO +* | *$O_2$ ⇌* | *$2NO_2$* |
|---|---|---|---|
| *n (initial)* | *0.645 mol* | *2.18 mol* | *0.76 mol* |
| *n (reacted/produced)*<br>*(↓) (↑)* | *0.24 x 2 = 0.48 mol ↑* | *0.24 mol ↑* | *0.24 x 2 = 0.48 mol ↓* |
| *n (equilibrium)* | *0.645 + 0.48 = 1.125 mol* | *2.18 + 0.24 = 2.42 mol* | *0.76 – 0.48 = 0.28 mol* |
| *[equilibrium] C =* $\frac{n}{V}$ | $\frac{1.125}{1.0}$ *= 1.125 M* | $\frac{2.42}{1.0}$ *= 2.42 M* | $\frac{0.28}{1.0}$ *= 0.28 M* |

$$K = \frac{[NO_2]^2}{[NO]^2 \times [O_2]}$$

$$= \frac{0.28^2}{1.125^2 \times 2.42} = 0.025597 = 0.026\ M^{-1}$$

**b.** Another equilibrium mixture consisting of the same gases was placed in a freezer. Analysis of this mixture at the lower temperature revealed that the moles of $NO_2$ present at equilibrium decreased by 0.25 mol. Is the formation of $NO_2$ described by the above equation an exothermic or endothermic process? Explain your answer.

*The fact that the equilibrium moles of the product, $NO_2$ decreased at the lower temperature suggests that a decrease in temperature is opposed by a net back reaction. Therefore the reverse reaction must be exothermic as it increases the temperature of the system. As a consequence the formation of $NO_2$ (forward reaction) must be endothermic.*

**c.** Calculate the pressure in atmospheres, of the vessel described in part **a.** when equilibrium was established.

$PV = nRT$

$$P = \frac{nRT}{V}$$

*n (gases present at equilibrium) = 1.125 + 2.42 + 0.28 = 3.825 mol*

$$P = \frac{3.825 \text{ x } 8.31 \text{ x } 298}{1.0} = 9{,}472.15 \text{ KPa} \div 101.3 = 93.506 = 94 \text{ atm}$$

**Question 5**

The equilibrium constant for the reaction,

$2H_2O$ (g) + $2Cl_2$ (g) ⇌ 4HCl (g) + $O_2$ (g) at 380 K is 4.8 x $10^{-4}$ M.

**a.** 5.0 x $10^{-4}$ mol of $Cl_2$ is mixed with $H_2O$ in a 3.0 L flask at $380^0$C. When equilibrium is reached 3.44 x $10^{-5}$ mol of $O_2$ is produced. Calculate the amount in mol, of $H_2O$ gas that was originally added to the flask.

| | $2H_2O$ + | $2Cl_2$ ⇌ | 4HCl + | $O_2$ |
|---|---|---|---|---|
| *n (initial)* | X = 6.789231 x $10^{-6}$<br>+<br>6.88 x $10^{-5}$ =<br>7.6 x $10^{-5}$ mol | 5.0 x $10^{-4}$ mol | 0 mol | 0 mol |
| *n (reacted/produced)* (↓) (↑) | 3.44 x $10^{-5}$ x 2 =<br>6.88 x $10^{-5}$ mol ↓ | 3.44 x $10^{-5}$ x 2 =<br>6.88 x $10^{-5}$ mol ↓ | 3.44 x $10^{-5}$x 4 =<br>1.376 x $10^{-4}$ mol ↑ | 3.44 x $10^{-5}$ mol ↑ |
| *n (equilibrium)* | n = c x v<br>= 2.263077 x $10^{-6}$<br>X 3.0 =<br>6.789231 x $10^{-6}$ | 5.0 x $10^{-4}$ – 6.88 x $10^{-5}$<br>= 4.312 x $10^{-4}$ mol | 1.376 x $10^{-4}$ | 3.44 x $10^{-5}$ mol |
| *C (equilibrium)* | 2.263077 x $10^{-6}$ M<br>Refer to calculation below. | $\frac{4.312 \text{ x } 10^{-4}}{3.0}$<br>= 1.437 x $10^{-4}$ M | $\frac{1.376 \text{ x } 10^{-4}}{3.0}$ =<br>4.58667 x $10^{-5}$ M | $\frac{3.44 \text{ x } 10^{-5}}{3.0}$<br>= 1.147 x $10^{-5}$ M |

$$K = \frac{[HCl]^4 \times [O_2]}{[H_2O]^2 \times [Cl_2]^2}$$

*The key to this question is to find the equilibrium concentration of $H_2O$. From this the equilibrium moles of $H_2O$ can be calculated. The initial moles of $H_2O$ can then be calculated by adding the equilibrium moles of $H_2O$ to the moles of $H_2O$ that were used up when the system reached equilibrium.*

$$4.8 \times 10^{-4} = \frac{(4.58667 \times 10^{-5})^4 \times 1.147 \times 10^{-5}}{\mathbf{X^2} \times (1.437 \times 10^{-4})^2}$$

$$\mathbf{X^2} = \frac{(4.58667 \times 10^{-5})^4 \times 1.147 \times 10^{-5}}{4.8 \times 10^{-4} \times (1.437 \times 10^{-4})^2}$$

$$\mathbf{X^2} = 5.12152 \times 10^{-12}$$

$$\mathbf{X} = \sqrt{5.12152 \times 10^{-12}} = 2.263077 \times 10^{-6}\ M$$

*Now go back to the table. The concentration of $H_2O$ at equilibrium is $2.263077 \times 10^{-6}$ M, therefore n ($H_2O$) at equilibrium = $2.263077 \times 10^{-6} \times 3.0 = 6.789231$ mol.*

*So the moles of $H_2O$ initially added = n ($H_2O$) at equilibrium + n ($H_2O$) reacted*

$= 6.789231 \times 10^{-6} + 6.88 \times 10^{-5} = 7.5589 \times 10^{-5} = 7.6 \times 10^{-5}$ mol

**b.** How would the position of equilibrium be affected, if the mixture was cooled down only enough to condense the $H_2O$ into a liquid?

*Condensing $H_2O$ (g) into $H_2O$ (l) will remove $H_2O$ (g) from the system. As a consequence the position of equilibrium will shift towards the reactants as the reverse reaction will compensate for this change by producing more $H_2O$ (g).*

**c.** 1.0 mole of $H_2O$ (g), 0.25 mol of $Cl_2$ (g), $3.12 \times 10^{-3}$ mol of HCl (g) and 0.0015 mol of $O_2$ (g) are placed in a 1.0 L gas jar at 380 K. Is this mixture at equilibrium? If it is not at equilibrium describe how this reaction will get to equilibrium.

*First of all calculate the calculation fraction, Q, for the mixture. As the gas jar is 1.0 L in volume, the concentration of each gas is equal to its moles.*

$$Q = \frac{(3.12 \times 10^{-3})^4 \times 0.0015}{1.0^2 \times 0.25^2} = 2.2742 \times 10^{-12} M$$

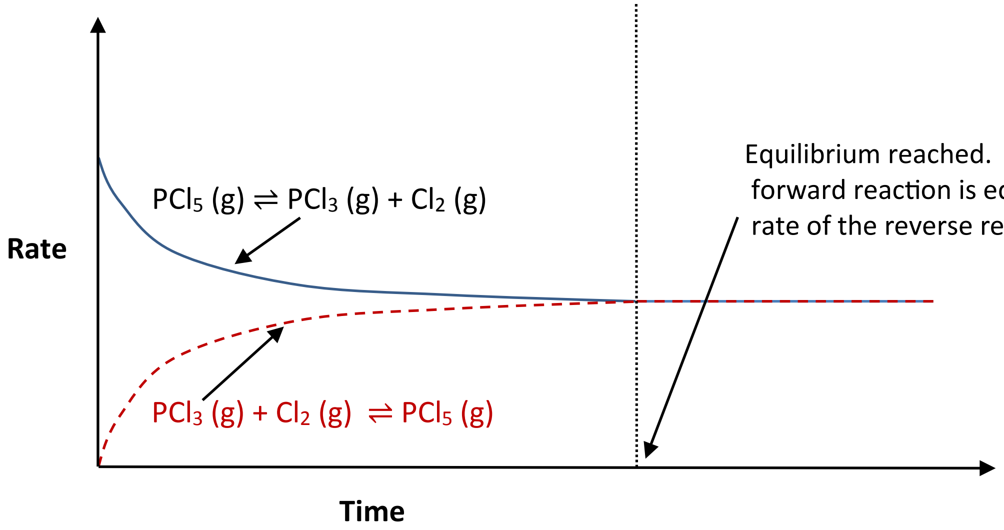
*At 380 K the equilibrium constant for this reaction is $4.8 \times 10^{-4}$ which is greater than Q. Therefore the mixture is not at equilibrium. In order for equilibrium to be reached, the concentration fraction Q, must increase from $2.72 \times 10^{-12}$ to $4.8 \times 10^{-4}$. Therefore the reaction will get to equilibrium by favouring the forward reaction as this will increase the concentration of the products and decrease the concentration of the reactants, resulting in an increase in the concentration fraction.*

**Question 6**
Some $PCl_5$ gas is placed into an empty gas jar and allowed to decompose according to the equation

$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$

Use collision theory to discuss how the rate of the forward and reverse reactions change as the reaction *approaches* and finally *achieves* equilibrium.

*When $PCl_5$ is added to an empty gas jar, the $PCl_5$ will start to decompose into $PCl_3$ and $Cl_2$ (forward reaction). The rate of this decomposition reaction will be at its highest just after the $PCl_5$ was added to the jar as the concentration of $PCl_5$ is at its highest and therefore the frequency of successful collisions between $PCl_5$ particles will also be at its highest. As the reaction proceeds the concentration of $PCl_5$ molecules starts to decrease as they are decomposed into products. As a consequence the frequency of successful collisions and hence the rate of the decomposition reaction starts to decrease. Initially the rate of the reverse reaction is zero as there are no products present. As the decomposition reaction proceeds the concentration of $PCl_3$ and $Cl_2$ starts to increase. As a consequence the frequency of successful collisions between $PCl_3$ and $Cl_2$ increases and hence the rate of the reverse reaction also starts to increase. So as the reaction approaches equilibrium, the rate of the forward reaction decreases and the rate of the reverse reaction increases. When equilibrium is reached the rate of the forward and reverse reaction become equal.*



**Question 7**
An important equation in the production of sulfuric acid is

$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g) \qquad \Delta H = -196 \text{ KJ mol}^{-1}$

**a.** What conditions of temperature and pressure would produce a high yield of $SO_3$?

*Low temperature and high pressure.*

❖ *In order to increase the yield of $SO_3$, the changes made to the system must cause the forward reaction to be favoured.*

*As the reaction is exothermic, the forward reaction will be favoured as temperatures are lowered. This is because the exothermic reaction produces heat and thus opposes the decrease in temperature.*

*The reactant side of this equation has 3 gas particles ($2SO_2$ and $O_2$) and the product side has 2 gas particles ($2SO_3$). If the pressure of the system is increased, the reaction will shift towards the products as this will reduce the number of molecules in the system and hence reduce the overall pressure of the system.*

**b.** What conditions of temperature and pressure would produce a fast reaction rate?

*High temperature and high pressure.*

**c.** Is there a conflict between the conditions that would give a high yield of $SO_3$ and the conditions that would give a fast reaction rate? Discuss your answer.

*Yes, there is a conflict with the temperature. Low temperature will give a high yield of $SO_3$ but at a slow reaction rate. High temperature will give a fast rate of reaction but a low yield of $SO_3$ .*

**Question 8**

Consider the following system

$A + B \rightleftharpoons C \quad \Delta H = -50 \text{ KJ mol}^{-1}$

If extra A is added to the system:

**a.** How would the position of equilibrium change? Discuss your answer.

*The position of equilibrium will shift towards to the products. A net forward reaction will remove some of the extra A added returning the system to equilibrium.*

**b.** How would the temperature of the system change? Discuss your answer.

*The temperature of the system will increase. As the reaction is exothermic, the shift in the equilibrium towards the products will result in the production of more heat.*

**c.** How would the value of K be affected? Discuss your answer.

*The value of K will be unaffected as the external change made to the system was the addition of the reactant A, not a change in temperature which is the only factor that can affect K.*

- *This can be a confusing question as the net forward reaction caused an increase in temperature. This can cause some students to conclude that K will change since the temperature was changed. This however, is not the case because the change in temperature was not caused by an external factor such as a flame. The external change made to the system was the addition of A and the change in temperature was as a result of the reaction shifting forwards. K will only be changed if the change in temperature is from an EXTERNAL SOURCE not as a result of a reaction shifting in a particular direction after Le Chatelier's principle has "kicked in".*

**Question 9**

Consider the following equilibrium reaction.

$Co(H_2O)_6^{2+}\ (aq) + 4Cl^-\ (aq) \rightleftharpoons CoCl_4^{2-}\ (aq) + 6H_2O\ (l)$

Some important information regarding this reaction are

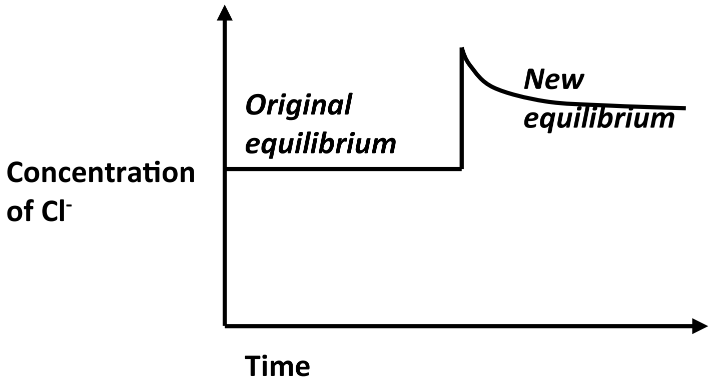
- $Co(H_2O)_6^{2+}$ has a red colour in solution.
- $CoCl_4^{2-}$ has a blue colour in solution.
- $Cl^-$ and $H_2O$ are colourless.

The following changes are made to this equilibrium system.

**a.** the addition of a few drops of concentrated hydrochloric acid.
**b.** the addition of a few drops of concentrated $AgNO_3$ solution.

For each change, discuss how the colour of the mixture at the NEW EQUILIBRIUM compares with the colour at the ORIGINAL EQUILIBRIUM. You should also state whether the concentration of $Cl^-$ ions has increased or decreased at the new equilibrium.

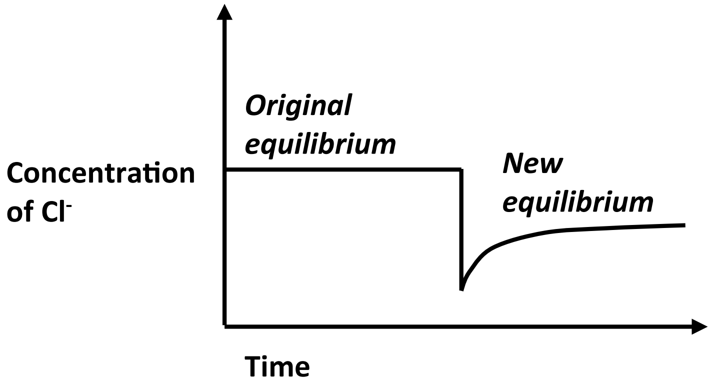
**a.** *The addition of concentrated HCl will increase the concentration of $Cl^-$ ions in the system as the HCl will dissociate into $H^+$ and $Cl^-$ ions: $HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$. The system will oppose the increase in $Cl^-$ concentration by shifting in the forward direction as the $Cl^-$ reacts with $Co(H_2O)_6^{2+}$. Once equilibrium is re-established the mixture will become more blue / less red due to the increase in the concentration of the blue $CoCl_4^{2-}$. The concentration of $Cl^-$ at the new equilibrium will be higher than it was at the original equilibrium even though the net forward reaction has removed some of the $Cl^-$ ions.*



**b.** *If concentrated $AgNO_3$ is added to the equilibrium mixture, $Ag^+$ will be present in the mixture as $AgNO_3$ dissociates into $Ag^+$ and $NO_3^-$ ions ($AgNO_3 \rightarrow Ag^+ + NO_3^-$). $Ag^+$ will react with $Cl^-$ to produce a precipitate of AgCl. The equation for this reaction is shown below.*

$Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$

*The concentration of $Cl^-$ in this system will be reduced by this reaction resulting in a net back reaction as the system attempts to increase the concentration of $Cl^-$. The net back reaction will increase the concentration of the red coloured* $Co(H_2O)_6^{2+}$ *resulting in the solution becoming more red / less blue in colour. The concentration of the $Cl^-$ at the new equilibrium will be lower than the concentration at the original equilibrium as the net back reaction will only partially replaces the $Cl^-$ ions that have been removed from the system. This is illustrated in the graph below.*



**Question 10**

In terms of equilibrium, explain why a person suffering from carbon monoxide poisoning has a reduction in the concentration of oxyhaemoglobin reaching their cells.

*Haemoglobin has a stronger attraction for CO than $O_2$. As a consequence when a person has breathed in CO, a large proportion of the haemoglobin molecules present in the blood surrounding the lungs will bind to CO molecules according to the following equilibrium reaction.*

$Hb + 4CO \rightleftharpoons Hb(CO)_4$   Kc = very large value

*As a consequence the amount of haemoglobin available for the equilibrium reaction between oxygen and haemoglobin is decreased. The equilibrium reaction between haemoglobin and oxygen is shown below.*

$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$

*As a consequence oxyhaemoglobin ($Hb(O_2)_4$) will decompose into haemoglobin and oxygen as the system opposes the decrease in haemoglobin concentration. Now there is a lower concentration of oxyhaemoglobin available for transportation to the cells.*

**Question 11**
Some $N_2O_4$ is placed inside a gas syringe and allowed to decompose until equilibrium is reached. The equation describing the reaction is

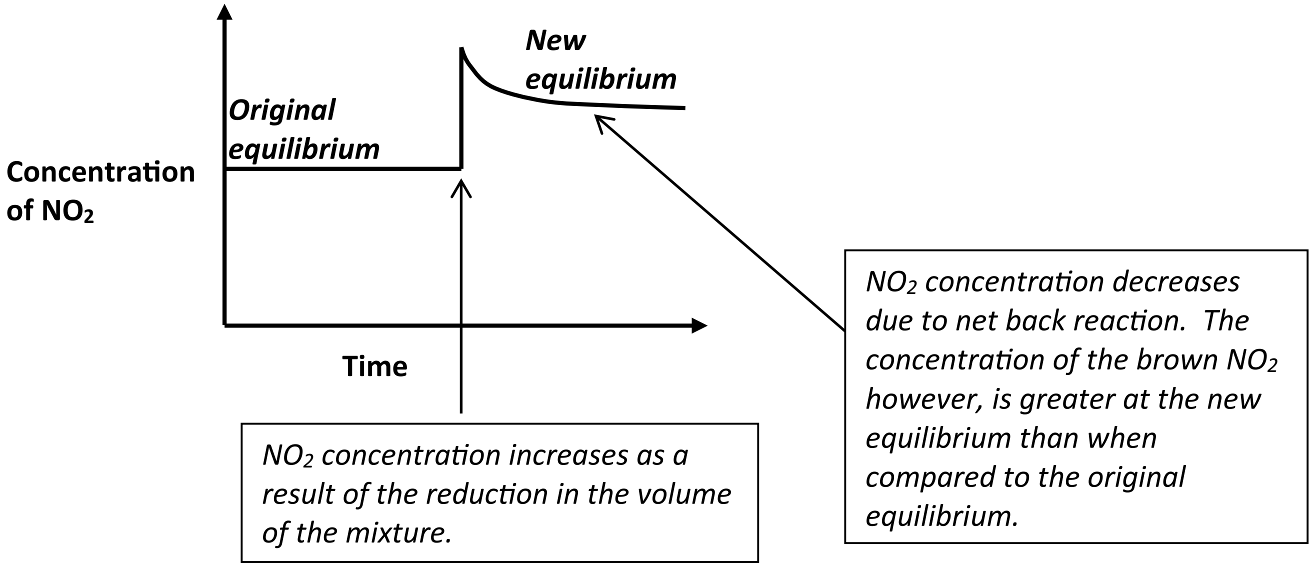
$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$N_2O_4$ is colourless and $NO_2$ is brown. The volume of the mixture is reduced at constant temperature and allowed to re-establish equilibrium.

**a.** How will the colour of the mixture at the new equilibrium compare with the colour before the volume was reduced. Discuss your answer.

*The brown colour at the new equilibrium will be darker than it was at the original equilibrium before the volume was reduced. This is because the reduction in volume increased the concentration of the brown coloured $NO_2$ at the new equilibrium.*

❖ *The reduction in volume of the mixture will cause a net back reaction to occur as there are less reactant molecules ($N_2O_4$) than there are product molecules ($2NO_2$), therefore the back reaction will reduce the pressure of the system. As the net back reaction is favoured, many students conclude that the brown colour of the mixture will be get lighter because some of the brown $NO_2$ is used up by the back reaction. This is incorrect because the reduction in volume of the mixture caused the concentration of the brown $NO_2$ gas to increase. Just after this, Le Chatelier's principle kicks in and the net back reaction occurs which reduces the concentration of $NO_2$.* ***The increase in $NO_2$ concentration when the volume is initially reduced is greater than the decrease in $NO_2$ concentration that occurs when the reaction shifts backwards. Therefore at the new equilibrium the $NO_2$ concentration is higher and hence the brown colour of the mixture is darker. This is well illustrated when viewing a time versus concentration graph:***



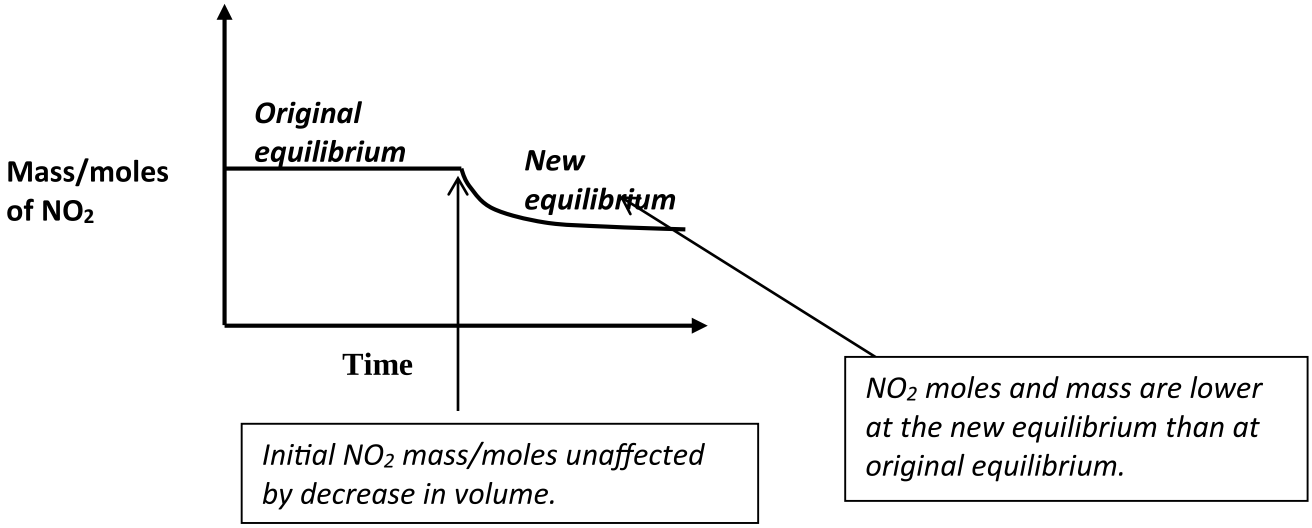
*$NO_2$ concentration increases as a result of the reduction in the volume of the mixture.*

*$NO_2$ concentration decreases due to net back reaction. The concentration of the brown $NO_2$ however, is greater at the new equilibrium than when compared to the original equilibrium.*

**b.** How will the moles and mass of the $NO_2$ at the new equilibrium compare with the original equilibrium?

*The moles and mass of* $NO_2$ *at the new equilibrium are less than at the original equilibrium before the volume was reduced.*

- *When the volume of the mixture is reduced, the initial concentration of the* $NO_2$ *will increase but the amount of* $NO_2$ *in moles and the mass of* $NO_2$ *remain the same. This is because reducing the volume will not change the actual number of* $NO_2$ *molecules that are initially present in the system. It just increases the concentration because the same number of* $NO_2$ *molecules have a smaller volume of space to move around in. When the reaction shifts backwards, the moles and mass of* $NO_2$ *will be reduced. Refer to the graph below.*



*Initial* $NO_2$ *mass/moles unaffected by decrease in volume.*

$NO_2$ *moles and mass are lower at the new equilibrium than at original equilibrium.*

**c.** How was the rate of the forward reaction affected by the reduction in volume? Discuss.

*The rate of the forward reaction was increased by the reduction in volume. This is because the reduction in volume increased the concentration of the* $N_2O_4$ *molecules which increased the likelihood of successful collisions / frequency of successful collisions between these reactant molecules.*

- *A common miss-conception with this question is to associate the net back reaction with a reduction in the rate of the forward reaction and an increase in the rate of the back reaction. According to collision theory, the reduction in the volume of gaseous reactants will increase the frequency of successful collisions between the molecules due to their increased concentration. This applies to both the forward and reverse reactions of a gaseous equilibrium system. As the reaction also needs to oppose the increase in pressure, the increase in the rate of the reaction that reduces the number of gas particles (in this case the back reaction) will be greater than the increase in* *rate of the other reaction (in this case the forward reaction.)* ***So the reduction in volume has caused the rates of both the forward and reverse reactions to increase but the increase in the rate of the reverse reaction was greater.***

The mixture is allowed to return to the original volume. Then it is placed inside an ice water bath. After a few minutes it is observed that the brown colour has become more intense.

**d.** Is the reaction exothermic or endothermic? Discuss your answer.

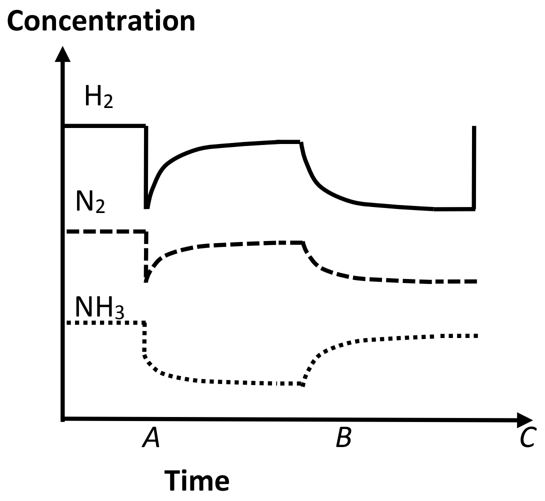
*This reaction is exothermic. When the system experienced an external decrease in temperature (from the ice water bath), the brown colour became more intense. This indicates that the system opposed the decrease in temperature by favouring the forward reaction which increased the concentration of brown $NO_2$. Therefore the forward reaction must be releasing heat into the system and is EXOTHERMIC.*

**Question 12**

The production of ammonia from nitrogen and hydrogen gas is of great industrial importance. The equation describing this reaction is shown below.

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g) \quad \Delta H = -$

The graph below shows the concentration of the reactants and products of an equilibrium mixture formed from this reaction. A number of changes are made to the system and these are shown on the graph.



**a.** How many times was the system at equilibrium?

*The reaction was at equilibrium 3 times.*

- *Each section of the graph that shows a horizontal line (constant concentration over time) represents an equilibrium system.*

**b.** What change was made to the system at the point labeled A on the graph?

*Decrease in pressure or increase in volume.*

- *At the point A, the concentration of all reactants and products in the system decreases. This is as a result of the volume of the mixture increasing causing the gas molecules to spread further apart as they take up the space in the larger volume. This decrease in the concentration of the gaseous mixture also causes a lowering of the overall gas pressure.*

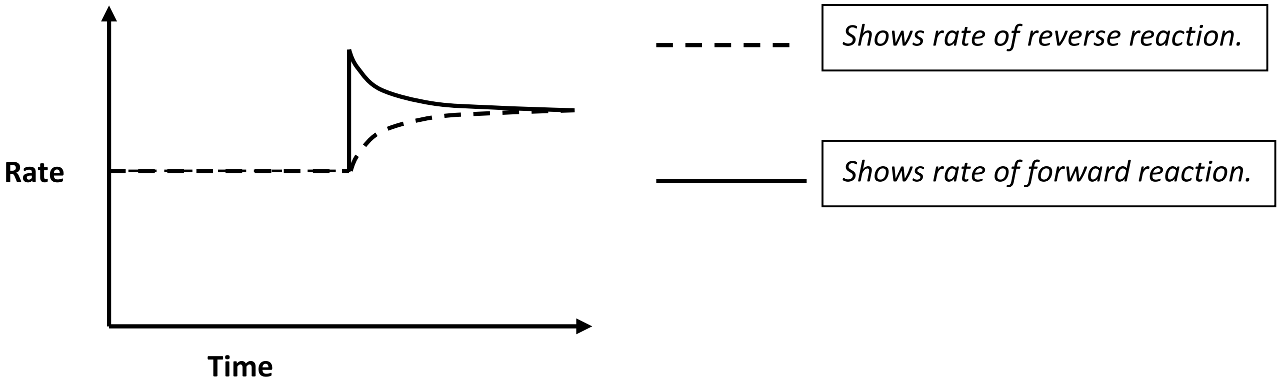
**c.** What change was made to the system at the point labeled B on the graph. Explain your answer.

*At the point labeled B the temperature of the system was decreased. At the point B on the graph, the concentration of the reactants* $H_2$ *and* $N_2$ *decrease and the concentration of the product,* $NH_3$*, increases. This shows that the change in temperature is causing a net forward reaction. The temperature of the system must have been decreased as the reaction is opposing the decrease in temperature by favouring the forward reaction which is releasing heat as it is exothermic (*$\Delta H = -$*).*

**d.** How would the value of the equilibrium constant at point B compare with the value at point A? Discuss your answer.

*At B the temperature of the system is lower than at A. As the reaction is exothermic, the lower temperature at B will result in the position of equilibrium favouring the products to a greater extent than at A. This means that the equilibrium mixture at B will have a greater proportion of products compared to reactants resulting in a higher equilibrium constant.*

**e.** A change was made at point C but the response of the system is not shown on the graph. Draw a sketch of a rate versus time graph that shows how the rates of the forward and reverse reactions were affected immediately after the change and when the system went back to equilibrium.



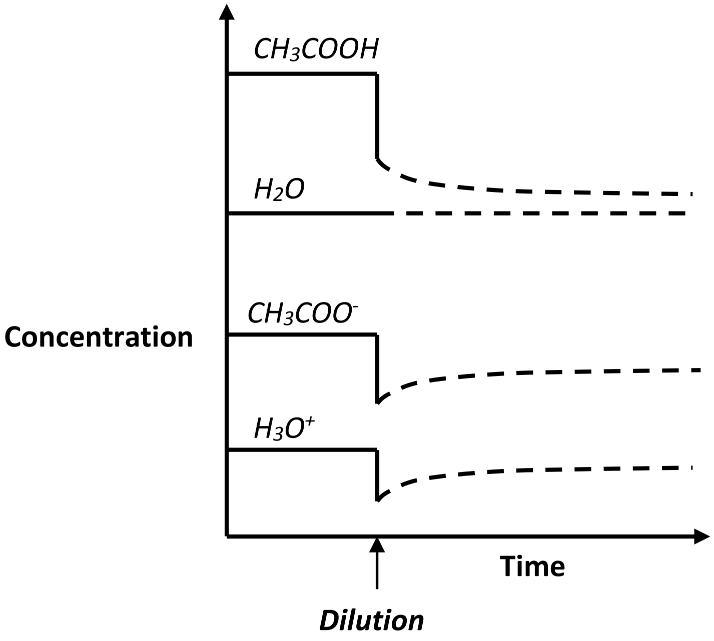
- *At point C, extra $H_2$ was added to the system. The increase in the $H_2$ concentration causes an instantaneous increase in the rate of the forward reaction as the frequency of successful collisions between $N_2$ and $H_2$ has been increased. As time goes by the rate of the forward reaction gradually decreases as the reactants get used up and the frequency of successful collisions between $N_2$ and $H_2$ decreases. Just after the $H_2$ was added, the increase in the rate of the forward reaction has also resulted in a net forward reaction as the rate of production of $NH_3$ by the forward reaction is greater than the rate of production of $N_2$ and $H_2$ by the reverse reaction. The resultant increase in the concentration of $NH_3$ has resulted in an increase in the frequency of successful collisions between $NH_3$ molecules, hence the rate of the reverse reaction starts to increase. Since the rate of the forward reaction gradually decreases and the rate of the reverse reaction gradually increases, eventually the rates of these 2 reactions will become equal and the system will go back to equilibrium.*

**Question 13**

Draw a rough sketch of a concentration versus time graph showing the reaction

$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$
*1 particle* *2 particles*

regaining equilibrium after it has been diluted with a large volume of water. Your graph must show the concentration of $CH_3COOH$, $H_2O$, $CH_3COO^-$ and $H_3O^+$ before and after the dilution.



- *The addition of water dilutes the system and causes the concentration of all aqueous species to decrease. The system opposes the dilution by favouring the forward reaction as this produces a greater number of aqueous particles resulting in an* *increase in the overall concentration of particles in the system. $H_2O$ (l) is not an aqueous ion or molecule so it is NOT counted as a reactant particle.*

- *The concentration of $H_2O$ in the equilibrium system is unaffected by the dilution. Water is a solvent in this equilibrium system so it cannot be diluted. The concentration of water in water is always 56 M regardless of whether it is pure water or an aqueous solution.*

**Question 14**

The weak acid, benzoic acid, with formula $C_6H_5COOH$ ionises in water according to the following equation:

$C_6H_5COOH$ (aq) + $H_2O$ (l) $\rightleftharpoons$ $C_6H_5COO^-$ (aq) + $H_3O^+$ (aq)

**a.** Discuss the effect on the equilibrium yield of $C_6H_5COO^-$ if

**iii.** a few drops of concentrated HCl is added to the system.

*HCl will dissociate into $H^+$ and $Cl^-$ ions. $H^+$ ions are a representation of $H_3O^+$ ions so the concentration of $H_3O^+$ in the system will increase which will be opposed by the system shifting backwards. The backwards reaction will use up $C_6H_5COO^-$ so the yield of $C_6H_5COO^-$ will be decreased.*

**iv.** a few drops of concentrated NaOH are added to the system.

*NaOH will dissociate into $Na^+$ and $OH^-$ ions. The $OH^-$ ions which are basic will react with the acidic $H_3O^+$ ions: $H_3O^+ + OH^- \rightarrow 2H_2O$. This will cause a reduction in the concentration of $H_3O^+$ which will be opposed by a net forward reaction as this will produce more $H_3O^+$. The net forward reaction will increase the yield of $C_6H_5COO^-$*

**b.** What would happen to the pH of the acid solution if it was diluted with a large amount of water?

*The dilution would cause the $H_3O^+$ concentration to decrease. As a consequence the pH will increase.*

**Question 15**
On planet Earth there is a cyclic movement of carbon dioxide gas between the atmosphere and bodies of water such as the oceans, lakes and rivers.

This can be represented by the following equilibria.

$CO_2\ (g) \rightleftharpoons CO_2\ (aq)$
$CO_2\ (aq) + H_2O\ (l) \rightleftharpoons H^+\ (aq) + HCO_3^-\ (aq)$

Use the above equations to help explain what effect rising levels of $CO_2$ in the atmosphere are having on the pH of the ocean.

*Rising levels of $CO_2$ will cause the concentration of $CO_2$ (g) in the first equation to increase. As a consequence this reaction will shift forwards causing the concentration of $CO_2$ (aq) to increase. Now the $CO_2$ (aq) in the second equation has increased causing this reaction to shift forwards resulting in an increase in concentration of $H^+$ in the ocean. The increased concentration of $H^+$ will cause the pH of the ocean to decrease.*

# Chapter 10 Review Questions – Solutions

## Multiple Choice

**Question 1**
The oxidation number of N in $NH_4NO_3$ is

**A.** -3.
**B.** +5.
**C.** +1.
[✓ **D.**] -3 and +5.

*$NH_4NO_3$ is made up of 2 ions, $NH_4^+$ and $NO_3^-$. The oxidation number of the N in each ion will be different:*

| $NH_4^+$ | $NO_3^-$ |
|---|---|
| $X + (4 x +1) = +1$ | $X + (3 x -2) = -1$ |
| $X + 4 = + 1$ | $X – 6 = -1$ |
| $X = +1 – 4 = -3$ | $X = -1 + 6 = +5$ |

**Question 2**
Consider the 4 statements below:

i A reductant donates electrons to an oxidising agent. *Correct.*
ii An oxidant is oxidised by a reducing agent. *Incorrect. An oxidant is reduced.*
iii A reducing agent is oxidised by an oxidant. *Correct.*
iv. A reductant is reduced by an oxidising agent. *Incorrect. A reductant is oxidised.*

Which of these 4 statements are INCORRECT?

**A.** All 4 statements
**B.** i and iii
**C.** ii, iii and iv
[✓ **D.**] ii and iv

**Question 3**
The half equation that shows the chemical species A, acting as a reducing agent is

**A.** $A \rightarrow A^{2-} + 2e^-$
**B.** $A + 2e^- \rightarrow A^{2-}$
[✓ **C.**] $A \rightarrow A^{2+} + 2e^-$
**D.** $A^{2+} + 2e^- \rightarrow A$

*A reducing agent undergoes oxidation so it must have electrons on the right hand side of the equation. If a neutral atom such as A loses electrons, it will gain a positive charge as the number of protons will now exceed the number of electrons.*

**Question 4**

$$\underset{\substack{\downarrow\\ \mathbf{+4}}}{Mn}\underset{\substack{\downarrow\\ -2}}{O_2}\,(s) + 4HCl\,(aq) \rightarrow Cl_2\,(g) + 2H_2O(l) + \underset{\substack{\downarrow\\ \mathbf{+2}}}{Mn}\underset{\substack{\downarrow\\ -1}}{Cl_2}\,(aq)$$

During this reaction the charge of Mn changes from

[✓ **A.**] +4 to +2 and $MnO_2$ is the oxidant. *A decrease in oxidation number means that reduction has occurred. Therefore $MnO_2$ is an oxidant.*
**B** +4 to -2 and HCl is the reductant.
**C.** from +4 to +2 and $MnO_2$ is the reducing agent.
**D.** +4 to 0 and $Cl_2$ is produced when $Cl^-$ ions are reduced.

**Question 5**

Which of the equations below represents a redox reaction?

*The equation that represents a redox reaction is the one where at least one element has undergone a change in oxidation number.*

**A.** $\underset{\substack{\downarrow\\ +1}}{Ag^+}\,(aq) + \underset{\substack{\downarrow\\ -1}}{Cl^-}\,(aq) \rightarrow \underset{\substack{\downarrow\\ +1}}{Ag}\underset{\substack{\downarrow\\ -1}}{Cl}\,(s)$

[✓ **B.**] $\underset{\substack{\downarrow\\ +1}}{H_2}\underset{\substack{\downarrow\\ -1}}{O_2}\,(al) \rightarrow \underset{\substack{\downarrow\\ 0}}{H_2}\,(g) + \underset{\substack{\downarrow\\ 0}}{O_2}\,(g)$

**C.** $\underset{\substack{\swarrow\\ +1}}{K}\underset{\substack{\searrow\\ -1}}{I}\,(aq) + \underset{\substack{\swarrow\\ +1}}{Na}\underset{\substack{\downarrow\\ -1}}{Cl}\,(aq) \rightarrow \underset{\substack{\downarrow\\ +1}}{Na}\underset{\substack{\searrow\\ -1}}{I}\,(aq) + \underset{\substack{\swarrow\\ +1}}{K}\underset{\substack{\searrow\\ -1}}{Cl}\,(aq)$

**D.** $\underset{\substack{\swarrow\\ +2}}{Cu}\underset{\substack{\downarrow\\ +6}}{S}\underset{\substack{\searrow\\ -2}}{O_4}\,(aq) \rightarrow \underset{\substack{\downarrow\\ +2}}{Cu^{2+}}\,(aq) + \underset{\substack{\downarrow\\ +6}}{S}\underset{\substack{\searrow\\ -2}}{O_4^{2-}}\,(aq)$

**Question 6**

The oxidation states of chromium in $\underset{\substack{\swarrow\\ \mathbf{+6}}}{Cr_2}\underset{\substack{\downarrow\\ -2}}{O_7^{2-}}$, $\underset{\substack{\swarrow\\ \mathbf{+6}}}{Cr}\underset{\substack{\searrow\\ -2}}{O_4^{2-}}$ and $\underset{\substack{\downarrow\\ \mathbf{+3}}}{Cr_2}\underset{\substack{\searrow\\ -2}}{O_3}$ are respectively

**A.** +12, +3 and +3.
**B.** +3, +6 and +6.
[✓ **C.**] +6, +6 and +3
**D.** +12, +6 and +6.

# Short Answers

## Question 1

What is the oxidation number of the underlined element?

| | | |
|---|---|---|
| **a.** | $\underline{Br_2}$ | *0* |
| **b.** | $O\underline{Br}^-$ | *+1* |
| **c.** | $F_2\underline{O}$ | *+2* |
| **d.** | $\underline{S_2}O_3^{2-}$ | *+2* |
| **e.** | $Ba\underline{O_2}$ | *-1* |

## Question 2

Write out the oxidation half equation, reduction half equation and overall equation for each of the following.

**a.** A solution of $Fe^{3+}$ions is reduced by iron metal. The product of the reaction is only $Fe^{2+}$ (aq).

$Fe (s) \rightarrow Fe^{2+}(aq)$

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ *oxidation*

$Fe^{3+}(aq) \rightarrow Fe^{2+}(aq)$

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ *reduction*

*To balance electrons multiply reduction equation by 2:*

$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$ *reduction*

*Now combine this equation with the oxidation half equation to get the full or overall equation:*

$Fe (s) + 2Fe^{3+}(aq) \rightarrow Fe^{2+}(aq) + 2Fe^{2+}(aq)$

$Fe (s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$

**b.** CuS (s) and nitric acid are allowed to react with each other to produce $CuSO_4$ (aq) and NO (g)

$CuS (s) \rightarrow CuSO_4 (aq)$

$CuS (s) + 4H_2O (l) \rightarrow CuSO_4 (aq) + 8H^+(aq) + 8e^-$ *oxidation*

$HNO_3 (aq) \rightarrow NO (g)$

$HNO_3 (aq) + 3H^+(aq) + 3e^- \rightarrow NO (g) + 2H_2O (l)$ *reduction*

*To balance electrons multiply oxidation reaction by 3 and reduction reaction by 8.*

$3CuS (s) + 12H_2O (l) \rightarrow 3CuSO_4 (aq) + 24H^+(aq) + 24e^-$

$8HNO_3 (aq) + 24H^+(aq) + 24e^- \rightarrow 8NO (g) + 16H_2O (l)$

*Now combine these 2 equations to get the overall equation.*

$3CuS\ (s) + 12H_2O\ (l) + 8HNO_3\ (aq) + 24H^+(aq) \rightarrow 3CuSO_4\ (aq) + 24H^+(aq) + 8NO\ (g) + 16H_2O\ (l)$

*Now cancel down the $H_2O$ and $H^+$ which appear on both sides of the equation in order to get the full equation.*

$3CuS\ (s) + 12H_2O\ (l) + 8HNO_3\ (aq) + 24H^+(aq) \rightarrow 3CuSO_4\ (aq) + 24H^+(aq) + 8NO\ (g) + 16H_2O\ (l)$
$-12H_2O$ $-24H^+$ $-24H^+$ $-12H_2O$

$3CuS\ (s) + 8HNO_3\ (aq) \rightarrow 3CuSO_4\ (aq) + 8NO\ (g) + 4H_2O\ (l)$

**c.** A solution of chromium (III) ions is oxidised into $Cr_2O_7^{2-}$ (aq) by $H_2O_2$ (aq) which is reduced into water.

$Cr^{3+}(aq) \rightarrow Cr_2O_7^{2-}(aq)$
$2Cr^{3+}(aq) + 7H_2O\ (l) \rightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$ *oxidation*

$H_2O_2\ (aq) \rightarrow H_2O\ (l)$

$H_2O_2\ (aq) + 2H^+(aq)\ 2e^- \rightarrow H_2O\ (l) + H_2O\ (l)$
$H_2O_2\ (aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O\ (l)$ *reduction*

*Multiply reduction reaction by 3 in order to balance the electrons.*

$3H_2O_2\ (aq) + 6H^+(aq) + 6e^- \rightarrow 6H_2O\ (l)$

*Now combine this equation with the oxidation half equation to get the overall equation:*

$2Cr^{3+}(aq) + 7H_2O\ (l) + 3H_2O_2\ (aq) + 6H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6H_2O\ (l)$

*Now cancel down the $H_2O$ and $H^+$ which appear on both sides of the equation in order to get the full equation.*

$2Cr^{3+}(aq) + 7H_2O\ (l) + 3H_2O_2\ (aq) + 6H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6H_2O\ (l)$
$-\ 6H_2O$ $-\ 6H^+$ $-\ 6H^+$ $-\ 6H_2O$

$2Cr^{3+}(aq) + H_2O\ (l) + 3H_2O_2\ (aq) \rightarrow Cr_2O_7^{2-}(aq) + 8H^+(aq)$

**Question 3**
When hot concentrated sulfuric acid is poured over solid zinc granules, zinc ions and $H_2S$ gas are produced.

**a.** Give the ionic oxidation half equation showing states.

$Zn\ (s) \rightarrow Zn^{2+}(aq) + 2e^-$

**b.** Give the ionic reduction half equation showing states.

$H_2SO_4(aq) + 8H^+(aq) + 8e^- \rightarrow H_2S\ (g) + 4H_2O\ (l)$

**c.** Give the full equation showing states.

*Multiply the oxidation half equation by 4.*

$4Zn\ (s) \rightarrow 4Zn^{2+}(aq) + 8e^-$

*Now combine this with the reduction half equation.*

$4Zn\ (s) + H_2SO_4\ (aq) + 8H^+(aq) \rightarrow 4Zn^{2+}(aq) + H_2S\ (g) + 4H_2O\ (l)$

**d.** Calculate the mass of zinc required to produce 1.0 L of $H_2S$ gas at a temperature of 35 $^0$C and pressure of 2.0 atm.

$\underline{4Zn\ (s)} + H_2SO_4\ (aq) + 8H^+(aq) \rightarrow 4Zn^{2+}(aq) + \underline{H_2S\ (g)} + 4H_2O\ (l)$

*X g*

*1.0 L*

$35^0C + 273 = 308\ K$

$2.0\ atm \times 101.3 = 202.6\ KPa$

$PV=nRT$

$$n(H_2S) = \frac{PV}{RT} = \frac{202.6 \times 1.0}{8.31 \times 308} = 0.079157\ mol$$

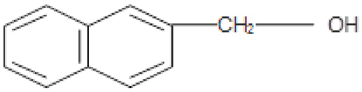
$n\ (Zn) = 4 \times 0.079157 = 0.316628\ mol$

$m\ (Zn) = 0.316628 \times 65.4 = 20.7074712 = 21\ g$

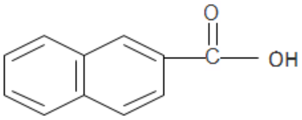
**Question 4**

An organic molecule, “molecule 1”, is transformed into “molecule 2”.

**molecule 1**



**Molecule 2**



Is the process of the transformation of molecule 1 into molecule 2 a reduction or oxidation reaction? Discuss your answer.

*Molecule 1 gains an oxygen atom and loses a H atom when it is transformed into molecule 2. Therefore the transformation of molecule 1 into molecule 2 is an oxidation process as oxidation is also defined as a gain oxygen and or loss of hydrogen.*

- *Due to the complex structures of these 2 molecules it would be impractical to try to use oxidation numbers to answer this question.*

**Question 5**

Consider the half equation below.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

**c.** Use oxidation numbers to show that the Cr has been reduced.

$$\underset{\underset{+6}{\downarrow}}{Cr_2}O_7^{2-} + 14H^+ + 6e^- \rightarrow 2\underset{\underset{+3}{\downarrow}}{Cr}^{3+} + 7H_2O$$

*Chromium has undergone a decrease in oxidation number therefore it has been reduced.*

**d.** Show that the Cr has been reduced by discussing the transfer of oxygen atoms.

*Chromium has lost oxygen atoms which shows that it has been reduced.*

**Question 6**

Use oxidation numbers to show that manganese atoms have been reduced in this half equation:

$$\underset{+7}{\underset{\uparrow}{MnO_4^-}} + \underset{+1}{\underset{\uparrow}{8H^+}} + 5e^- \rightarrow \underset{+2}{\underset{\uparrow}{Mn^{2+}}} + \underset{+1}{\underset{\uparrow}{4H_2O}}$$

*The oxidation state of the Mn as decreased from +5 at the start of the reaction to +2 at the end of the reaction so it has undergone reduction.*

*The oxidation state of the H has remained at +1 so it has neither been reduced nor oxidised.*

# Chapter 11 Review Questions – Solutions

**Question 1**
When Pb metal is placed in a $H_2O_2$ solution at standard conditions, the most likely outcome will be that

**A.** the $H_2O_2$ will decompose into $O_2$ and $H^+$ ions.
**B.** the Pb metal will increase in mass and the concentration of $H_2O_2$ will decrease.
[✓ **C.**] the Pb metal will decrease in mass.
**D.** the concentration of $Pb^{2+}$ ions surrounding the Pb metal will decrease.

*According to the electrochemical series table, Pb is a reductant and is below the oxidant* $H_2O_2$*. Therefore a spontaneous redox reaction will occur between Pb and* $H_2O_2$*. Pb metal is oxidised into* $Pb^{2+}$ *and as a consequence its mass will decrease.*

**Question 2**
Which combination will all reduce a solution of $Sn^{4+}$ ions?

[✓ **A.**] Sn (s), Li (s), Ni (s) and $H_2$ (g)
**B.** $F^-$ (aq), $H_2O$ (l), $Br^-$ (aq) and $I^-$ (aq)
**C.** $F_2$ (g), $H_2O_2$ (aq), $Au^+$ (aq) and $Cl_2$ (g)
**D.** Cu (s), $Sn^{2+}$, $I^-$ (aq) and S (s)

$Sn^{4+}$ *is an oxidant and the only chemical species that will cause its reduction are those on the right hand side of the table (reductants) and below* $Sn^{4+}$*, hence response A.*

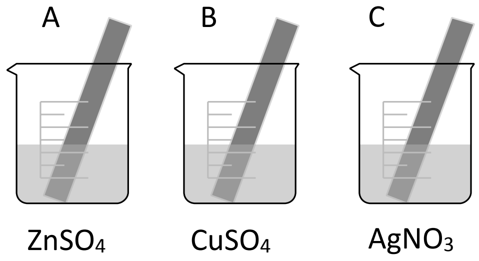
**Question 3**
Storing pieces of silver metal in a solution of $Sn(NO_3)_2$ (aq) will

**A.** result in the loss of the silver metal through oxidation.
**B.** prevent the reduction of silver ions into silver metal.
**C.** cause the concentration of $Sn^{2+}$ ions to increase.
[✓ **D.**] prevent the silver metal from being oxidised by $Cl_2$ gas.

*Ag is a reductant and is above the oxidant* $Sn^{2+}$ *on the electrochemical series table. As a consequence they will not react spontaneously. Therefore responses A, B, and C are out as they all involve reaction between Ag (s) and* $Sn^{2+}$ *(aq).* $Cl_2$ *gas is an oxidant that is above Ag on the table so they can react spontaneously.* $Sn^{2+}$ *is also a reductant that is below Ag on the electrochemical series table. As a consequence it is a stronger reductant than Ag and will react with* $Cl_2$ *gas in preference to Ag metal.*

**Question 4**

The 3 beakers shown below labelled A, B and C have a piece of Zn metal immersed in a solution.



The beakers that will produce a coating of metal on the Zn after a period of time are

**A.** A, B and C
**B.** A and B.
[✓ **C.**] B and C.
**D.** C only.

*$Cu^{2+}$ and $Ag^{+}$ are oxidants that are above the reductant, Zn, on the electrochemical series table. Therefore $Cu^{2+}$ and $Ag^{+}$ will react spontaneously with Zn and undergo reduction according to the following equations:*

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$

*The Cu and Ag metal produced will form a coating over the surface of the Zn metal.*

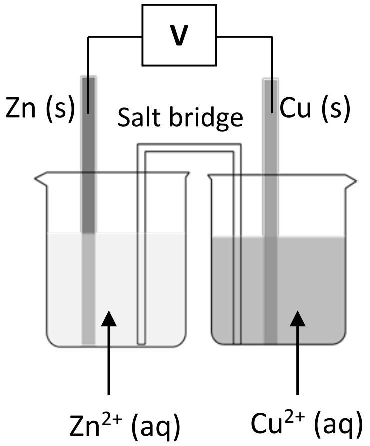
**Question 5**
A half cell contains $Fe(NO_3)_2$ and $Fe(NO_3)_3$ solutions. An appropriate electrode for this half cell would be

**A.** Fe (s)
[✓ **B.**] graphite
**C.** $Fe^{2+}$ (aq)
**D.** $Fe^{3+}$ (aq)

*$Fe^{2+}$ and $Fe^{3+}$ are both aqueous ions and are unable to form an electrode. Therefore an inert electrode such as graphite is required for such a half cell.*

*Questions 6 and 7 refer to the following information.*

The galvanic cell shown below is known as the Daniel cell. It contains the $Zn^{2+}$/Zn half cell and the $Cu^{2+}$/Cu half cell.



**Question 6**
While this cell is discharging, the salt bridge allows

**A.** electrons to pass through it from the anode through to the cathode.
**B.** cations to pass into the cathode through the external circuit.
[✓ **C.**] anions to migrate towards the anode.
**D.** cations to neutralise the negative charge accumulating around the anode.

**Question 7**
In order to change the direction of electron flow through the external circuit, the $Zn^{2+}$/ Zn half cell should be replaced with a

[✓ **A.**] $Ag^{+}$/Ag half cell.
**B.** $Mn^{2+}$/Mn half cell.
**C.** $Ca^{2+}$/Ca half cell.
**D.** None of the above.

*When the $Zn^{2+}$/Zn half cell is connected to the $Cu^{2+}$/Cu half cell, the electrons flow from the Zn to the Cu through the external circuit as the $Zn^{2+}$/Zn half cell is lower in the table and will therefore contain the strongest reductant (Zn). If the $Ag^+$/Ag half cell is connected to the $Cu^{2+}$/Cu half cell, the $Cu^{2+}$/Cu is the lower half cell. Now the Cu electrode will undergo oxidation and the electrons will flow in the opposite direction. That is, away from the $Cu^{2+}$/Cu half cell where as in the original cell (containing $Zn^{2+}$/Zn) the electrons were flowing towards the $Cu^{2+}$/Cu half cell.*

**Question 8**

The information below relates to the following half cells:

$A^+$ (aq) / A (s)
$B^{2+}$ (aq) / B (s)
$C^{2+}$ (aq )/ C (s)
$D^{3+}$ (aq) / D (s)

When A (s) is immersed in a solution of $C^{2+}$ (aq), the solid C is produced. When A (s) is placed in a solution of $B^{2+}$ (aq), no changes are observed. D (s) loses mass when placed in a solution of $B^{2+}$ (aq).

The list that shows the oxidants in order of increasing oxidising strength is

**A.** C, A, B and D.
**B.** D, B, A and C.
**C.** $C^{2+}$, $A^{2+}$, $B^{2+}$ and $D^{3+}$.
[✓ **D.**] $D^{3+}$, $B^{2+}$, $A^{2+}$ and $C^{2+}$.

*Produce a "mini" electrochemical series table from the information. When viewing any half cell, the species on the left hand side is always an oxidant and the one on the right hand side is always a reductant. Eg. $A^+$ (aq) / A (s)*

↓ ↓

*Oxidant Reductant*

*A (s) reacts with $C^{2+}$(aq) to produce C (s). This shows that A is causing the reduction of $C^{2+}$. Therefore A (s) is on the right hand side of the table and below the position of $C^{2+}$ (aq). The 2 equations showing the position of these 2 half cells should be written out as they would appear on the electrochemical series table.*

$C^{2+}$ (aq) + $2e^-$ → C (s)
$A^+$ (aq) + $e^-$ → A (s)

*When A (s) is placed in $B^{2+}$ no reaction occurs. Therefore the oxidant $B^{2+}$ must be below the reductant A (s).*

$C^{2+}$ (aq) + $2e^-$ → C (s)
$A^+$ (aq) + $e^-$ → A (s)

*$B^{2+}$ (aq) + 2e$^-$ → B (s)*

*D (s) loses mass in a solution of $B^{2+}$ (aq). This shows that the $B^{2+}$ (aq) is causing the oxidation of D (s). Therefore D (s) must be below $B^{2+}$ (aq) on the table. Here is the final table.*

*$C^{2+}$ (aq) + 2e$^-$ → C (s)*
*$A^+$ (aq) + e$^-$ → A (s)*
*$B^{2+}$ (aq) + 2e$^-$ → B (s)*
*$D^{3+}$ (aq) + 3e$^-$ → D (s)*

*On the left hand side of the table we have the oxidants. The higher up the table they are the stronger they are. Therefore the oxidants in order of increasing strength are*

*$D^{3+}$, $B^{2+}$, $A^+$ and $C^{2+}$.*

**Question 9**
When connected to the standard $H^+/H_2$ half cell, half cell Z causes the pH in the $H^+/H_2$ half cell to increase. When half cell Z is placed in the $Fe^{2+}/Fe$ half cell, the mass of the Fe electrode increases. Half cell Z is

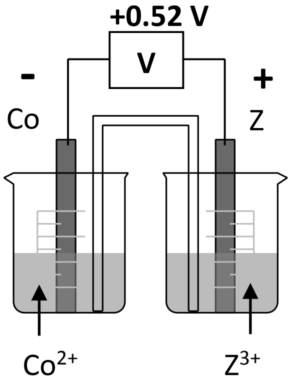
**A.** $Cu^{2+}/$ Cu
[✓ **B.**] $Mn^{2+}/$ Mn
**C.** $Ag^+/$ Ag
**D.** $Br_2$ / 2Br$^-$

*If half cell Z causes the pH of the $H^+/H_2$ half cell to increase, then it must be causing the reduction of $H^+$ ions as this will decrease the concentration of $H^+$ in the solution and hence increase the pH. Therefore the Z half cell is undergoing oxidation and the $H^+/H_2$ half cell reduction.* ***Half cell Z must be below $H^+/H_2$ on the table.***

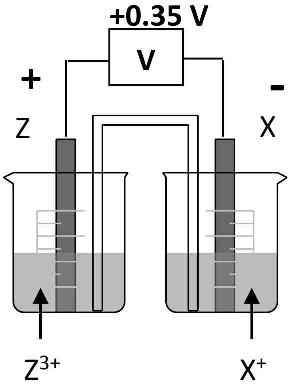
*If half cell Z is below $H^+/H_2$ then it must also be below half cell $Fe^{2+}/Fe$ as it causing the reduction of $Fe^{2+}$ into Fe solid. Only half cell $Mn^{2+}/$ Mn is below both $H^+/H_2$ and $Fe^{2+}/Fe$.*

*Questions 10 and 11 relate to the following information.*

The galvanic cell shown below is constructed from the half cells $Co^{2+}$/Co and $Z^{3+}$/Z.



This galvanic cell is constructed from the half cells $Z^{3+}$/Z and $X^+$/X.



**Question 10**

Which list contains the reductants from these 2 galvanic cells ordered in increasing reducing strength?

**A.** Co, X and Z.
[✓ **B.**] Z, X and Co.
**C.** Co, X and Z.
**D.** X, Co and Z

*Construct a "mini" electrochemical series table using the information. From the first cell it can be seen that half cell $Z^{3+}$ /Z is above $Co^{2+}$/Co as the $Z^{3+}$/ Z half cell is the cathode.*

$Z^{3+} + 3e^- \rightarrow Z$
$Co^{2+} + 2e + 2e^- \rightarrow Co$

*In the second cell, $Z^{3+}$/ Z is the cathode so it must be above $X^{+}$ / X. In both cells, $Z^{3+}$ / Z is the cathode so it must be the highest of all the half cells. The half cell $Co^{2+}$/ Co must be the lowest one as the potential difference between it and $Z^{3+}$ / Z is higher than the potential difference $Z^{3+}$ / Z and $X^{+}$ / X. Therefore on the electrochemical series table, the gap between $Z^{3+}$/ Z and $Co^{2+}$/ Co is greater than between $Z^{3+}$/ Z and $X^{+}$/ X. Hence the table would be:*

$Z^{3+} + 3e^{-} \rightarrow Z$
$X^{+} + e^{-} \rightarrow X$
$Co^{2+} + 2e^{-} \rightarrow Co$

*An alternative method would be to calculate the $E^{0}$ of each half cell and arrange them from highest to lowest to construct the mini electrochemical series table.*

*$Co^{2+}$ / Co half cell* $E^{0} = -0.28$ V *(from the electrochemical series table)*

*Now the $E^{0}$ of the $Z^{3+}$ / Z can be worked out from the first cell:*

*Potential difference = $E^{0}$ oxidant – $E^{0}$ reductant*
$+0.52 = \mathbf{Z} - -0.28$
$+0.52 = \mathbf{Z} + 0.28$
$\mathbf{Z} = 0.52 - 0.28 = +0.24$ V

*So $E^{0}$ of $Z^{3+}$ / Z = +0.24 V*

*Use the second cell to calculate the $E^{0}$ of $X^{+}$ / X*

$+0.35 = 0.24 - \mathbf{X}$
$0.35 - 0.24 \mathbf{= -X}$
$0.11 = \mathbf{-X}$
$\mathbf{X} = -0.11$ V

*So $E^{0}$ of $X^{+}$ / X = -0.11 V*

$Z^{3+} + 3e^{-} \rightarrow Z$ $E^{0} = +0.24$ V
$X^{+} + e^{-} \rightarrow X$ $E^{0} = -0.11$ V
$Co^{2+} + 2e^{-} \rightarrow Co$ $E^{0} = -0.28$ V

*On the table the reductants are on the right hand side and they increase in strength when moving down the table. Therefore the reductants listed in order of increasing reducing strength = Z, X and Co.*

**Question 11**

The $E^0$ value of the $X^+/X$ half cell is

**A.** + 0.35 V
**B.** + 0.59 V
**C.** + 0.52 V
[✓ **D.**] - 0.11 V

*Refer to the working out for question 10.*

**Question 12**

Methane gas is fed into a fuel cell using an acidic electrolyte. While this cell is discharging the reaction occurring at the positive electrode is

**A.** $CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$
[✓ **B.**] $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ *From the electrochemical series table.*
**C.** $2H^+ + 2e^- \rightarrow H_2$
**D.** $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

*Questions 13 and 14 refer to the following:*

Nickel cadmium cells are secondary cells that are used as a power supply for many portable devices such as power tools. The full equation when this cell is discharging is

$Cd + 2NiOH + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

**Question 13**

When this cell is discharging, the reaction occurring at the negative electrode is

[✓ **A.**] $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
**B.** $2NiOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$
**C.** $2Ni(OH)_2 + 2OH^- \rightarrow 2NiOH + 2H_2O$
**D.** $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$

*During discharge the negative electrode is the anode. Using oxidation numbers it can be seen that Cd undergoes oxidation:*

*ON of Cd = 0*
*ON of Cd in $Cd(OH)_2$ Work with the charge of the 2 hydroxide ions ($OH^-$)*
*Cd +-2 = 0*
*Cd – 2 = 0*
*Cd = +2*

*Therefore response A is correct. Response A is the only oxidation half equation given so no other options are viable.*

**Question 14**
When this cell is recharging, the reaction occurring at the negative electrode is

**A.** $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$
**B.** $2NiOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$
**C.** $2Ni(OH)_2 + 2OH^- \rightarrow 2NiOH + 2H_2O$
**[✓ D.]** $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$

*During recharging, the negative electrode is the cathode and it must show the opposite reaction to what is occurring when the cell is discharging.*

*That is during recharging, the reaction occurring at the cathode will be the reverse of the reaction that was occurring at the anode during discharge. Therefore response D*

**Question 15**
A year 12 chemistry student constructs an electrochemical cell in the lab. This cell consists of the following.

- A half cell made from Cu (s) and $Cu(NO_3)_2$ (aq).
- A half cell made from $CuSO_4$ (aq) and Zn (s).
- A salt bridge made from a piece of filter paper that was soaked in potassium nitrate solution.

When these 2 half cells are connected by wires and a salt bridge, the main energy transformation that is occurring is

**A.** Chemical → Electrical
**[✓ B.]** Chemical → Heat
**C.** Electrical → Chemical
**D.** Chemical → Heat → Electrical

*When these 2 half cells are connected with wires and a salt bridge, no electricity will flow between them because one of the half cells contains a reductant, Zn (s) that is in contact with an oxidant,* $Cu^{2+}$ *(aq). As the* $Cu^{2+}$ *is above the Zn on the electrochemical series table, the Zn will be oxidised and the electrons will be gained by the* $Cu^{2+}$ *ions making direct contact with the Zn. This is a spontaneous and exothermic redox reaction that will produce heat. No electrical energy will be produced because no electrons will flow through the wires from the* $Zn^{2+}$ *(aq) to the Cu (s) in the other half cell.*

**Question 16**
A lithium-ion cell is stored in a refrigerator.  As a consequence of these storage conditions it is expected that

**A.** when the cell is taken out of the refrigerator and placed straight into an appliance, the appliance will operate at its best performance.
**B.** this cell will be able to be recharged only a small number of times.
[✓ **C.**] the life of this cell will be prolonged.
**D.** when the cell is taken out of the refrigerator and placed straight into an appliance, the appliance will operate at its best performance but will go flat very quickly.

*At low temperatures, the side reactions that limit the life of the cell will be slowed down so the life of the cell will be prolonged.*

## Short Answers

**Question 1**
Explain the following observations.

**a.** A gold ring that has been immersed in water for years shows very little sign of corrosion (rust).

*On the electrochemical series table, gold (Au) is a reductant and is above the reduction half equation occurring between* $O_2$ *and* $H_2O$*. Therefore there will be no spontaneous reaction occurring between Au and* $H_2O$ *and* $O_2$*.*

**b.** Lithium metal and fluorine gas react explosively when mixed together.

*Li is a reductant and is below* $F_2$ *on the electrochemical series table so the 2 chemicals will react spontaneously with each other. The EMF for the reaction is very high as there is a large gap between* $F_2$ *and Li on the electrochemical series table so the extent of the reaction is very high. This high EMF means that a great amount of electrical energy would be produced if these 2 chemical species were connected in an electrochemical cell. Since they are just made to react directly with each other, a great amount of heat energy will be produced instead which can cause an explosion.*

**c.** A piece of Cu is immersed in $Ag^+$ (aq) and shows no sign of reaction even though the electrochemical series table predicts that a reaction should occur.

*It is likely that the reaction is not occurring at standard conditions. The temperature may not be at 25* $^0$*C or the concentration of the* $Ag^+$*(aq) may not be 1.0 M.*

- *Do not mention that the pressure may not be 0.987 atm (100 KPa). This only applies if there is a gas taking part in the reaction which is not the case here. Also do not just say that the conditions are not SLC. You need to specifically refer to the relevant conditions of either gas pressure, temperature or solution concentration.*

*Another valid is answer:*

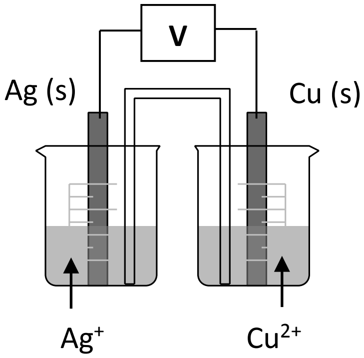
*The rate of reaction may be too slow and as a result is unable to be observed.*

**d.** At SLC conditions, a piece of Mg is allowed to stand in a solution of $Fe(NO_3)_3$ and no reaction is observed.

*The rate of reaction may be too slow and as a result is unable to be observed.*

**Question 2**

The galvanic cell shown below consists of a $Cu^{2+}$/Cu half cell and a $Ag^+$/ag half cell.



**a.** Give the name of the anode.

*Copper.*

- *Cu is lower on the table than the other reductant, Ag, so it is the anode. It is incorrect to state that the* $Cu^{2+}$*/Cu half cell is the anode. The anode is the actual electrode where oxidation is occurring. It is not the whole half cell.*

**b.** Give the name of the cathode.

*Silver*

- $Ag^+$ *is higher on the table than the other oxidant* $Cu^{2+}$*. It is incorrect however, to state that the cathode is* $Ag^+$*. The cathode is the electrode where the reduction reaction is occurring. The* $Ag^+$ *is undergoing reduction on the surface of the cathode which is made from Ag metal.*

**c.** Give the anode half equation showing states.

$Cu (s) \rightarrow Cu^{2+} (aq) + 2e^-$

**d.** Give the cathode half equation showing states.

$Ag^+ (aq) + e^- \rightarrow Ag (s)$

**e.** Give the full equation showing states.

*Multiply reduction half equation by 2 to balance electrons:*

$2 \times Ag^+ + e^- \rightarrow Ag = 2Ag^+ (aq) + 2e^- \rightarrow 2Ag(s)$

*Combine this with the oxidation half equation:*

$Cu (s) + 2Ag^{+} (aq) \rightarrow Cu^{2+} (aq) + 2Ag (s)$

**f.** Give the formulae of suitable electrolytes for each half cell.

*$Cu(NO_3)_2$ for half cell on the right and $AgNO_3$ for half cell on the left.*

- *Always use nitrate ions as they will always form a soluble compound with any positive ion.*

**g.** Explain why the anode loses mass and the cathode gains mass.

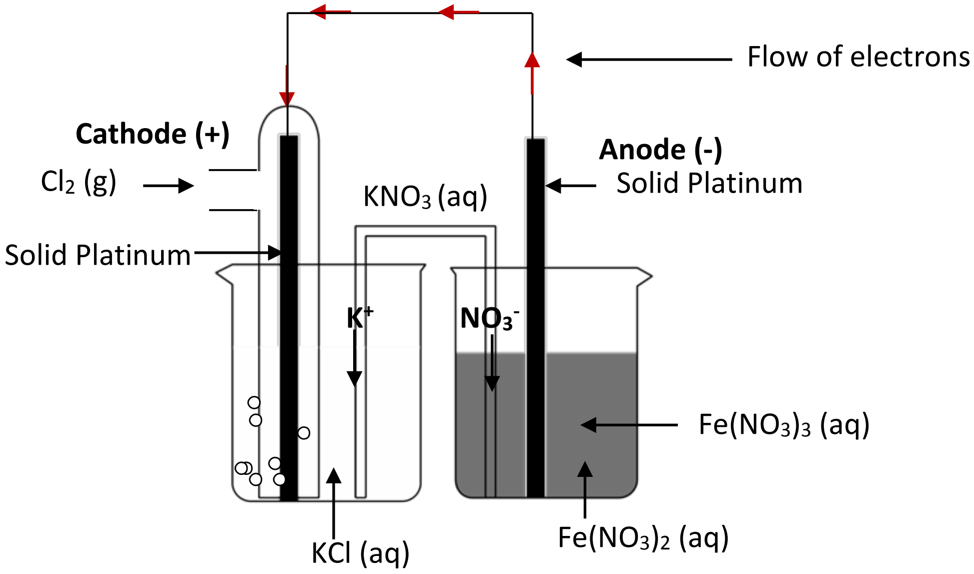
*The anode loses mass because solid copper metal is oxidised into $Cu^{2+}$ ions which dissolve into the surrounding electrolyte. As a consequence the copper anode is gradually losing mass as it dissolves into the surrounding electrolyte. At the cathode $Ag^{+}$ ions are reduced into Ag (s). The silver produced by this reaction deposits onto the surface of the silver electrode making its mass increase.*

**Question 3**

An electrochemical cell is to be constructed from a $Fe^{3+}/Fe^{2+}$ half cell and a $Cl_2/Cl^-$ half cell.

**a.** Draw a labelled sketch of this cell. Your sketch must include the following.

- Anode and cathode including polarities.
- Names of materials used for the electrodes.
- Formulae of appropriate solutions for each half cell.
- The formulae of the solution used for the salt bridge.
- The direction of movement of electrons through the external circuit.
- The direction of movement of cations and anions from the salt bridge.



**b.** Give the electrode half equations and the full equation.

*Anode (-):* $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
*Cathode (+):* $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

*Full equation:*

*Multiply anode equation by 2 to balance electrons.*

$2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$

$2Fe^{2+}(aq) + Cl_2(g) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

**c.** Give 3 reasons why the solution you chose for the salt bridge was suitable.

- $KNO_3$ *is cheap and readily available.*
- $K^+$ *is a very weak oxidant and* $NO_3^-$ *is a very weak reductant and oxidant so they are unlikely to take part in the redox reactions occurring at the electrodes.*
- $KNO_3$ *has high solubility in water.*

**d.** Calculate the predicted cell potential for this cell.

*Potential difference =* $E^0$ *(higher half cell) –* $E^0$ *(lower half cell)*
$= +1.36 - +0.77$
$= +0.59\ V$

**Question 4**
With reference to the electrochemical series table, explain why silver nitrate is not an appropriate solution to use for a salt bridge.

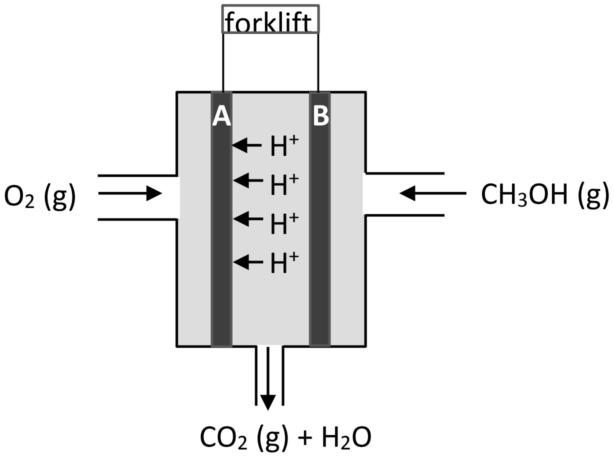
$Ag^+(aq)$ *is high on the electrochemical series table and is a strong oxidant so it may take part in the reduction reaction occurring at the cathode or it may react with the reductant at the anode.*

**Question 5**
What are the factors that have prevented the use of fuel cells for the large scale generation of electrical energy?

*They are very expensive to produce and maintain.* $H_2/O_2$ *fuel cells have the problem of the hydrogen gas being dangerous to store as it is highly flammable and explosive.*

**Question 6**

A direct methanol fuel cell (DMFC) can be used to power vehicles such as forklifts. Methanol is fed into the anode and oxygen gas into the cathode. A proton exchange membrane allows for the movement of $H^+$ ions into the cathode area.



**a.** Which electrode, A or B is positive?

*A is positive.*

❖ *With fuel cells $O_2$ is always fed into the cathode (+).*

**b.** Give the half equation for the reaction occurring at the anode.

$CH_3OH + H_2O\,(l) \rightarrow CO_2\,(g) + 6H^+(aq) + 6e^-$

**c.** Give the half equation for the reaction occurring at the cathode.

*From the electrochemical series table:*

$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l)$

❖ *The $H^+$ ions in the electrolyte show that this is an acid fuel cell, hence the $H^+$ ions in the oxidation half cell.*

**d.** Give the full equation.

$CH_3OH + H_2O\,(l) \rightarrow CO_2\,(g) + 6H^+(aq) + 6e^-$ (X 2)
$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l)$ (X 3)

$2CH_3OH + 2H_2O\,(l) \rightarrow 2CO_2\,(g) + 12H^+(aq) + 12e^-$
$3O_2\,(g) + 12H^+\,(aq) + 12e^- \rightarrow 6H_2O\,(l)$

$2CH_3OH + 2H_2O\ (l) + 3O_2\ (g) + 12H^+\ (aq) \rightarrow 2CO_2\ (g) + 12H^+(aq) + 6H_2O\ (l)$
*Cancel out* $H^+$ *and* $H_2O$

$$2CH_3OH + 2H_2O\ (l) \mathbf{- 2H_2O(l)} + 3O_2\ (g) + 12H^+\ (aq) \mathbf{- 12H^+\ (aq)}$$
$$\rightarrow 2CO_2\ (g) + 12H^+(aq) \mathbf{- 12H^+\ (aq)} + 6H_2O\ (l) \mathbf{- 2H_2O\ (l)}$$

$2CH_3OH\ (g) + 3O_2\ (g) + \rightarrow 2CO_2\ (g) + 4H_2O\ (l)$

**e.** Why is it important for $H^+$ ions to be allowed to flow from electrodes B to A?

*At the cathode (electrode A)* $H^+$ *ions are removed by the reduction reaction. This would make negative charge accumulate around the cathode and the flow of electrons through the external circuit would cease. The movement of* $H^+$ *ions towards the cathode replaces the* $H^+$ *ions that were removed by the reduction reaction. This maintains a neutral charge around the cathode.*

*At the anode (electrode B), the oxidation of* $CH_3OH$ *produces* $H^+$ *ions which would cause the accumulation of positive charge around the anode. This accumulation of positive charge would prevent the flow of electrons through the external circuit. These ions are allowed to move away from the anode so the accumulation of positive charge around the anode does not occur.*

**f.** It is possible for the membrane to only allow the movement of negative ions. Explain how this would maintain the neutrality of charges at the anode and cathode. Assume the electrolyte contains $HNO_3$.

$NO_3^-$ *ions from the electrolyte could flow from the cathode towards the anode in order to maintain neutral charge at both electrodes. The consumption (using up) of* $H^+$ *ions at the cathode would cause negative charge to build up around the cathode as the* $NO_3^-$ *are losing their* $H^+$ *partners which used to balance out their negative charge. This is counteracted by* $NO_3^-$ *ions moving away from the cathode. When* $NO_3^-$ *ions cross over into the anode they can balance out the positive charge from the* $H^+$ *ions produced from the oxidation of* $CH_3OH$*.*

**g.** Give one advantage that a fuel cell has over a traditional combustion engine as the power source for the forklift.

*It converts chemical energy directly into electrical energy which is more efficient than a combustion engine which converts chemical energy into heat energy.*

- *Heat energy is very easily lost and only a fraction of the heat energy will be converted into the kinetic energy of the fork lift. With the fuel cell, a much greater proportion of the electrical energy produced will be converted into the kinetic energy of the fork lift.*

**h.** Give one advantage that a traditional combustion engine has over a fuel cell as the power source for the forklift.

*A combustion engine is cheaper to build and run than a fuel cell.*

**Question 7**

A special type of hydrogen / oxygen fuel cell has molten $Li_2CO_3$ as the electrolyte. The separator between the anode and cathode allows for the movement of $CO_3^{2-}$ ions. The full equation and anode half equation for when this cell discharges are shown below.

Full equation

$2H_2 + O_2 \rightarrow 2H_2O$

Anode half equation

$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

**a.** Write out the cathode half equation. States of matter do not need to be shown.

*Subtract the anode half equation from the full equation. First of all multiply the anode half equation by 2 because in the full equation the $H_2$ has a coefficient of 2.*

$2H_2 + 2CO_3^{2-} \rightarrow 2H_2O + 2CO_2 + 4e^-$

$2H_2 + O_2 - 2H_2 - 2CO_3^{2-} \rightarrow 2H_2O - 2H_2O - 2CO_2 - 4e^-$

*The $H_2$ will be eliminated from the left hand side of the equation and the $H_2O$ from the right hand side.*

$O_2 - 2CO_3^{2-} \rightarrow - 2CO_2 - 4e^-$

*Now move $-2CO_3^{2-}$ to the product side so it becomes $+2CO_3^{2-}$. Move $-2CO_2$ and $-4e^-$ over to the reactant side of the equation so they can become $+2CO_2$ and $+4e^-$. Now the cathode half equation is:*

$O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$

**b.** Describe and justify the movement of $CO_3^{2-}$ ions through this fuel cell.

*The $CO_3^{2-}$ ions will move from the cathode towards the anode in order to maintain neutrality of charge at the anode and cathode and hence allow electrons to move through the external circuit. At the anode $CO_3^{2-}$ ions are removed by the oxidation reaction. This would make the charge at the anode positive except for the fact that the lost $CO_3^{2-}$ ions are replaced by $CO_3^{2-}$ ions from the cathode.*

*The cathode reaction produces $CO_3^{2-}$ ions which would make the cathode gain a negative charge. This does not happen however, because $CO_3^{2-}$ ions move away from the cathode and towards the anode.*

**Question 8**

A nickel metal hydride battery is a special type of secondary cell that uses a hydrogen absorbing alloy as the negative electrode (MH) when the cell is discharging. The full equation for when the cell is recharging is shown below.

$M (s) + H_2O (l) + Ni(OH)_2 (s) + OH^- (aq) \rightarrow MH(s) + OH^- (aq) + NiOOH (s) + H_2O (l)$

The oxidation half equation for when the cell is discharging is shown below.

$MH (s) + OH^- (aq) \rightarrow M (s) + H_2O (l) + e^-$

**a.** Give the full formula of the reductant during the recharging process.

*Using oxidation numbers it can be seen that Ni is undergoing oxidation during the recharging process, which is represented by the full equation at the start of the question.*

*$Ni(OH)_2$ (on reactant side of equation)*

$Ni + 2 \times -1 = 0$ *Using $OH^-$ in charge of -1*
$Ni - 2 = 0$
$Ni = +2$

*NiOOH on product side of the equation.*

$Ni - 2 - 1 = 0$
$Ni - 3 = 0$
$Ni = +3$

*So during recharging the oxidation number of Ni increases from +2 to +3. Therefore Ni is undergoing oxidation. The formula of the reductant must include the whole formula of the compound, not just the Ni:*

*Formula of reductant = $Ni(OH)_2$*

**b.** Write out the half equation for the reaction occurring at the positive electrode when the cell is recharging. States of matter must be shown.

*If the oxidation reaction occurring at the anode during discharge is reversed, this will give the reduction reaction occurring at the cathode during recharge. That is, it will give the cathode (-) reaction during recharge:*

$M\ (s) + H_2O\ (l) + e^- \rightarrow MH\ (s) + OH^-\ (aq)$ *(this is the reverse of the oxidation reaction during discharge given in the question.)*

*If this half equation is subtracted from the full equation during recharge, what is left will be the oxidation half equation for the recharging process (equation at the positive electrode).*

$M\ (s) + H_2O\ (l) + Ni(OH)_2\ (s) + OH^-\ (aq)\ \mathbf{- M\ (s) - H_2O\ (l) - e^-}$
$\rightarrow MH(s) + OH^-\ (aq) + NiOOH\ (s) + H_2O\ (l)\ \mathbf{- MH\ (s) - OH^-\ (aq)}$

$Ni(OH)_2\ (s) + OH^-\ (aq) \rightarrow NiOOH\ (s) + H_2O\ (l) + e^-$

- ❖ *You might be tempted to work out this equation by trying to write out a half equation by adding $H_2O$ to balance O atoms and adding $H^+$ ions to balance H atoms etc. This only works when the reaction is occurring in* ***acidic media*** *where there are $H^+$ ions in the solution. This reaction is occurring in an alkaline environment which is evident by the $OH^-$ ions in the full equation given at the start of the question.*

*Alternatively this equation can be worked out using the fake acid method.*

$Ni(OH)_2\ (s) \rightarrow NiOOH\ (s)$
$Ni(OH)_2\ (s) \rightarrow NiOOH\ (s) + H^+\ (aq)$
$Ni(OH)_2\ (s) \rightarrow NiOOH\ (s) + H^+\ (aq) + e^-$

$Ni(OH)_2\ (s) \rightarrow NiOOH\ (s) + H^+\ (aq) + \mathbf{OH^-\ (aq)} + e^-$
$Ni(OH)_2\ (s) \rightarrow NiOOH\ (s) + \mathbf{H_2O\ (l)} + e^-$
$Ni(OH)_2\ (s) + OH^-\ (aq) \rightarrow NiOOH\ (s) + H_2O\ (l) + e^-$

**c.** Give the formula of the oxidant when the cell is discharging.

*If the full equation given at the start of this question is reversed, it will give the full equation for when the cell is discharging:*

$MH(s) + OH^-\ (aq) + NiOOH\ (s) + H_2O\ (l) \rightarrow M\ (s) + H_2O\ (l) + Ni(OH)_2\ (s) + OH^-\ (aq)$

*Using oxidation numbers it can be seen that Ni has undergone a decrease in oxidation number:*

| $NiOOH$ | $Ni(OH)_2$ |
|---|---|
| $Ni - 2 - 1 = 0$ | $Ni + 2 \times -1 = 0$ |
| $Ni - 3 = 0$ | $Ni - 2 = 0$ |
| $Ni = +3$ | $Ni = +2$ |

*Ni has undergone a decrease in oxidation number, therefore the oxidant during discharge is NiOOH.*

# Chapter 12 Review Questions – Solutions

## Multiple Choice

### Question 1

During the electrolysis of 100 mL of distilled water, the gases produced at the negative and positive electrodes are respectively

**A.** oxygen and hydrogen
[✓ **B.**] hydrogen and oxygen
**C.** oxygen and oxygen
**D.** hydrogen and hydrogen

*During the electrolysis of water, $H_2O$ is reduced at the negative electrode producing $H_2$ gas and $OH^-$. At the positive electrode $H_2O$ is oxidised into $O_2$ and $H^+$.*

### Question 2

When comparing electrolysis and galvanic cells it is correct to say that

**A.** oxidation occurs at the negative electrode in both types of cells.
[✓ **B.**] oxidants migrate to the cathode in both types of cells.
**C.** oxidation occurs at the positive electrode only in galvanic cells.
**D.** in electrolysis cells reduction occurs at the anode.

### Question 3

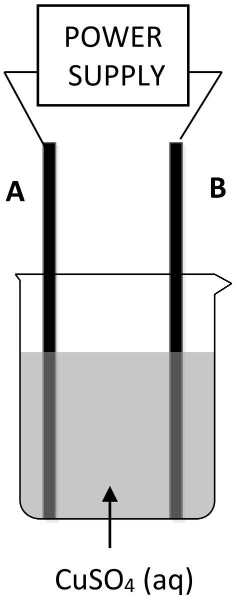
The electrolysis of a 1.0 M solution of NaCl will produce the same products at the anode and cathode as the electrolysis of

**A.** distilled water and 1.0 M $Fe(NO_3)_2$
**B.** 1.0 M $HNO_3$
**C.** 1.0 M $CuSO_4$
[✓ **D.**] 1.0 M $Al(NO_3)_3$

*When 1.0 M NaCl is electrolysed the strongest reductant, $H_2O$ (l) is oxidised into $O_2$ and $H^+$ and the strongest oxidant, $H_2O$ (l) is reduced into $H_2$ and $OH^-$. When 1.0 M $Al(NO_3)_3$ is electrolysed, $H_2O$ (l) is the strongest reductant and oxidant so the products at the anode and cathode will be the same as for the electrolysis of 1.0 M NaCl.*

**Question 4**

Consider the electrolysis cell below.



After this cell has been operating for about 30 minutes the mass of electrode B has increased and the concentration of the $CuSO_4$ in the electrolyte has decreased. Which of the statements regarding this cell is correct?

[✓ **A.**] Electrode A is made from graphite and electrode B is connected to the negative terminal of the power supply.

**B.** Electrodes A and B are both made from copper.

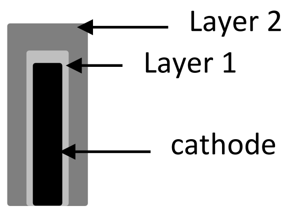
**C.** Electrode B is connected to the positive terminal of the power supply and electrode A is made from platinum.

**D.** Electrode B is connected to the positive terminal of the power supply and electrode A is connected to the negative terminal of the power supply.

*The only way for electrode B to gain mass is for the strongest oxidant in the solution, $Cu^{2+}$(aq), to be reduced into Cu (s) on the surface of electrode B. Therefore electrode B must be the cathode and connected to the negative terminal of the power supply. Electrode A must be the positive electrode and made from an inert material such as platinum or graphite. If it was made from copper, Cu (s), would be a much stronger reductant than $H_2O$ (l) and it would be reduced into $Cu^{2+}$ ions. This would result in the concentration of the $CuSO_4$ remaining constant rather than decreasing as was stated in the question.*

*Questions 5 and 6 refer to the following information.*

A solution containing 3 different ionic compounds is electrolysed at standard conditions. After several hours of electrolysis the cathode is removed and analysis shows that 2 different layers of material have deposited on the cathode during this time. The cathode is shown below.



**Question 5**
The solution that was electrolysed could have been a mixture of

**A.** $AgNO_3$ , NaCl and distilled water
**B.** $Al(NO_3)_3$ , $KNO_3$ and $NaNO_3$
[✓ **C.**] $Ni(NO_3)_2$, $AgNO_3$ and $Ca(NO_3)_2$
**D.** NaCl, $Mn(NO_3)_2$ and $Al(NO_3)_3$

*Only 2 layers of material formed on the cathode so of the 3 ionic compounds present in the solution, only 2 contained metal ions that were reduced into solid metal at the cathode. $Ni^{2+}$(aq) and $Ag^+$ (aq) are both stronger oxidants than $H_2O$ so they can be reduced into Ni (s) and Ag (s) respectively. $Ca^{2+}$ (aq), $Al^{3+}$ (aq) and $Na^+$ (aq) are below $H_2O$ on the electrochemical series table so are weaker oxidants than $H_2O$ and cannot be reduced into solid metals.*

**Question 6**
The composition of layers 1 and 2 could not be

| | **Layer 1** | **Layer 2** |
|---|---|---|
| [✓ **A.**] | Ag | Cu |
| **B.** | Zn | Ag |
| **C.** | Co | Ag |
| **D.** | Al | Li |

*The first layer of metal on the cathode must form from the reduction of the metal ion that is the strongest oxidant in the aqueous solution. If an aqueous solution contains $Ag^+$ (aq) and $Cu^{2+}$ (aq), the $Ag^+$ (aq) will be reduced first as it is the stronger oxidant. Therefore the first layer of material on the cathode would be Ag (s). Once all of the $Ag^+$ ions have been reduced , the weaker oxidant $Cu^{2+}$ will be reduced into Cu (s) which would form the second layer of material on the cathode.*

**Question 7**

An iron nail is to be coated with zinc metal in order to protect it from corrosion. The zinc metal can be coated onto the surface of the nail using electrolysis. During this process

**A.** the iron nail is connected to the negative of the power supply where it is oxidised.
**B.** $Zn^{2+}$ ions migrate to the nail where they are oxidised into Zn (s)
[✓ **C.**] An electrode of Zn (s) is oxidised at the positive electrode in order to maintain a constant electrolyte concentration.
**D.** the iron nail is attached at the positive electrode where it will act as a cathode.

**Question 8**

During the electrolysis of a dilute $MgCl_2$ solution, the ions and molecules that will migrate towards the negative electrode are

**A.** $Mg^{2+}$
**B.** $H_2O$
[✓ **C.**] $Mg^{2+}$ and $H_2O$
**D.** $Mg^{2+}$, $Cl^-$ and $H_2O$

*$Mg^{2+}$ and $H_2O$ are the only oxidants present in a $MgCl_2$ (aq) solution so they will both be attracted to and migrate towards the cathode. It is only the strongest oxidant, in this case $H_2O$, that will be reduced at the cathode.*

**Question 9**

Which of the following metals cannot be produced from the electrolysis of an aqueous solution containing its cation?

**A.** Cu
[✓ **B.**] Al
**C.** Ag
**D.** Zn

*An aqueous solution of $Al^{3+}$ ions cannot be reduced into solid Al at a cathode as $H_2O$ is a stronger oxidant and will be preferentially reduced at the cathode.*

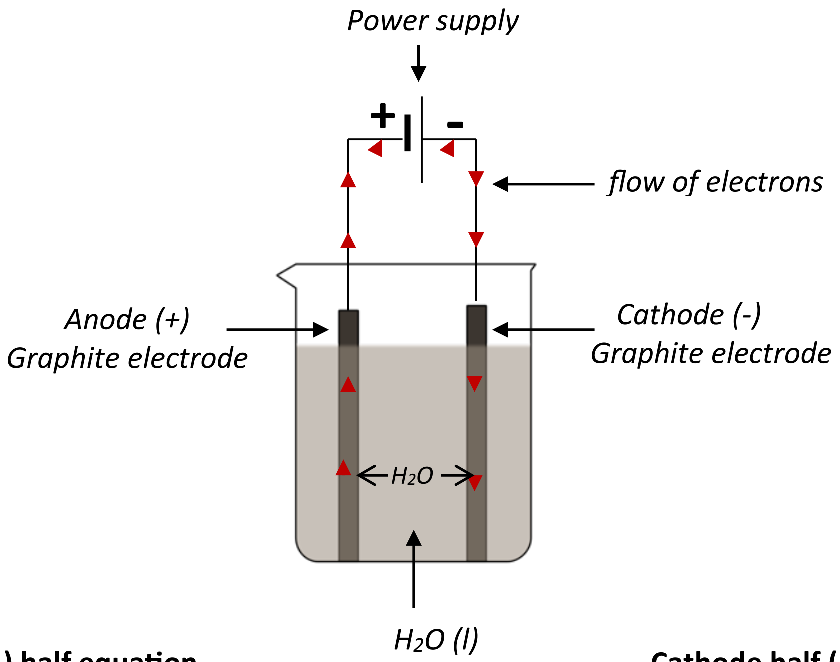
- *The only way to produce solid Al metal by electrolysis is to electrolyse a molten (melted into a liquid) compound containing $Al^{3+}$ ions such as $Al(NO_3)_3$. As there is no water present, $Al^{3+}$ is the only oxidant present and will be reduced into solid Al at the cathode without any interference from water.*

## Short Answers

**Question 1**

Draw cells showing the electrolysis of the following solutions. Graphite electrodes are present in all cells. Your diagrams must be labelled and include the power supply, anode, cathode and the movement of electrons through the wires connecting the electrodes and power supply. You must include equations for the electrode reactions. States of matter must be shown.

**a.** distilled water



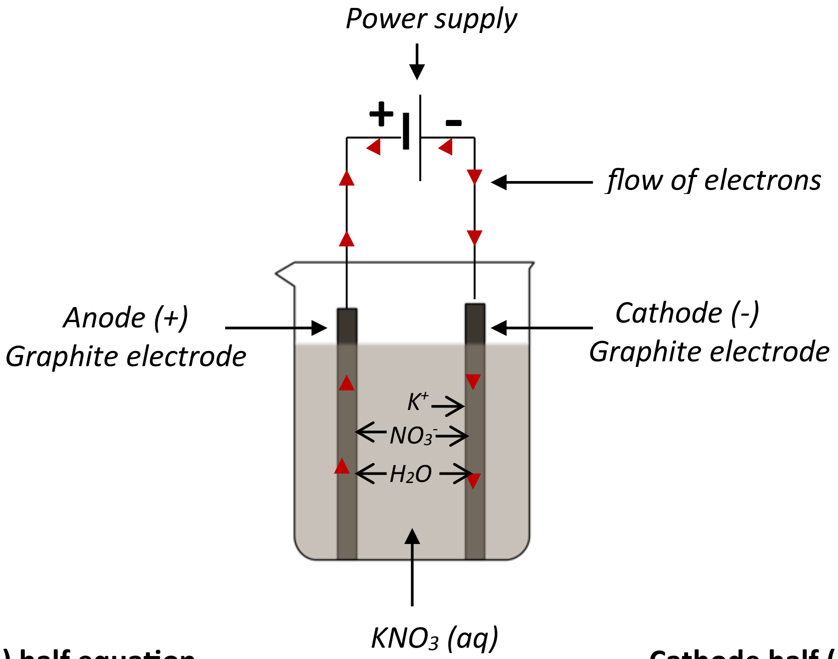
**Anode (+) half equation**

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

**Cathode half (-) half equation**

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

**b.** 1.0 M $KNO_3$



**Anode (+) half equation**

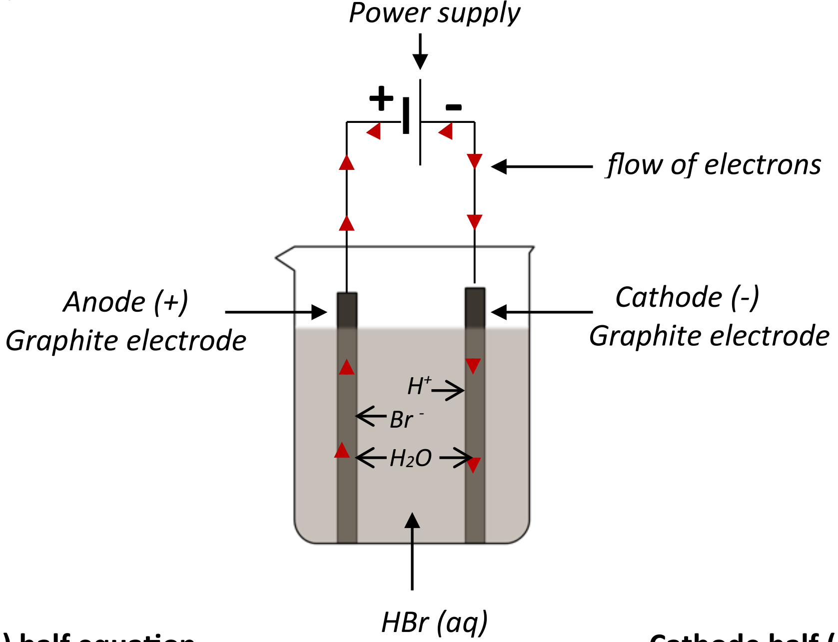
$2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$

**Cathode half (-) half equation**

$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 2OH^- (aq)$

*$K^+$ and $NO_3^-$ are oxidants so in the diagram they have been shown migrating to the cathode. They are not reduced there however, because $H_2O$ is a stronger oxidant. In a similar way $NO_3^-$ migrates to the anode because it is also a reductant but $H_2O$ which is the stronger of the two.*

**c.** 1.0 M HBr



**Anode (+) half equation**

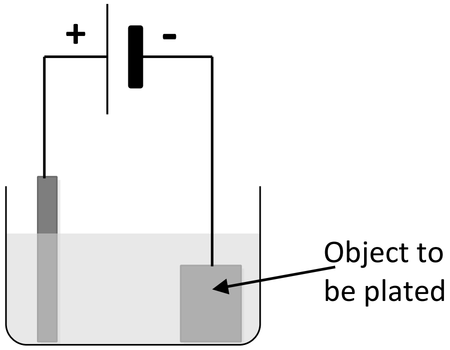
$2Br^- (aq) \rightarrow Br_2 (l) + 2e^-$

**Cathode half (-) half equation**

$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

**Question 2**

The diagram below shows part of an electrolysis cell that is going to be used to plate copper onto the surface of an object. The object to be plated is connected at the negative electrode.



**a.** Give a suitable electrolyte for this cell.

*$CuSO_4$ or $Cu(NO_3)_2$*

- *Any ionic compound containing the $Cu^{2+}$ ion will do provided it is soluble in water.*

**b.** From what material should the electrode connected to the positive terminal of the power supply be made from?

*Solid copper: Cu (s)*

**c.** In reference to this cell, explain why electrolytic cells do not need a salt bridge.

*With electrolytic cells the oxidation and reduction reactions occur in the same container which keeps the charge in the container neutral which allows electrons to flow through the external circuit. That is the oxidation reaction cancels out the negative charge produced at the cathode and the reduction cancels the positive charge produced at the anode.*

*In this copper plating cell, Cu (s) is oxidised at the anode:*

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$

*Every time a Cu atom is oxidised ,a $Cu^{2+}$ ion is released into the solution which would create a positive charge in the cell. This however, does not occur because over at the cathode $Cu^{2+}$ ions are removed from the solution due the reduction of $Cu^{2+}$ ions into Cu (s):*

$Cu^{2+}\ (aq) + 2e \rightarrow Cu\ (s)$

*Another way of looking at it:*

*At the cathode, $Cu^{2+}$ ions are reduced into Cu (s). This removes $Cu^{2+}$ ions from the solution which could make the solution accumulate a negative charge because the negative ions from the electrolyte, eg. $SO_4^{2-}$ are losing their $Cu^{2+}$ partner which used to cancel out their negative charge to zero. Negative charge is not accumulated in the cell because over at the anode Cu (s) is oxidised into $Cu^{2+}$ (aq) which dissolves into the solution and replaces the $Cu^{2+}$ ions that were lost by the reduction reaction at the cathode. These $Cu^{2+}$ ions that are produced at the anode can balance out the negative charge of the $SO_4^{2-}$ ions.*

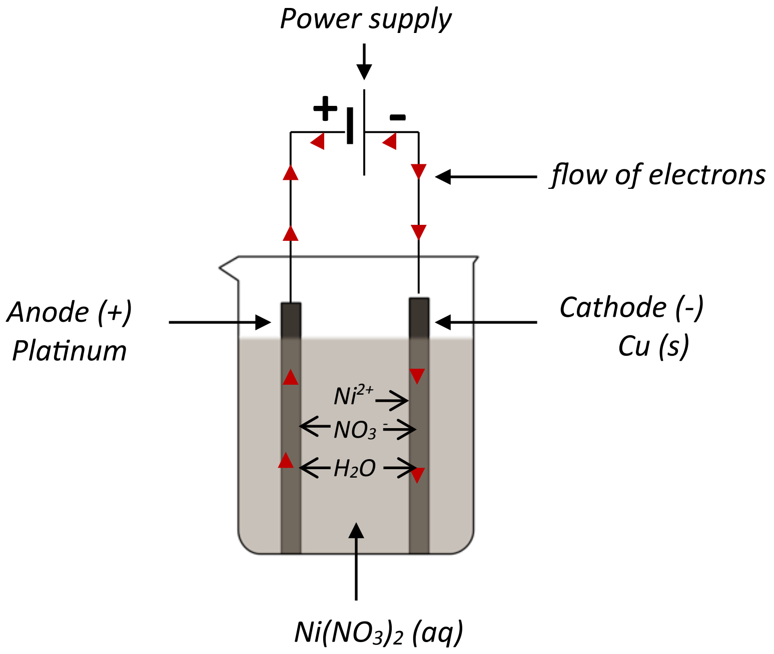
**d.** In reference to this cell, explain why the concentration of the electrolyte remains constant during the operation of an electroplating cell.

*The concentration of the electrolyte remains constant because each time a $Cu^{2+}$ ion from the electrolyte is removed by its reduction into Cu (s) at the cathode, it is replaced by the oxidation of a Cu atom into $Cu^{2+}$(aq) at the anode.*

**Question 3**

An electrolytic cell consists of a copper cathode and a platinum anode. The electrolyte is $Ni(NO_3)_2$.

- *It helps to draw the cell.*



**a.** Give the electrode half equations for this cell.

**Anode:** $2H_2O (l) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$
**Cathode:** $Ni^{2+} (aq) + 2e^- \rightarrow Ni (s)$

- *A common error with this type of question is to identify Cu (s) as the strongest reductant and give the anode half equation as*

  *Cu (s) → $Cu^{2+}$ (aq) + $2e^-$*

  *This is not possible because the Cu (s) is attached at the* ***cathode not the anode.*** *Even though Cu (s) is the strongest reductant it can only be oxidised it if it is attached at the anode. While at the cathode, Cu (s) will not be able to react at all. It will act in a similar way to an inert electrode and just allow electrons to flow through it which will be gained by the strongest oxidant, $Ni^{2+}$. As the Cu (s) is not attached at the anode, the only species that can be oxidised at the anode is $H_2O$ (l).*

**b.** If the electrolyte has a volume of 250.00 mL and a concentration of 1.00 M, calculate the concentration of the electrolyte after 2.00 A of electricity have passed through the cell for a time of 25.00 minutes.

*Q = I x t*
*= 2.00 x 25.00 x 60 = 3,000 c*

*n ($e^-$) =* $\frac{3,000}{96,500}$ *= 0.0310881 mol of electrons passed through the cell.*

*$Ni^{2+}$ (aq) + $2e^-$ → Ni (s)*

*n ($Ni^{2+}$) that gained the electrons and were reduced into Ni (s) = n ($e^-$) x ½*
*= 0.0310881 x ½*
*= 0.0155441 mol*

*n ($Ni^{2+}$) originally in cell = c x v*
*= 1.0 x 0.250.00 = 0.250 mol of $Ni^{2+}$ or $Ni(NO_3)_2$*

*n ($Ni^{2+}$) remaining in cell = n ($Ni^{2+}$) originally in cell – n ($Ni^{2+}$) removed by reduction*
*= 0.250 – 0.0155441 = 0.2344559 mol*

*C ($Ni^2$ or $Ni(NO_3)_2$) remaining in the cell =* $\frac{n}{v}$ = $\frac{0.2344559}{0.2500}$ *= 0.9378236 = 0.938 M*

**c.** Explain why the reaction occurring at the cathode may change after this cell has been operating for a long period of time.

*As time goes by the concentration of $Ni^{2+}$ ions in the electrolyte will get lower and lower as $Ni^{2+}$ ions are reduced into Ni (s). Once all of the $Ni^{2+}$ ions are removed from the electrolyte, the next strongest oxidant, $H_2O$ (l) ,will be reduced at the cathode:*

*$2H_2O$ (l) + $2e^-$ → $H_2$ (g) + $2OH^-$ (aq)*

- *Even before all of the $Ni^{2+}$ ions have been used up, the $H_2O$ may start to react at the cathode. This is because once the concentration of $Ni^{2+}$ gets well below 1.0 M, the electrochemical series table can no longer predict that it will be reduced in preference to the water. Recall that the electrochemical series table can only predict reactions for electrolyte concentrations that are at 1.0 M. As the $Ni^{2+}$ is a significantly stronger oxidant than $H_2O$, it is not likely that the $H_2O$ will be reduced before all of the $Ni^{2+}$ ions have been removed.*

**Question 4**

A cathode has 0.0962 mol of metal deposited onto its surface during the electrolysis of an aqueous solution of unknown identity. For a time of 25.0 minutes 12.36 A of electricity were passed through this cell.

**a.** Calculate the oxidation number of the cation dissolved in this electrolyte.

*Find the moles of the electrons that have passed through the cell:*

$Q = I \times t$
$= 12.36 \times 25.0 \times 60 = 18{,}540\ c$

$$n(e^-) = \frac{18{,}540}{96{,}500} = 0.1921244\ mol$$

*Therefore 0.1921244 mol of electrons were gained by 0.0962 mol of the metal cations in the electrolyte.*

*Find the ratio between the moles of electrons and moles of metal produced or ions reduced at the cathode.*

$$M^{x+} \quad + \quad x\,e^- \quad \rightarrow \quad M$$

0.0962 mol    0.1921244

$$\frac{0.0962}{0.0962} \qquad \frac{0.1921244}{0.0962}$$

1    2

*Therefore the charge (oxidation number) of the metal cations is +2.*

**b.** What is the identity of the metal deposited at the cathode if its mass increased by 5.0 g?

*The increase in mass of the metal is equivalent to the moles of metal ions reduced / solid metal produced at the cathode.*

*Find the molar mass of the metal:*

$$M = \frac{m}{n} = \frac{5.0}{0.0962} = 51.975 \text{ g mol}^{-1}$$

*The metal is Chromium (Cr). On the data book Cr has a molar mass of 52.0 g mol$^{-1}$*

**Question 5**

During an experiment to determine the value of Avogadro's number, 19,510.3 c of charge are passed through molten sodium chloride. The volume of $Cl_2$ gas collected at the anode at a temperature of 310 K and pressure of 1.5 atm is equal to 1.74 L.

**a.** Use the data provided to calculate Avogadro's number.

$PV = nRT$

$$n(Cl_2) = \frac{PV}{RT} = \frac{1.5 \text{ x } 101.3 \text{ x } 1.74}{8.31 \text{ x } 310} = 0.102633 \text{ mol}$$

$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq)$

$n(e^-) = n(Cl_2) \text{ x } 2$

$= 0.102633 \text{ x } 2 = 0.205266 \text{ mol}$

*Now find the charge of 1.0 mol of electrons (F) using the equation:*

$Q = n(e^-) \text{ x } F$

$$F = \frac{Q}{n(e-)}$$

$$F = \frac{19{,}510.3}{0.205266} = 95{,}048.86 \text{ c}$$

*Divide this charge of 1.0 mol of electrons by the charge of just 1 electron (refer to data book) in order to find the actual number of electrons in 1.0 mol of electrons. This will be equal to Avogadro's number.*

$$\frac{95{,}048.86}{1.6 \text{ x } 10^{-19}} = 5.94055 \text{ x } 10^{23} = 5.9 \text{ x } 10^{23}$$

**b.** What error in the above experiment could cause a calculation of Avogadro's number to be higher than the true value? Explain your answer.

*Loss of $Cl_2$ gas at the anode. This would give a lower volume of $Cl_2$ which would lead to a lower calculated moles of $Cl_2$. This would lead to a lower calculated moles of electrons. When the charge of 1.0 mole of electrons is determined, the charge of* 19,510.3 c *will be divided by a lower number of electrons leading to a higher calculated charge for 1.0 mol of electrons:*

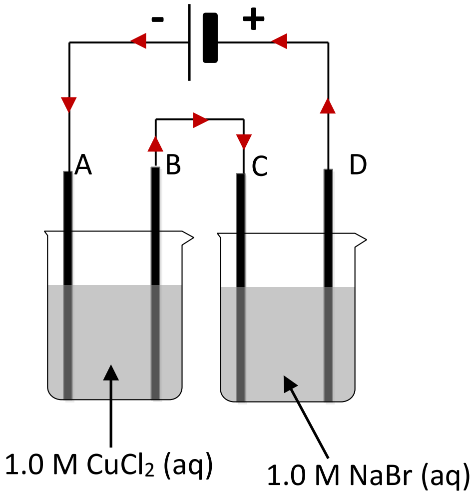
$$F = \frac{Q}{n\ (e-)} = \text{HIGHER VALUE}$$

*Lower value*

*This greater value for the charge of 1.0 mol of electrons when divided by $1.6 \times 10^{-19}$ c will give a greater value for Avogadro's constant.*

**Question 6**

The diagram below shows 2 electrolysis cells connected in series. All of the electrodes are made from platinum and the volume of each solution is 400.0 mL



**a.** Give the half equations showing states, for the reactions occurring at electrodes A, B, C and D.

*A (-): $Cu^{2+}$ (aq) + $2e^-$ → Cu (s)*
*B (+): $2H_2O$ (l) → $O_2$ (g) + $4H^+$ (aq) + $4e^-$*
*C (-): $2H_2O$ (l) + $2e^-$ → $H_2$ (g) + $2OH^-$ (aq)*
*D (+): $2Br^-$ (aq) → $Br_2$ (l) + $2e^-$*

**b.** What mass of material will be deposited at electrode A if 0.025 mol of reductant has been oxidised at electrode D?

- *When electrolysis cells are connected in series, the number of electrons flowing into and out of each cell is always the same. That is, the number of electrons flowing out of each anode (electrodes B and D) is equal to the number of electrons flowing into each cathode (electrodes A and C).*

  *At electrode D:*
  $2Br^- (aq) \rightarrow Br_2 (l) + 2e^-$

  $n (e^-) = n (Br^-)$
  $= 0.025$ *mol*

  *So 0.025 mol of electrons are produced when 0.025 mol of* $Br^-$ *are oxidised. This means that 0.025 mol of electrons flowed out of electrode D. Therefore the 0.025 mol of electrons flowed into the electrode A.*

*At electrode A,* $Cu^{2+}$ *was reduced into Cu solid.*

$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s)$

$n (Cu)$ *produced* $= ½ \times n (e^-)$
$= ½ \times 0.025 = 0.0125$ *mol*

$m (Cu) = 0.0125 \times 63.5 = 0.79375 = 0.79$ *g of material produced at electrode A*

**c.** What current in amps, is needed in order to change the concentration of $Br^-$ ions to 0.75 M during a 2.0 hour period.

$n (Br^-)$ *initially added to the cell on the right* $= c \times v$
$= 1.0 \times 0.4000 = 0.4000$ *mol*

$n (Br^-)$ *present in 400.0 mL if concentration reduced to 0.75 M* $= c \times v$
$= 0.75 \times 0.4000$
$= 0.3000$ *mol*

$n (Br^-)$ *that must be oxidised to change*
*the concentration from 1.0 M to 0.75 M* $= 0.4000 – 0.3000 = 0.1000$ *mol*

$n (e^-)$ *produced from the oxidation of 0.1000 mol of* $Br^-$*:*

$2Br^- (aq) \rightarrow Br_2 (l) + 2e^-$

$n (e^–) = n (Br^-) = 0.1000$ *mol*

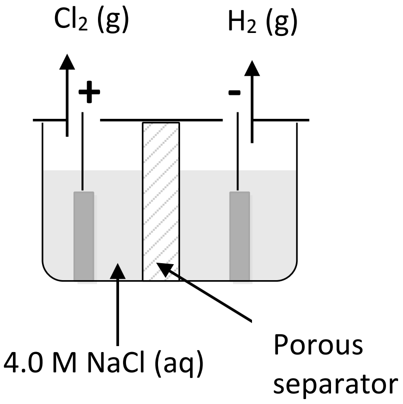
*$Q = n(e^-) \times 96{,}500$*
*$= 0.1000 \times 96{,}500 = 9650$ c*

*$Q = I \times t$*

$$I = \frac{Q}{t} = \frac{9650}{(2 \times 60 \times 60)} = 1.340278 = 1.3\ A$$

**Question 7**

Sodium hydroxide is produced industrially using the membrane cell which is shown below.



The electrode reactions are

**Anode**
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

**Cathode**
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The electrolyte is first poured in at the positive electrode. Water and $Na^+$ ions are able to move through the separator and enter the negative electrode. $Cl^-$ ions are unable to pass through the separator.

**a.** Explain why the reaction at the anode is able to occur even though the electrochemical series table predicts that $H_2O$ should be oxidised in preference to $Cl^-$ ions.

*The electrochemical series table can only be used to predict reactions occurring at standard conditions where solution concentrations are equal to 1.0 M. The concentration of the NaCl is 4.0 M so at this concentration it is possible for $Cl^-$ to be oxidised in preference to $H_2O$ even though the table lists $H_2O$ as the stronger reductant.*

**b.** Explain how sodium hydroxide is able to be produced at the negative electrode.

*At the negative electrode (cathode), the only oxidant present that can undergo reduction is water:*

$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$

*The porous separator allows* $Na^+$ *ions to pass from the anode to the cathode. Sodium hydroxide is produced when the* $Na^+$ *ions react with the* $OH^-$ *ions that were produced by the reduction of* $H_2O$ *at the cathode:*

$Na^+\ (aq) + OH^-\ (aq) \rightarrow NaOH\ (aq)$

**c.** How does the porous separator help to ensure that the sodium hydroxide produced at the cathode is of high purity?

*The porous separator does not allow* $Cl^-$ *ions from the 4.0 M NaCl solution poured in at the anode to pass through to the cathode where NaOH is produced. Therefore the NaOH will not be contaminated with NaCl.*

**d.** Why must the products at the 2 electrodes not be allowed to make contact with each other?

*The* $Cl_2$ *gas produced at the anode can react spontaneously with the* $H_2$ *gas produced at the cathode. This reaction can generate heat energy which may cause fires and / or explosions.*

**e.** What current of electricity would be required to produce 2.0 tonnes of $Cl_2$ gas during a 24 hour period?

$2Cl^- \rightarrow Cl_2\ (g) + 2e^-$

$$n\ (Cl_2) = \frac{2.0 \text{ x } 10^6}{71\ .0} = 28{,}169.014 \text{ mol}$$

$n\ (e^-) = 28{,}169.014 \text{ x } 2 = 56{,}338.028 \text{ mol}$

$Q = n\ (e^-) \text{ x } 96{,}500$
$\quad = 56{,}338.028 \text{ x } 96{,}500 = 5{,}436{,}619{,}702 \text{ c}$

$Q = I \text{ x } t$

$$I = \frac{Q}{t} = \frac{5{,}436{,}619{,}702}{24 \text{ x } 60 \text{ x } 60} = 62{,}923.84 = 6.3 \text{ x } 10^4 \text{ A}$$

**f.** How many joules of electrical energy are required to produce 2.0 tonnes of sodium hydroxide? The voltage of the electricity is equal to 100.0 v.

*First of all we need to calculate the moles of NaOH:*

$n\ (NaOH) = \frac{2{,}000{,}0000}{40.0} = 50{,}000$ *mol of NaOH*

$n\ (OH^-) = n\ (NaOH) = 50{,}000$ *mol*

$n\ (e^-)$ *can be calculated from the equation:*

$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$

$n\ (e^-) = n\ (OH^-) = 50{,}000$ *mol*

$Q = n\ (e^-) \times 96500$

$= 50{,}000 \times 96{,}500 = 4{,}825{,}000{,}000$ *c*

$E = V \times Q$

$= 100.0 \times 4{,}825{,}000{,}000 = 4.825 \times 10^{11} = 4.8 \times 10^{11}$ *J*