

HSC Chemistry – Module 5: Equilibrium & Acid Reactions – Static & Dynamic Equilibrium Study Notes

Inquiry question: What happens when chemical reactions do not go through to completion?

Students:

- conduct practical investigations to analyse the reversibility of chemical reactions, for example:
 - cobalt(II) chloride hydrated and dehydrated
 - iron(III) nitrate and potassium thiocyanate
 - burning magnesium
 - burning steel wool
- model static and dynamic equilibrium and analyse the differences between open and closed systems
- analyse examples of non-equilibrium systems in terms of the effect of entropy and enthalpy, for example:
 - combustion reactions
 - photosynthesis
- investigate the relationship between collision theory and reaction rate in order to analyse chemical equilibrium reactions

Reversibility of Chemical Reactions

In some cases, chemical reactions are reversible, and in other cases chemical reactions are not.

Non-reversible Chemical Reactions

A non-reversible chemical reaction is one that can only move in **one direction**. This means that all of the reactants will form products, but the products are not able to reverse and form the reactants (unless a new and separate reaction takes place). Non-reversible chemical reactions are signified by a **completion** sign (\rightarrow). Non-reversible chemical reactions can also be known as **completion reactions**.

Common examples of completion reactions include:

- ✓ Acid + Base – e.g. $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$
- ✓ Acid + Metal – e.g. $3\text{H}_2\text{SO}_{4(\text{aq})} + 2\text{Al}_{(\text{s})} \rightarrow \text{Al}_2(\text{SO}_4)_{3(\text{aq})} + 3\text{H}_{2(\text{g})}$
- ✓ Burning metal – e.g. $2\text{Ca}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow 2\text{CaO}_{(\text{s})}$
- ✓ Photosynthesis – $6\text{CO}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{C}_6\text{H}_{12}\text{O}_{6(\text{aq})} + 6\text{O}_{2(\text{g})}$
- ✓ Respiration – $\text{C}_6\text{H}_{12}\text{O}_{6(\text{aq})} + 6\text{O}_{2(\text{g})} \rightarrow 6\text{CO}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})}$

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Reversible Chemical Reactions

A reversible chemical reaction is one that is able to move in **both** the forward and reverse direction. This means that reactants can form products (reaction proceeds forward), as well as products forming reactants (reaction proceeds in the reverse). This is all occurring in the same system, and **does not** require new and separate reactions. This is compared to completion reactions, where only the products are formed (and reforming reactants require a new and separate reaction). Reversible chemical reactions are signified by an equilibrium sign (\rightleftharpoons). Reversible reactions are also known as **equilibrium reactions**.

Common example of equilibrium reactions include:

- ✓ Dissolution of weak acids in water
 - $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{CH}_3\text{COO}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$
 - $\text{H}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{HCO}_3^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})}$
- ✓ Saturated solutions
 - $\text{NaCl}_{(\text{s})} \rightleftharpoons \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$ when enough NaCl is added to water that it stops dissolving
 - $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{aq})}$ since $\text{CO}_{2(\text{g})}$ has low solubility in water, only a small proportion of it will dissolve in water.

Throughout this topic, you will come across many more examples of reversible chemical reactions.

Practical Investigations

During your time at school, you would have conducted a variety of practical investigations to determine the reversibility of chemical reactions. Some include:

- ✓ Cobalt(II) chloride hydrated and dehydrated
- ✓ Iron(III) nitrate and potassium thiocyanate
- ✓ Burning magnesium
- ✓ Burning steel wool

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Cobalt(II) chloride hydrated and dehydrated



Anhydrous Cobalt(II) Chloride



Cobalt(II) Chloride Hexahydrate

In this experiment, cobalt(II) chloride hydrated (or hydrous cobalt(II) chloride) is **pink** and when dehydrated to form anhydrous cobalt(II) chloride it turns **blue**.

- Initially start off with hydrous cobalt(II) chloride, which is pink. This is placed in an evaporating basin, and the Bunsen burner is used to heat the substance.
 - The cobalt(II) chloride will start to turn blue when heated, since it is losing water.
- A couple drops of water is then added to the blue anhydrous cobalt(II) chloride.
 - The blue anhydrous cobalt(II) chloride will then turn pink signifying that it is once again becoming hydrated.

So is this chemical reaction reversible?

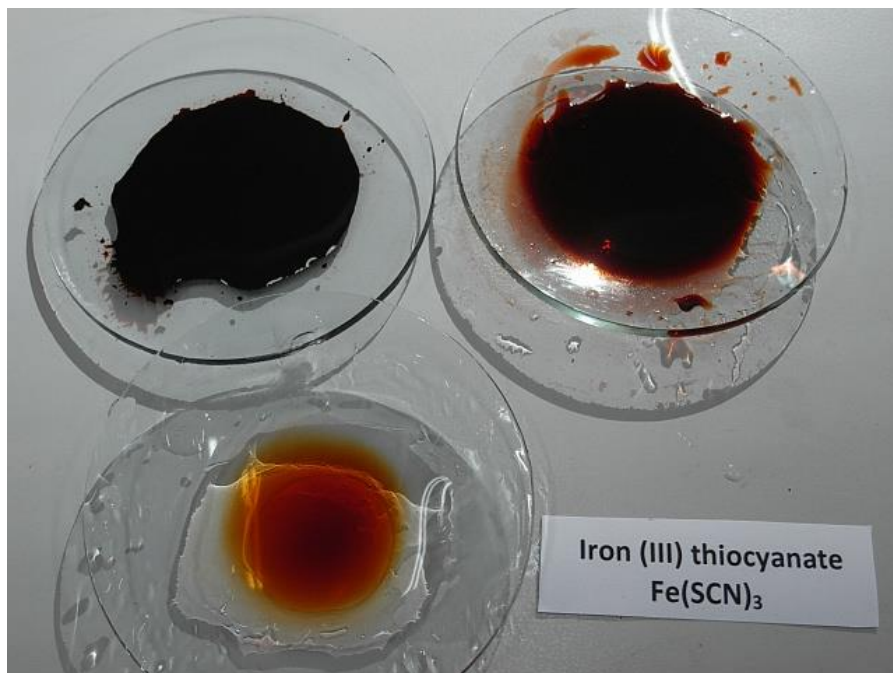
Yes, it is.

Here is the equation: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{CoCl}_{2(s)}$

It can be seen that the reaction can go forwards and backwards.

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Iron(III) nitrate and potassium thiocyanate



In this experiment, when $\text{Fe}(\text{NO}_3)_3$ reacts with KSCN , it will form a complex ion called iron thiocyanate, FeSCN^{2+} .

The simplified equation is $\text{Fe}^{3+}_{(\text{aq})} + \text{SCN}^{-}_{(\text{aq})} \rightleftharpoons \text{FeSCN}^{2+}_{(\text{aq})}$

The Fe^{3+} ion is yellow and SCN^{-} ion is colourless, whereas the FeSCN^{2+} complex ion is blood red.

There's a couple variations to this experiment:

1. Changing concentrations of KSCN and $\text{Fe}(\text{NO}_3)_3$
 - a. When more KSCN is added, this **increases the concentration of SCN^{-} ions** in the system. As a result, the equilibrium will move to the **right-hand side** (or forward reaction), to remove the extra amount of SCN^{-} ions (*factors that affect equilibrium will be explained in following chapters*). This will make extra FeSCN^{2+} and will induce a **more** blood-red colour.
 - b. $\text{Fe}(\text{NO}_3)_3$ can be removed by precipitating it out with phosphate ions. When it is precipitated out, this **decreases the concentration of Fe^{3+} ions** in the system. As a result, the equilibrium will move to the **left-hand side** (or reverse reaction), to increase the amount of Fe^{3+} ions. There will be less FeSCN^{2+} and will induce a **less** blood-red colour.
2. Changing temperatures:
 - a. When temperature is **increased**, the reaction will shift to the **endothermic side** (*will be covered in future chapters*). Since this reaction is exothermic, the **left-hand side is endothermic**, thus it will **shift to the reverse reaction**. This will mean **less FeSCN^{2+}** available and will induce a **less** blood-red colour.

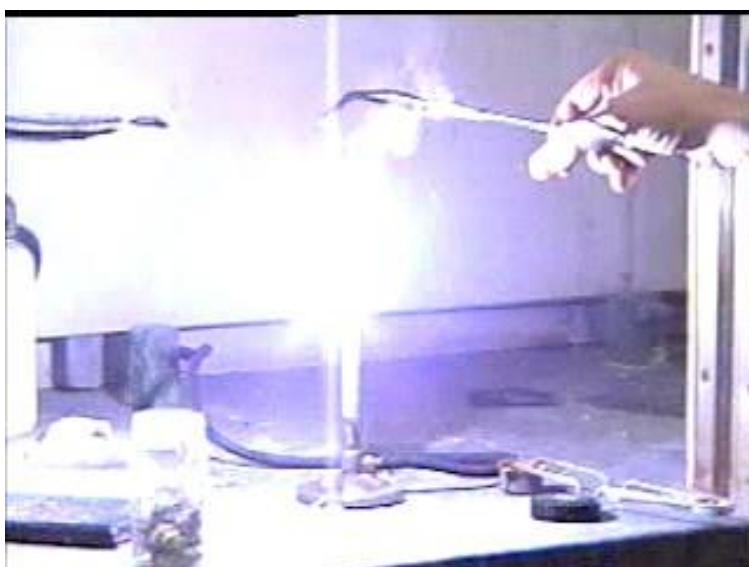
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- b. When temperature is **decreased**, the reaction will shift to the **exothermic side**. Since this reaction is exothermic, the right-hand side is exothermic, thus it will **shift to the forward reaction**. This will mean **more** FeSCN^{2+} produced and will induce a **more** blood-red colour.

So is this chemical reaction reversible?

Yes, it is. This is because the colours are able to change and revert back to its original colour as well.

Burning magnesium

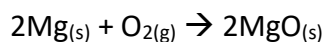


This should be a well-known experiment, since it should have been conducted back in year 10.

When magnesium or an **active** metal is burnt, it will become a metal oxide.

Active metal + oxygen gas \rightarrow Metal oxide

Magnesium is quite active, and will react with oxygen gas to form magnesium oxide:



Magnesium is placed in a crucible and heated using the Bunsen burner. When there is a flash of bright light, this signifies that the magnesium has reacted with oxygen. Magnesium oxide is powdery and white in colour, and should coat the magnesium metal.

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So is this reaction reversible?

No, as it very difficult to return back to magnesium metal, unless you undergo as series of new chemical reactions. You cannot change the temperature or concentration or other factors during this reaction to return magnesium oxide back to magnesium.

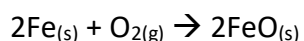
Therefore, this reaction **goes to completion** and is **not in equilibrium**.

Burning steel wool



As with burning magnesium, this will follow the same equation.

Steel is primarily made up of iron and will react as iron(II):



Steel wool is also placed in a crucible and heated using the Bunsen burner. Iron oxide is also white and powdery, and will coat the steel wool.

So is this reaction reversible?

No, as it very difficult to return back to Fe metal, unless you undergo as series of new chemical reactions. You cannot change the temperature or concentration or other factors during this reaction to return iron oxide back to iron.

Therefore, this reaction **goes to completion** and is **not in equilibrium**.

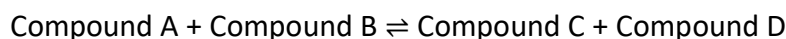
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Static and Dynamic Equilibriums

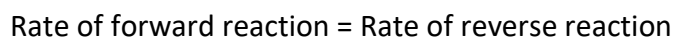
What is an equilibrium?

An equilibrium reaction is a type of **reversible reaction**. As stated above, the notation for equilibrium is \rightleftharpoons .

A common example of an equilibrium reaction is:



In this equilibrium, Compound A is reacting with Compound B to form Compound C and Compound D (forward). A defining factor of an equilibrium is that at the **same time**, Compound C is reacting with Compound D to form Compound A and Compound B. This means that when a system is at equilibrium, $\text{Compound A} + \text{Compound B} \rightarrow \text{Compound C} + \text{Compound D}$, and $\text{Compound C} + \text{Compound D} \rightarrow \text{Compound A} + \text{Compound B}$ are occurring at the **same rate**. Essentially at equilibrium, the amount of reactants and products **stay constant** and **do not change**, unless there is a **disturbance** acting on it.

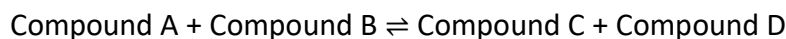


Dynamic Equilibrium

One type of equilibrium is **dynamic equilibrium** and it is essentially what has been explained above.

- ✓ Dynamic equilibrium is reversible.
- ✓ Rate of the forward reaction is equal to the rate of the reverse reaction.
 - However, the rates of the forward and reverse reaction are not **zero**, which means that there are always reactants becoming products, and always products becoming reactants. Both forward and reverse reactions are occurring at the **same rate**, unless there is a disturbance.
 - E.g. it is $2=2$, not $0=0$
- ✓ Only occurs in a **closed system**.

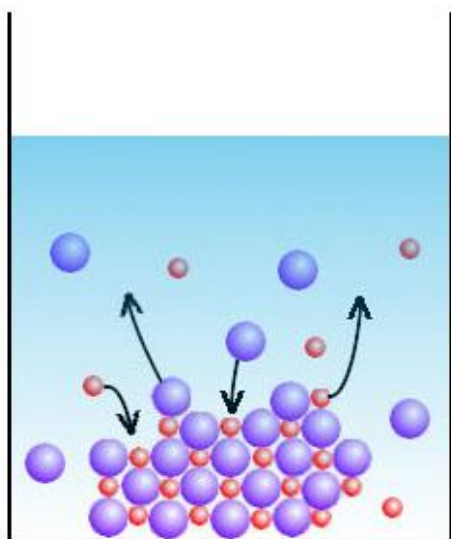
The generic chemical equation would be:



Examples would be:

- ✓ A saturated solution of $\text{NaCl}_{(s)} \rightleftharpoons \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$

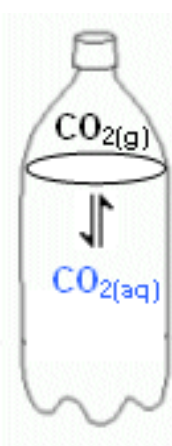
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Eventually, the rate of dissolution will equal the rate of precipitation. The solution will be in equilibrium, but the ions will continue to dissolve and precipitate.

At all times, there will be molecules of $\text{NaCl}_{(s)}$ dissolving to become $\text{Na}^+_{(aq)}$ and $\text{Cl}^-_{(aq)}$. At the same time, equal numbers of $\text{Na}^+_{(aq)}$ and $\text{Cl}^-_{(aq)}$ are precipitating to become $\text{NaCl}_{(s)}$. Therefore, when one mole of $\text{NaCl}_{(s)}$ dissolves into its ions, one mole of $\text{Na}^+_{(aq)}$ and $\text{Cl}^-_{(aq)}$ will precipitate at the same time. This shows that the rate of the forward reaction is equal to rate of the reverse reaction, since there will always be the same moles of $\text{NaCl}_{(s)}$ and $\text{Na}^+_{(aq)}/\text{Cl}^-_{(aq)}$ unless there is a disturbance (such as temperature).

✓ An unopened soft drink can/bottle $\text{CO}_{2(g)} \rightleftharpoons \text{CO}_{2(aq)}$



- Gases, including $\text{CO}_{2(g)}$ have a very low solubility in water and other liquids. Therefore, it is very easy for the soft drink to lose its fizziness (presence of $\text{CO}_{2(aq)}/\text{H}_2\text{CO}_{3(aq)}$).
- When the bottle or can of soft drink is unopened, there is a dynamic equilibrium taking place microscopically:

When one molecule of $\text{CO}_{2(g)}$ enters the water and becomes $\text{CO}_{2(aq)}$, one molecule of $\text{CO}_{2(aq)}$ will come out of solution and become $\text{CO}_{2(g)}$. The rate of the forward reaction is equal to the rate of the reverse reaction, and so the moles of $\text{CO}_{2(g)}$ and $\text{CO}_{2(aq)}$ will not change, unless there is a disturbance.

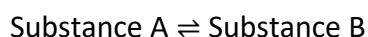
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Static Equilibrium

Another type of equilibrium is **static equilibrium**.

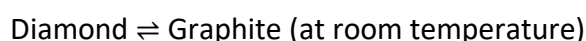
- ✓ Static equilibrium is a type of reaction that is considered **irreversible**.
- ✓ Rate of the forward reaction is equal to the rate of the reverse reaction.
 - However, the rate of the forward reaction is essentially **zero** and the rate of the reverse reaction is also essentially **zero**.
 - That means no reactants are forming products and no products are forming reactants.
 - E.g. $0=0$
- ✓ Usually occurs in closed systems, but sometimes in open.

The generic equation is:

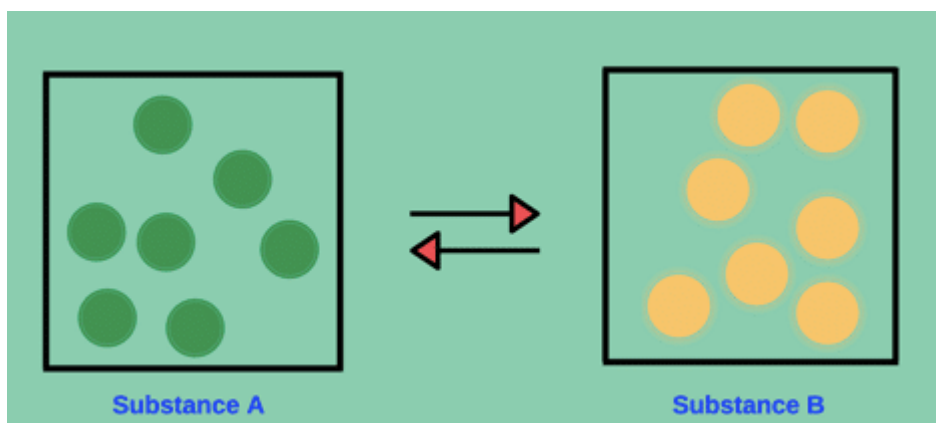


The difference between static and dynamic equilibrium is that static equilibrium **does not change, and will not change at a molecular level**.

For example:



- Diamond and graphite are allotropes, and diamond is able to transform into graphite (more stable allotrope of carbon) if the temperature is high enough.
- However, at room temperature it will take billions of years for that to occur, thus it is assumed that there is **no molecular change**.



As seen in this diagram, the number of diamond and graphite will not change. Even at a molecular level or microscopically, and molecules of substance A are not forming into substance B and the same number is forming vice versa (unlike dynamic equilibrium).

Note: However, the rate of the forward and reverse reactions are equal for both dynamic and static equilibrium. The difference is that in static equilibrium, this rate is $0=0$.

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Open and Closed Systems

A **closed system** does not involve the exchange of substances, materials and/or matter with the external environment. In other words, the system **does not interact with the environment**.

For example, in the soft drink can/bottle, the liquid, CO₂ equilibrium inside the can does not interact with the environment outside the can. When the can/bottle is unopened, the gases are kept inside and cannot escape to the environment. Therefore, this is a closed system.

In the salt example, since no gases are involved, the water and solid cannot escape to the external environment. Hence, this is also a closed system.

An **open system** involves the **interaction and exchanging** [of substances] **with the external environment**. For example, if the soft drink can is left open, then there would be a continual escape of gas into the environment, and hence this is an open system.

Dynamic equilibrium can only exist in a **closed system**, because for this equilibrium to form, substances cannot be affected by the surroundings, unless there is a disturbance enacted on it. If the soft drink can is left opened, then gases will continue to move out, and an equilibrium may never be reached.

Enthalpy and Entropy

Enthalpy

Enthalpy is **total internal energy** present inside a system, and is denoted through the letter 'H'. ΔH is the **change in enthalpy**, and is the change in internal heat energy that is lost or gained by the system.

- A positive ΔH shows that the system has gained heat energy from the surroundings. This is an endothermic reaction.
- A negative ΔH shows that the system has lost heat energy into the surroundings. This is an exothermic reaction.

Entropy

Entropy is the **number of ways** energy can be distributed in a system. It is a measure of randomness and is also a measure of the possible arrangements the atoms in the system can have. Entropy is denoted by 'S', with ΔS being the change in entropy.

Gases have the greatest entropy as they have the greatest number of ways they can interact, followed by aqueous solutions, liquids and solids.

The entropy of a system can be increased by:

1. Increasing the energy of the system (such as through increasing temperature)

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- More collisions, so more particles are able to interact, which increases the number of ways the energy is distributed.
2. Increasing the number of species in the system
 - More collisions, so more particles are able to interact, which increases the number of ways the energy is distributed.
3. Increase the volume of the species
 - Increased space, so increased number of ways particles can collide.

You will have to investigate the ΔH and ΔS of a variety of chemical reactions:

Photosynthesis

$6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$ (Note: At room temperature, the state of glucose is solid, hence why solid is used instead of aqueous)

Enthalpy: Positive as it is an endothermic reaction.

Entropy: Negative as left-hand side has liquid, whilst the right-hand side has solid. Both sides have 6 moles of gas, thus the substance that counts will be the liquid and solid. Liquids have greater entropy than solids, therefore the entropy decreases as the reactants are becoming products.

Combustion

$2\text{C}_8\text{H}_{18}(\text{l}) + 25\text{O}_2(\text{g}) \rightarrow 16\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l})$

Enthalpy: Negative as it is an exothermic reaction. All combustion reactions are exothermic.

Entropy: Positive as there are less (25) moles of gas on the left-hand side, and more (34) moles of gas on the right-hand side.

A negative enthalpy and positive entropy gives you a spontaneous reaction.

Collision Theory and Reaction Rates

Collision theory refers to products to forming from the successful collision of reactant molecules. A successful collision needs the following:

1. Sufficient speed – to have sufficient energy to break the bonds.
2. Correct orientation – so the correct products are formed.

To increase the rate of reaction, you will need to increase the rate of successful collisions. Hence, you will have to increase the kinetic energy of the system, by increasing the temperature or you will need to make sure the molecules are colliding in the correct orientation.

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There are a couple ways to affect the rate of reaction:

- ✓ Temperature of system
 - This increases the kinetic energy of the system, and will increase the number of collisions. If there are more collisions, then there should be an increased chance of successful collisions.
- ✓ Pressure (volume) of system
 - By increasing the pressure or decreasing the volume of the system, there is less space available for the reactants to collide with one another. If there is less space, this increases the number of collisions, then there should be an increased chance of successful collisions.
- ✓ Concentration of reactants
 - By increasing the concentration of reactants, there are more opportunities for collisions, then there should be an increased chance of successful collisions.
- ✓ Surface area of reactants
 - By increasing the surface area, you increase the available space for molecules to successfully collide with one another. Think of trying to dissolve Panadol in water – is it faster to dissolve when it is crushed up or when it is a full tablet.
- ✓ Presence of catalyst
 - This lowers the activation energy of the reaction, hence less energy is required for the reaction to proceed.