Surfing

NATIONAL CHEMISTRY

Unit 3 Equilibrium, Acids and Redox Reactions

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Contents

Introduction

Each book in the *Surfing* series contains a summary, with occasional more detailed sections, of all the mandatory parts of the syllabus, along with questions and answers.

All types of questions – multiple choice, short response, structured response and free response – are provided. Questions are written in exam style so that you will become familiar with the concepts of the topic and answering questions in the required way.

Answers to all questions are included.

A topic test at the end of the book contains an extensive set of summary questions. These cover every aspect of the topic, and are useful for revision and exam practice.

Words To Watch

account, account for State reasons for, report on, give an account of, narrate a series of events or transactions.

analyse Interpret data to reach conclusions.

annotate Add brief notes to a diagram or graph.

apply Put to use in a particular situation.

assess Make a judgement about the value of something.

calculate Find a numerical answer.

clarify Make clear or plain.

classify Arrange into classes, groups or categories.

comment Give a judgement based on a given statement or result of a calculation.

compare Estimate, measure or note how things are similar or different.

construct Represent or develop in graphical form.

contrast Show how things are different or opposite.

create Originate or bring into existence.

deduce Reach a conclusion from given information.

define Give the precise meaning of a word, phrase or physical quantity.

demonstrate Show by example.

derive Manipulate a mathematical relationship(s) to give a new equation or relationship.

describe Give a detailed account.

design Produce a plan, simulation or model.

determine Find the only possible answer.

discuss Talk or write about a topic, taking into account different issues or ideas.

distinguish Give differences between two or more different items.

draw Represent by means of pencil lines.

estimate Find an approximate value for an unknown quantity.

evaluate Assess the implications and limitations.

examine Inquire into.

explain Make something clear or easy to understand.

extract Choose relevant and/or appropriate details.

extrapolate Infer from what is known.

hypothesise Suggest an explanation for a group of facts or phenomena.

identify Recognise and name.

interpret Draw meaning from.

investigate Plan, inquire into and draw conclusions about.

justify Support an argument or conclusion.

label Add labels to a diagram.

list Give a sequence of names or other brief answers.

measure Find a value for a quantity.

outline Give a brief account or summary.

plan Use strategies to develop a series of steps or processes.

predict Give an expected result.

propose Put forward a plan or suggestion for consideration or action.

recall Present remembered ideas, facts or experiences.

relate Tell or report about happenings, events or circumstances.

represent Use words, images or symbols to convey meaning.

select Choose in preference to another or others.

sequence Arrange in order.

show Give the steps in a calculation or derivation.

sketch Make a quick, rough drawing of something.

solve Work out the answer to a problem.

state Give a specific name, value or other brief answer.

suggest Put forward an idea for consideration.

summarise Give a brief statement of the main points.

synthesise Combine various elements to make a whole.

Chemical Equilibrium System

1 Chemical Systems

In this course you will be looking at chemical equilibrium systems. So we will look first at what is meant by a system, and then what is meant by equilibrium.

You can think of a **system** as any part of the Universe that is being studied. Sometimes a system can be very large, such as a whole ocean. A system can also be relatively small, such as the contents of a test tube.

In chemistry, the systems we study can be either open or closed; they can involve either physical changes or chemical reactions; and the changes taking place can either go to completion or be reversible.

Open and closed systems

An **open system** is one which interacts with its environment – this means that both energy and matter can move in and out of the system. Energy and matter are constantly moving between the system and the environment.

In a **closed system**, energy may still be able to flow in and out, between the system and the environment, but matter cannot enter or leave the system. (If you are also studying physics, note that this definition is different in physics.)

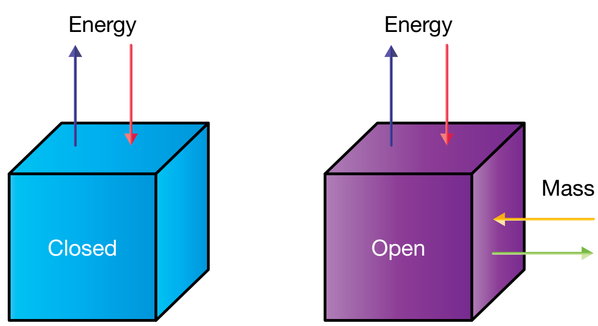


Figure 1.1 Open and closed systems.

A physical change

You will recall that a physical change is one in which no new substances are made, for example a change of state. The particles stay the same, but they may move differently, speeding up or slowing down. This may occur in an open or a closed system.

If we heat water in a container without a lid, then we have a **physical change** (evaporation) taking place in an **open system**.

If we put the lid on, then we have the same **physical change** taking place, but in a **closed system**. Heat can go in, but no matter can enter or leave the saucepan.

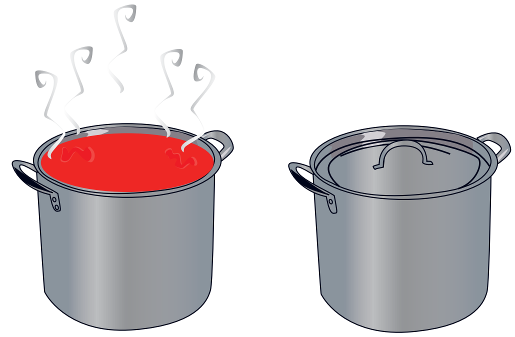


Figure 1.2 A physical change in an open and a closed system.

A chemical change

You will recall that a chemical change is one in which one or more new substances are formed, for example combustion, the action of acids on active metals, synthesis and decomposition.

Chemical changes can also occur in both open and closed systems.

Reversible reactions

Sometimes, when a physical or a chemical change occurs in a closed system, the products will recombine and reform the reactants. The forward and reverse reactions will continue to occur at the same time. This reaction would be called a reversible reaction.

All physical changes and some chemical reactions are reversible, they can go in both directions under suitable conditions.

Reversible physical changes

Physical changes are easily reversed, for example evaporation and condensation are reversible.

In a sealed container, water will evaporate:

$$H_2O(l) \rightarrow H_2O(g)$$

At the same time water vapour will condense:

$$H_2O(g) \rightarrow H_2O(l)$$

This is a reversible physical change, so we can show it by using arrows going in both directions.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Reversible chemical reactions

Many chemical reactions that you have seen in the laboratory **go to completion and cannot be reversed**. For example, neutralisation reactions, reactions involving combustion, and reactions between metals and acids all go to completion. And of course you cannot turn a cake back into the ingredients – such as flour, eggs, sugar and milk – used to make it.

Figure 1.3 Combustion reactions are not reversible.

However, there are also many chemical reactions that are **reversible in a closed system**; both the forward and the reverse reactions can occur at the same time.

Under suitable conditions, in a closed system, as the products build up, they may start to re-form the reactants. Both the forward and reverse reaction will then take place at the same time. This can only happen if nothing escapes from the container. If for example a gas escapes, both reactions cannot occur. Remember, the reaction system must be closed to be reversible.

As in physical changes, we show a reversible chemical reaction by using arrows going in both directions. Here are some examples of reversible chemical reactions.

- **Dinitrogen tetroxide** is a colourless gas that decomposes at room temperature to form brown nitrogen dioxide gas. In a sealed container, the reverse reaction also occurs, with some nitrogen dioxide combining to re-form dinitrogen tetroxide.

  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

- An important reversible reaction that you will learn more about later is the **ionisation of water** to form hydrogen and hydroxide ions.

  $H_2O(aq) \rightleftharpoons H^+(aq) + OH^-(aq)$

- Many reversible reactions occur in **living organisms**, for example, reactions involved in the transport of oxygen and carbon dioxide around the body in blood.

  Haemoglobin + $O_2(g) \rightleftharpoons$ oxyhaemoglobin.

  $CO_2(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$

- We also make use of some reversible reactions. For example, some eyeglasses have **photochromatic lenses** that darken in ultraviolet light. These work by means of a reversible reaction. They contain substances such as a silver halide which darkens in UV light, making the lens darker. Indoors the reaction reverses and the lenses become clear again.

Some reactions that go to completion can, under the right conditions, become reversible. For example, at some stage you will have heated calcium carbonate and watched it decompose into calcium oxide and carbon dioxide.

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

You probably bubbled the gas produced through limewater, which turned milky, showing that the gas was carbon dioxide.

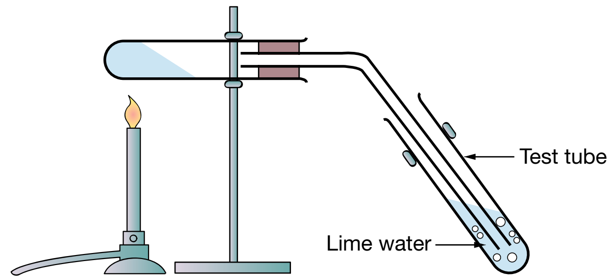


Figure 1.4 Decomposing calcium carbonate.

Note that this is an open system. There is a stopper in the test tube, but the carbon dioxide gas produced is escaping from the system through the tubing.

Heat energy is going into the system and matter (CO_2 gas) can escape. This is a **chemical change** in an **open system**.

However, if you were able to heat calcium carbonate gently in a closed container, heat energy would be going in, but no reactants or products could enter or leave. This would be a **chemical change** in a **closed system**.

This is not something you would do in a school laboratory. You would never enclose a reaction that produces a gas as this would not be safe. However, in an industrial situation, with containers that can withstand pressure, this reaction could be enclosed. In that case, some of the products – calcium oxide and carbon dioxide – would recombine to form calcium carbonate. The reverse reaction would occur.

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

Both forward and reverse reactions would be taking place at the same time, and we would have a reversible reaction in a closed system.

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

Modelling reversible reactions

In reversible reactions, the forward and reverse reactions both occur at the same time. We can model this reversible process using a dance – where some couples can be coming together and joining the dance floor (forward reaction) and, at the same time, other couples can be leaving the dance floor and moving apart (reverse reaction – they are becoming reactants again).

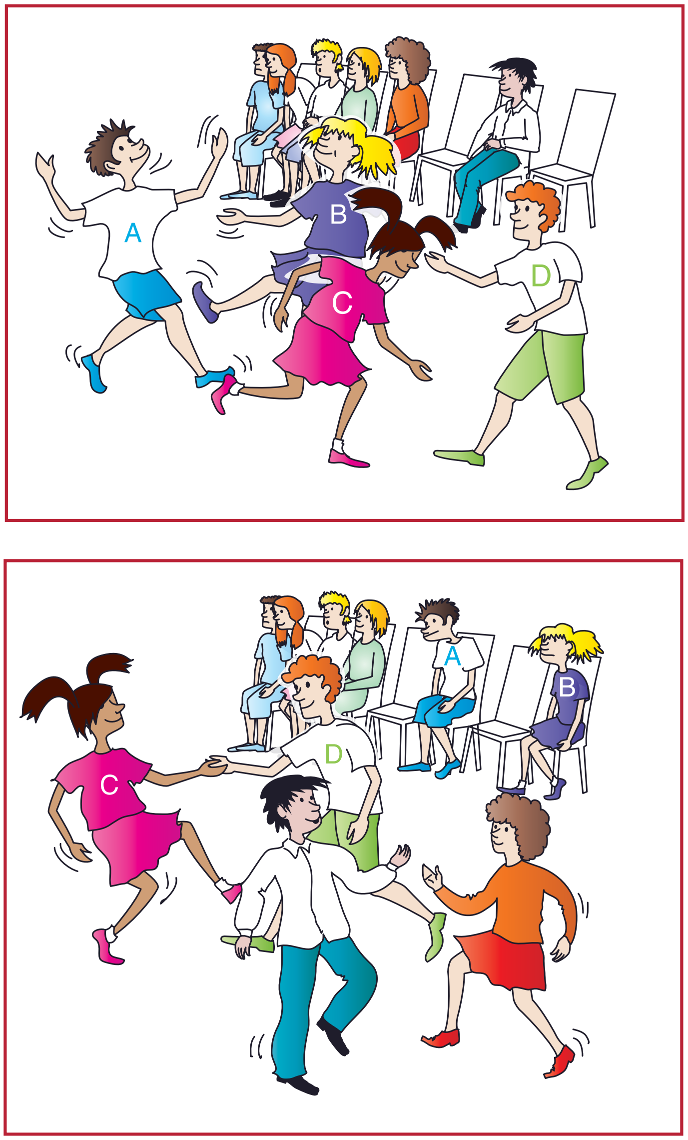


Figure 1.5 Modelling a reversible reaction.

If you just glanced at this dance floor you might think there were no changes, because there is always the same number of people dancing. But, looking closely, you will see that changes are taking place continuously – different people are constantly getting up to dance and replacing others who sit down. The same happens in a reversible reaction – there are always some particles interacting and others breaking up.

If the number of people joining the dance is the same as the number that are leaving, then we say the system is in a state of **dynamic equilibrium**. It is dynamic – there is constant change. It is in equilibrium – it seems to be staying the same.

You will learn more about equilibrium in the next lessons.

QUESTIONS

1. Recall the differences between a physical and a chemical change.
2. Describe the meaning of the following terms.
   (a) A system.
   (b) Open system.
   (c) Closed system.
   (d) Reversible reaction.
3. Some chemical reactions are reversible.
   (a) Write word equations for the following reversible reactions.
      (i) $FeCl_3(s) + 3H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3HCl(aq)$
      (ii) $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(l)$
      (iii) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
      (iv) $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
      (v) $3O_2(g) \rightleftharpoons 2O_3(g)$
   (b) Write symbolic equations for the following reversible reactions.
      (i) Sulfur dioxide + oxygen $\rightleftharpoons$ sulfur trioxide
      (ii) Nitrogen + hydrogen $\rightleftharpoons$ ammonia
      (iii) Nitrogen dioxide $\rightleftharpoons$ dinitrogen tetroxide
      (iv) Phosphorus pentachloride $\rightleftharpoons$ phosphorus trichloride + chlorine
      (v) Hydrogen + iodine $\rightleftharpoons$ hydrogen iodide
4. The first person to realise that chemical reactions could be reversible was the French chemist Claude Louis Berthollet. He observed salt lakes where he saw solid calcium carbonate being formed by a reaction between sodium carbonate and calcium chloride which are both dissolved in the lake water.
   (a) Write an equation for this reaction.
   (b) Berthollet also noticed that sodium carbonate was being deposited as a solid around the edges of the lake, and he realised that the reverse reaction must also have been occurring at the same time. Write an equation for this reverse reaction.
   (c) Write these reactions as an equilibrium reaction.
5. Find out why photochromatic lenses do not work in some situations, e.g. in some cars.
6. Explain why Figure 1.5 can be described as a model of dynamic equilibrium.
7. Research what is meant by steady state equilibrium.
8. Check your knowledge with this quick quiz.
   (a) A system in which energy and matter can move in and out is described as being ....
   (b) A reaction which can occur in the forward and the reverse directions is described as being ......

2 Equilibrium

A **saturated solution** contains as much solute dissolved in the solvent as is possible at that temperature. If a **saturated solution is placed in a closed container** and left standing, a reversible reaction will take place.

For example, if a saturated solution of nickel chloride is placed in a closed container and left standing, nickel chloride crystals will ionise and re-form simultaneously.

$NiCl_2(s) \rightarrow Ni^{2+}(aq) + 2Cl^-(aq)$

$Ni^{2+}(aq) + 2Cl^-(aq) \rightarrow NiCl_2(s)$

Eventually, if the conditions (such as temperature) remain the same, the **two reactions will occur at the same rate**. When this happens we say there is a system in **dynamic equilibrium**.

The contents of the closed container will look as if nothing is happening – the green of the beaker contents will stay the same and the amount of solid nickel sulfate will stay the same.

But if we could see the atoms and ions, we would notice that, inside that closed system, some nickel chloride crystals ($NiCl_2$) breaking up into ions (Ni^{2+} and Cl^-), and at the same time some nickel ions and chloride ions uniting to produce tiny nickel chloride crystals. As one breaks up, another forms, so the concentration of ions in the solution does not change.

$Ni^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons NiCl_2(s)$

The actual ions present in crystals and solution are continuously changing places. When both processes are occurring at the same rate, the system is in equilibrium.

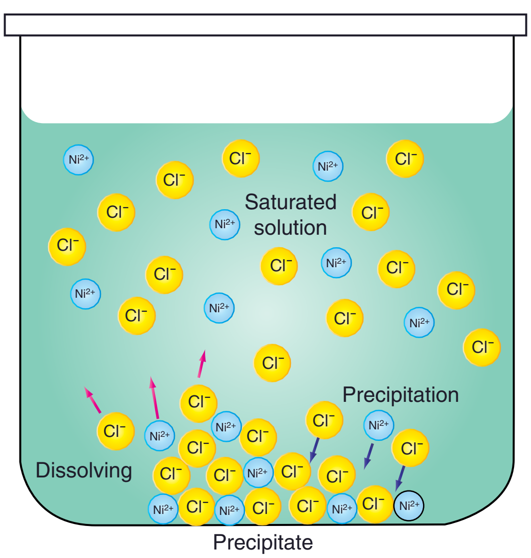


Figure 2.1 Nickel(II) chloride solution in equilibrium.

For different reactions, reaching equilibrium may take anything from milliseconds to many years.

The **characteristics of an equilibrium system** are:

1. It is a **closed system**. No matter enters or leaves the system. When a closed system is at equilibrium, there can be no overall energy changes either. If a **reversible reaction** is to reach and maintain equilibrium, then **no matter or energy can enter or leave** the system. If the energy changes in a closed system, the equilibrium will change. So there cannot be equilibrium if energy is lost or gained from the system.
2. It involves a reversible reaction and, at equilibrium, the **rate of the forward reaction equals the rate of the reverse reaction**. So if we graph rate versus time for each reaction, the lines will meet and become the same straight line.

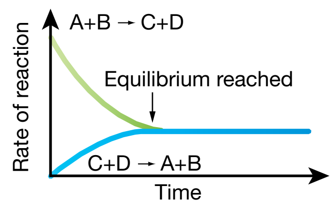


Figure 2.2 Equilibrium and rate of reaction.

3. The **macroscopic properties** (ones you can see) **stay constant** – there is no change in state, colour, temperature or pressure.
4. **Concentrations of all reactants and products stay constant**. Notice that although the concentration at equilibrium stays the same (constant), the concentration of reactants does not have to be equal to the concentration of products.

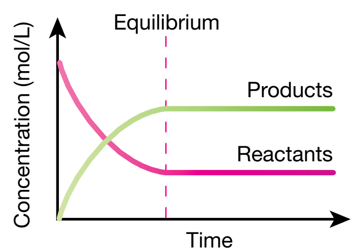


Figure 2.3 Concentration and equilibrium.

5. **Continuous changes** occur at the atomic level, with products forming and breaking up at equal rates (it is a dynamic process) but we cannot see these changes (macroscopic properties are constant).

QUESTIONS

1. (a) Outline what is meant by a reversible reaction.
   (b) Identify a macroscopic property you could observe to determine when a reversible reaction reaches equilibrium.
   (c) Explain why chemical equilibrium systems are described as being dynamic rather than static.

2. Each of the following situations would have constant macroscopic properties. Classify each as being in either a steady state, static equilibrium or dynamic equilibrium.
   (a) A cylinder of nitrogen gas in a room kept at a constant pressure and temperature.
   (b) A Bunsen burner turned to the hot flame and burning steadily.
   (c) A tank with water entering at the same rate as it is running out of the tap.
   (d) A chemical reaction represented as $A \rightleftharpoons B$ where [A] and [B] are constant but not equal.

3. Figure 2.1 shows a saturated solution of nickel chloride.
   (a) What is meant by a 'saturated solution'?
   (b) Describe the movement of ions in the solution.
   (c) Describe how you will know when this solution reaches equilibrium.
   (d) Use an equation to represent the saturated nickel(II) chloride at equilibrium

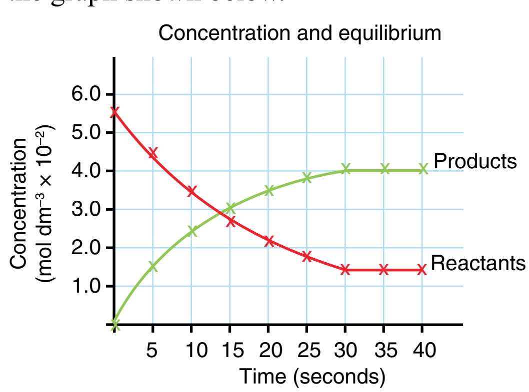
4. Outline the five characteristics of an equilibrium system.

5. Explain how the concentration of reactants can stay constant at equilibrium even though the reaction is still proceeding.

6. (a) Outline trends occurring in the concentration/time graphs in Figure 2.3.
   (b) Explain why both graphs in Figure 2.2 finish as the same straight line.

7. Can a liquid such as ethanol, develop into an equilibrium system if placed in a closed container?

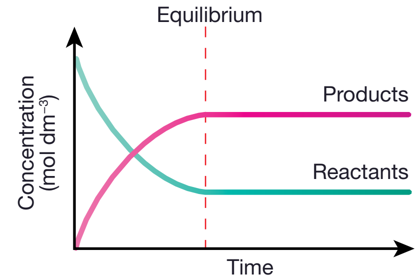
8. Two colourless solutions contain ferric (Fe^{3+}) ions and thiocyanate (SCN^-) ions. These two ions react when mixed to form a complex ion which is red in colour and has the formula $FeSCN^{2+}$.
   $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$
   Solutions containing equal concentration of the two ions were mixed and the reaction was allowed to come to equilibrium. The concentration of reactants and products was constantly monitored to produce the graph shown below.



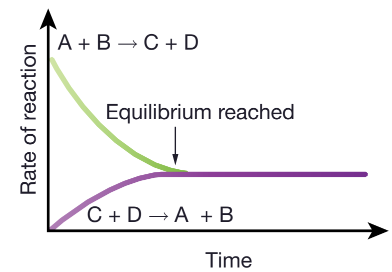
   Identify the time at which equilibrium was reached and justify your answer.

9. Describe an equilibrium system that you observed in the science laboratory.

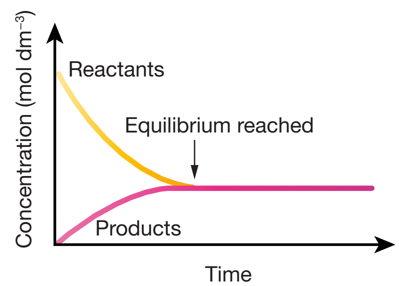
10. The graphs below illustrate two characteristics of systems at equilibrium.
   Graph X
   (i)



   Graph Y
   (ii)

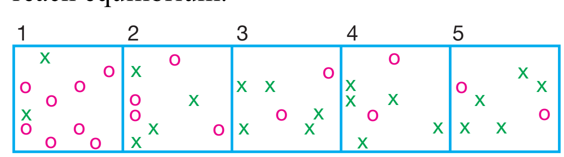


   (a) Outline the characteristic illustrated by each graph.
   (b) Compare graphs X and Y above with the graph Z below.
   Graph Z:



   Does graph (iii) represent a characteristic of all systems at equilibrium? Justify your answer.

11. In the following series of diagrams, molecules of $NO_2(g)$ (shown as O) are reacting to produce $N_2O_4(g)$ (shown as X). Eventually the two gases reach equilibrium.



   (a) At which stage is equilibrium reached? Justify your answer.
   (b) Is this a physical or a chemical equilibrium? Explain.

12. Check your knowledge with this quick quiz.
   (a) At equilibrium, what becomes constant?
   (b) At equilibrium, what must be equal?

3 Explaining Equilibrium

Equilibrium position

The position of an equilibrium refers to where the equilibrium lies with reference to the equation. This is defined by the relative concentrations of products and reactants. The equilibrium position tells us whether the forward or reverse reaction is favoured. For example, look at the following equilibrium.

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

If this reaction is taking place in a sealed container, under constant conditions, it will eventually reach equilibrium. It does not matter whether you start with sulfur dioxide and oxygen or with sulfur trioxide in your container, as long as the conditions such as temperature are identical, you will still reach the same equilibrium.

This equilibrium can be described as lying to the left or the right. If the equilibrium position is described as being to the left (it favours the reverse reaction) that means there are higher concentrations of sulfur dioxide and oxygen in the container than of sulfur trioxide. If the equilibrium lies to the right (it favours the forward reaction) then more sulfur trioxide is present in the container at equilibrium.

What affects equilibrium position?

The equilibrium position can be affected by **temperature**, **pressure and concentrations**, and you will be looking at these later. However, the presence of a **catalyst** has no effect on the equilibrium position. Adding a catalyst will speed up the reaction in both directions, so that equilibrium is reached sooner, but it will not affect the position of the equilibrium – whether it lies to the left or to the right.

The relative **activation energies of the forward and reverse reactions** also help to determine the reversibility of reactions and the position of the equilibrium. To understand this, you may need to revise the differences between endothermic and exothermic reactions and the concept of activation energy.

Exothermic/endothermic reactions

You will recall that in a reversible reaction, the reaction in one direction is be exothermic and the reaction in the other direction is endothermic. For example, in the equilibrium reaction, $SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$:

The forward reaction, $SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, is exothermic, as it involves the release of energy.

The reverse reaction, $2SO_3(g)\ ) \rightarrow SO_2(g) + O_2(g)$, absorbs energy and is endothermic.

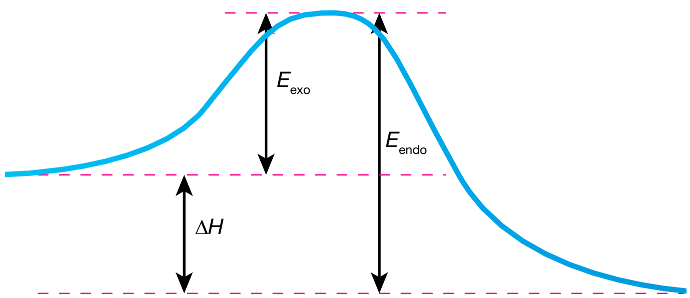
Activation energy in reversible and equilibrium reactions

You will recall that activation energy is the energy particles need to have if they are to interact. In other words, colliding particles react if they have energy equal to or greater than the activation energy for that reaction.

The **reversibility** of chemical reactions is related to the activation energies of the forward and reverse reactions. Many chemical reactions go to completion because the activation energy is low (lots of particles have enough energy to react when they collide) and also because the products have less energy than the reactants.

Many other reactions do not occur because the activation energy is too high (the colliding particles do not have enough energy to react) and the reactants are more stable than the products.

In the reaction $A + B \rightleftharpoons C + D$, particles A and B have enough energy to react (activation energy E_A for the forward reaction is reached). And at the same time, particles C and D also have enough energy to react (activation energy E_A for the reverse reaction is also reached). The reaction can proceed in both directions, so we say it is reversible.



E_{exo} = activation energy for the forward reaction

E_{endo} = activation energy for the reverse reaction

ΔH = the difference between the activation energies.

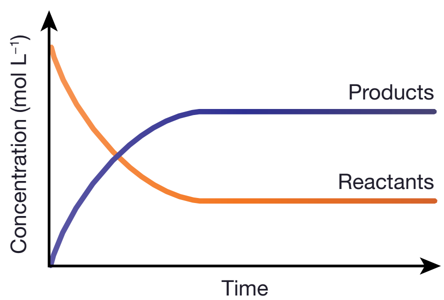
Figure 3.1 Energy profile for a reversible reaction.

The relative activation energies of the forward and reverse reactions help determine not only whether or not a reaction is reversible, but also the **position of the equilibrium**.

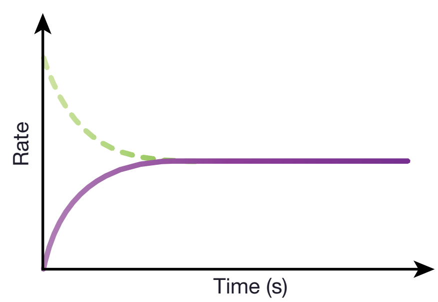
- If the activation energies are similar, both reactants and products will be present in significant amounts.
- If the forward reaction has a higher activation energy, then equilibrium will lie to the left.
- If the reverse reaction has higher activation energy, the equilibrium position will favour the reactants.

QUESTIONS

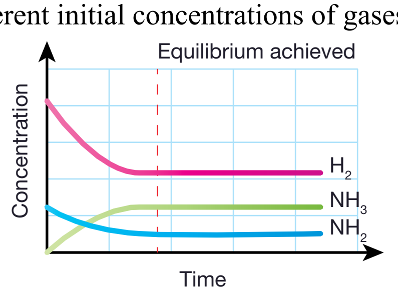
1. (a) If you observe a reversible chemical reaction in a closed system, how can you tell when it reaches equilibrium?
   (b) What is meant by the position of an equilibrium reaction?
2. Explain the reversibility of chemical reactions in terms of activation energies of the forward and reverse reactions.
3. Chemical reactions can be exothermic or endothermic.
   (a) Recall the difference between endothermic and exothermic reactions and tabulate your answer.
   (b) Draw energy profiles to illustrate an exothermic and an endothermic reaction.
   (c) Sketch the energy profile for a reversible reaction with the forward reaction as endothermic. Show how the activation energy varies for the forward and reverse reactions.
4. On each of the graphs below, mark the position when equilibrium is reached. Justify your answer.
   (a)



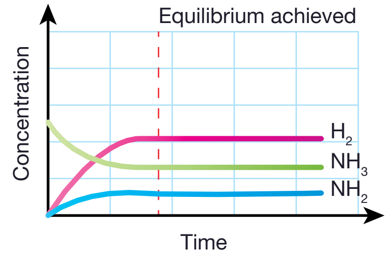
   (b)



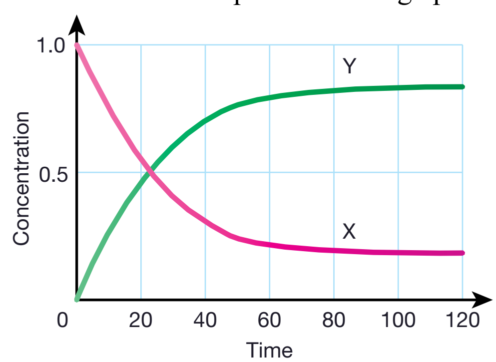
5. Nitrogen and hydrogen react to form ammonia which decomposes to form hydrogen and nitrogen gas. In a closed container, under constant conditions, this mixture will reach equilibrium.
   $N2(g) + 3H2(g) \rightleftharpoons 2NH3(g)$.
   The graphs show equilibrium being achieved from different initial concentrations of gases.
   (i)



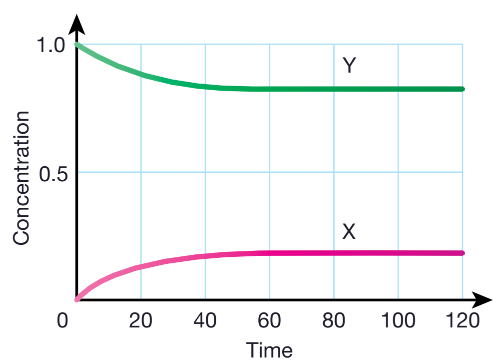
   (ii)



   (a) Compare the initial concentrations of hydrogen, nitrogen and ammonia illustrated in graphs (i) and (ii).
   (b) Write the forward reaction for each graph.
   (c) Compare the final concentrations of gases in graphs (i) and (ii).
6. The two graphs below illustrate a simple reversible reaction, $X \rightleftharpoons Y$. In one graph the chemist starts with only chemical X present in the sealed reaction vessel. In the other graph the reaction commences with only chemical Y present. In each case the reaction is carried out under the same conditions. Account for similarities and differences in the shapes of the two graphs.
   (a)



   (b)



7. Check your knowledge with this short quiz.
   (a) If equilibrium position lies to the left, would you expect to see a greater concentration of reactants or products in the container?
   (b) Chemical equilibrium is considered to be (static/dynamic).
   (c) In a reversible reaction, the activation energy for an exothermic reaction is (greater/smaller) than that for an endothermic reaction.
   (d) Can the addition of a catalyst affect equilibrium position?

4 Changing Equilibrium

The position of an equilibrium reaction can be disturbed by:

- Changing the **temperature**.
- Changing the **concentration** – removing or adding more of any reactant or product.
- Changing the **pressure** – this applies only when one or more reactants or products is a gas.

When any of these conditions change, the equilibrium is upset. Rates of the forward and reverse reactions change. Then, after a while, the system again settles into a new dynamic equilibrium. But this new equilibrium is not the same as the original equilibrium. The concentrations of reactants and/or products will be different.

We say that the position of the equilibrium has changed and we describe it as having moved to the left (towards the reactants) or to the right (towards the products). Below are two examples.

Changing concentration

Figure 4.1 shows a system which reaches equilibrium and this is then disrupted by the addition of more reactant.

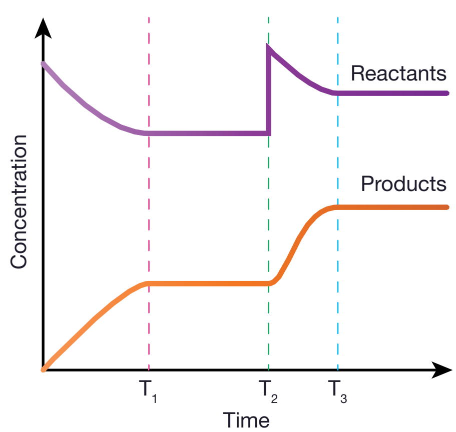


Figure 4.1 Effect on concentration when a system at equilibrium is disturbed.

From time 0 to T_1 equilibrium is being reached.

Between T_1 and T_2 we know the system is at equilibrium because the concentration of the reactants is constant (graph is a horizontal line) and also the concentration of the products is constant (graph is a horizontal line).

Then, **at time T_2**, something happens – the spike in the graph at T_2 indicates that more reactant is added at this time, increasing the concentration suddenly.

Between T_2 and T_3 the system is adjusting to the change.

At time T_3 a new equilibrium position has been reached and now the concentrations are again constant.

However, notice that, at the new equilibrium position, the concentrations of the reactants and products have changed – they differ from the earlier equilibrium concentrations. **The equilibrium position has moved**. In this case, the concentration of the products has increased more than the concentration of the reactants has increased. This is what we mean when we say that the equilibrium position has shifted towards the products (to the right) – the yield of products is higher.

Changing temperature

Figure 4.2 below shows a typical concentration/time graph for an equilibrium system in which equilibrium is disturbed by **changing the temperature** of the system at time T_2. Notice the concentration change is gradual, there is no sharp peak (as there is when a chemical is added to the system). By T_3 a new equilibrium position has been reached and in this case the equilibrium position has moved left, favouring the reactants.

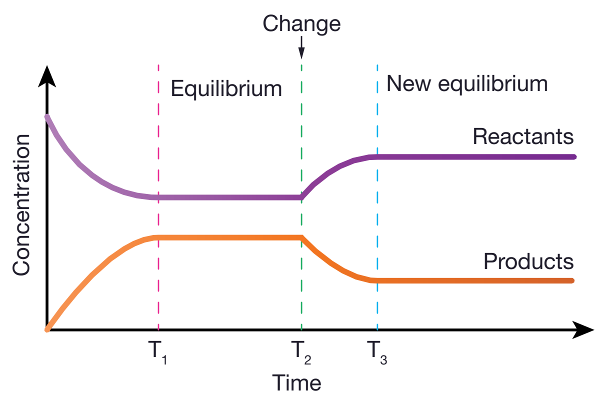


Figure 4.2 Effect on an equilibrium system when temperature is changed.

You will be looking at more graphs like these later.

QUESTIONS

1. Identify three changes in conditions that can affect the position of an equilibrium.
2. What is the effect on the concentrations of reactants and products when:
   (a) An equilibrium position moves left?
   (b) An equilibrium position moves right?
3. Answer the following questions about Figure 4.2.
   (a) What is happening between time 0 and T_1?
   (b) How do you know this system is in equilibrium between time T_1 and T_2?
   (c) Compare the new equilibrium position to the original equilibrium position.

5 Equilibrium and Temperature

Changing the temperature at which a reversible reaction is taking place will change its equilibrium position. For example, look at the decomposition of dinitrogen tetroxide.

Decomposition of dinitrogen tetroxide

At room temperature, dinitrogen tetroxide is a colourless gas that decomposes to form the dark brown gas, nitrogen dioxide. This reaction is reversible. While the N_2O_4 is decomposing, some of the NO_2 molecules are combining to form N_2O_4.

$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Colourless		dark brown

This reaction, carried out in a sealed flask, will soon reach equilibrium and there will be no further visible change – as long as the temperature is kept constant.

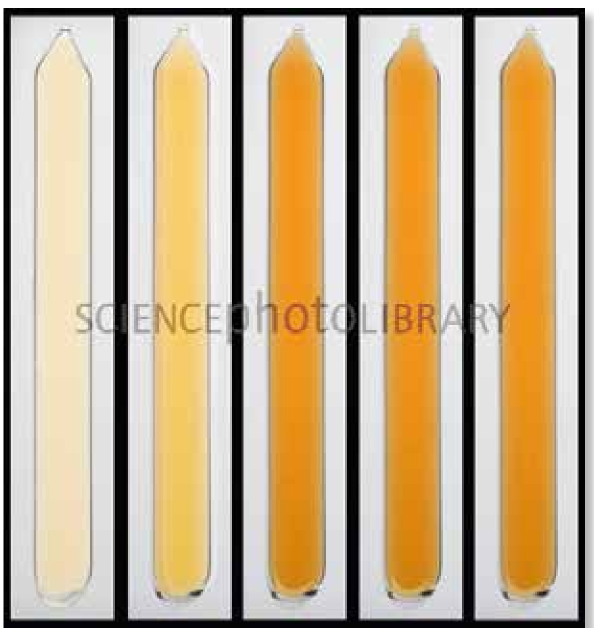


Figure 5.1 Successive photos of a mixture of N2O4 and NO2 as equilibrium is reached.

If you increase the temperature of the surroundings, for example by putting the flask in a bowl of hot water, the equilibrium will be disturbed and eventually a new equilibrium will be established. In this case the forward reaction will be favoured (you will see why shortly). The new equilibrium position will be towards the right – this means that there will be a greater percentage of NO_2 present in the flask and the mixture will look a darker brown.

If temperature is decreased, the opposite happens, the equilibrium moves left and the brown colour fades.

Explaining effects of temperature on equilibrium position

Carrying out a reversible reaction at a higher temperature will increase the rate of reaction for both the forward and the reverse reactions – but they will increase by different amounts. The higher the activation energy, the greater the effect of temperature on reaction rate will be.

Increasing the temperature at which a reversible reaction takes place, will favour whichever reaction is endothermic. Think of it like this – an endothermic reaction absorbs heat energy – so when you heat an endothermic reaction, it will absorb the added heat and increase its reaction rate.

Conversely, decreasing the temperature favours the exothermic reaction which has the lower activation energy.

This means that when the temperature at which the reaction occurs is changed, the direction in which the equilibrium position will shift depends on which reaction is endothermic and which is exothermic.

For example, the decomposition of dinitrogen tetroxide is endothermic in the forward direction.

$N_2O_4(g) \rightarrow 2NO_2(g)$ ΔH is positive.

The reverse reaction is exothermic.

$2NO_2(g) \rightarrow N_2O_4(g)$ ΔH is negative.

When the reaction vessel is at a higher temperature, the endothermic reaction is favoured, and so the mixture at the higher temperature will contain a higher concentration of NO_2. A different equilibrium position will be established.

QUESTIONS

1. Recall three factors that, when changed, can alter the equilibrium position of a reversible reaction.
2. State whether each of the following reactions is endothermic or exothermic.
   (a) $A + B \rightleftharpoons C + D$ + heat
   (b) $A + B$ + heat $\rightleftharpoons C + D$
   (c) $A + B \rightleftharpoons C + D$, ΔH = negative
   (d) $A + B \rightleftharpoons C + D$, ΔH = positive
3. Describe the effect of the following changes on the equilibrium reaction, $A + B \rightleftharpoons C + D$ + heat.
   (a) Decrease the reaction temperature.
   (b) Increase the reaction temperature.
4. Consider the equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.
   (a) Figure 5.1 shows a series of photos of a container of dinitrogen tetroxide gas as some of it spontaneously decomposes to nitrogen dioxide gas. At which position is equilibrium first reached? Justify your answer.

(b) At 21°C, the mixture, at equilibrium, will contain about 16% nitrogen dioxide and will appear light brown. At 100oC, it will contain about 90% nitrogen dioxide and it will look dark brown. Use this information to explain whether the forward, or reverse reaction is endothermic.

5. The following equilibrium reaction is exothermic in the forward direction.

$FeCl_3(s) + 3H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3HCl(aq)$

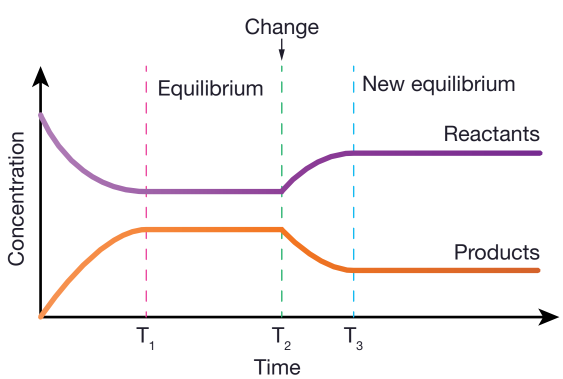
Iron(III) chloride is a yellow/orange colour, depending on its concentration. Whereas iron(III) hydroxide is a reddish brown colour as illustrated below.

Anhydrous iron(III) chloride (before adding water)	Iron(III)hydroxide (forms when water is added to iron(III) chloride)
	

(a) Predict any colour change you would expect to occur when the reaction temperature is changed.

(b) Describe the effect of increasing the reaction temperature on the equilibrium position of this reaction.

6. In Chapter 4 you looked at the following graph showing changes in the equilibrium position due to a temperature change. The changes in this system were brought about by an increase in temperature.

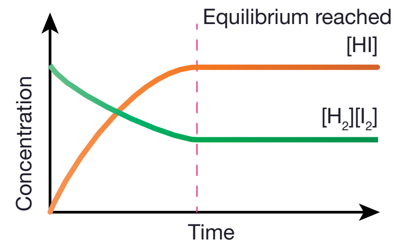


(a) Compare the equilibrium concentrations, as shown by this graph, at a lower and a higher temperature.

(b) Based on this information, deduce whether the forward reaction is endothermic or exothermic.

7. Hydrogen and iodine react to form hydrogen iodide. In a sealed container, under stable conditions, this system will reach equilibrium.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\ \Delta H = -51$ kJ



(a) Is this reaction endothermic or exothermic in the forward direction?

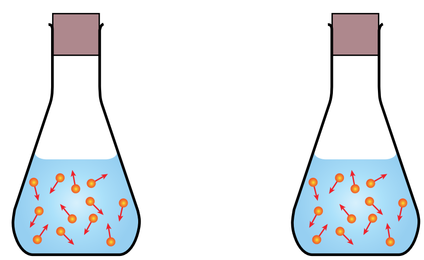
(b) If this reaction is carried out at a lower temperature, at the new equilibrium position the concentration of hydrogen iodide will be (larger/smaller) because the equilibrium will have shifted to the (left/right).

(c) Sketch what the above graph would look like if this reaction were carried out at a lower temperature.

8. A liquid such as ethanol, in a sealed container, reaches equilibrium with its vapour if conditions are kept constant.

Ethanol(l) $\rightleftharpoons$ ethanol(g)

Two identical flasks are set up, each containing the same amount of ethanol. Flask A is placed in a water bath at 25°C. Flask B is placed in a water bath maintained at 40°C. The conditions for each flask are kept constant so that equilibrium can be achieved.



(a) Copy the diagram to show what is happening in each flask at equilibrium.

(b) How do the flask B contents compare with the contents of flask A?

9. Check your knowledge with this quick quiz.

(a) When the equilibrium reaction is maintained at a higher temperature, the rate of both forward and reverse reactions (increases/decreases/stays the same). The rate will increase more for whichever reaction is (endothermic/exothermic).

(b) Which gas is colourless, N_2O_4 or NO_2?

(c) Is the decomposition of nitrogen tetroxide endothermic or exothermic?

Answers

1 Chemical Systems

1. A physical change – No new substance is produced, particles stay the same and it is usually easy to reverse. Examples include change of state – melting, evaporation, condensation.
   A chemical change – A new substance forms, particles are changed as atoms are rearranged and it is usually difficult to reverse.
2. (a) A system refers to any part of the Universe that is being studied.
   (b) An open system is one that interacts with its environment – energy and matter can move between the system and its environment.
   (c) A closed system does not interact with its environment – energy can move in and out of the system but matter cannot.
   (d) A reversible reaction is one that goes in both directions – forward and in reverse.
3. (a) (i) Iron(III) chloride + water $\rightleftharpoons$ iron(III) hydroxide + hydrochloric acid
   (ii) Copper sulfate (hydrated) $\rightleftharpoons$ anhydrous copper sulfate + water
   (iii) Ammonium chloride $\rightleftharpoons$ ammonia + hydrogen chloride
   (iv) Carbon dioxide + water $\rightleftharpoons$ carbonic acid
   (v) Oxygen $\rightleftharpoons$ ozone
   (b) (i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   (ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (iii) $2NO_2(g) \rightleftharpoons N_2O_4(g)$
   (iv) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   (v) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
4. (a) $Na_2CO_3(aq) + CaCl_2(aq) \rightarrow CaCO_3(s) + 2NaCl(aq)$
   (b) $CaCO_3(s) + 2NaCl(aq) \rightarrow Na_2CO_3(s) + CaCl_2(aq)$
   (c) $Na_2CO_3(aq) + CaCl_2(aq) \rightleftharpoons CaCO_3(s) + 2NaCl(aq)$
5. Photochromatic lenses darken with exposure to ultraviolet radiation (not to sunlight). Some cars have tinted windows which do not let the UV rays in, so the lenses do not darken.
6. The individual students represent ions in a solution. Each pair of dancers represents a unit of product. At equilibrium, the concentration of reactants stays the same – the number of students sitting stays the same – there are always six in this diagram. The concentration of products also stays the same – there are always two couples dancing. It is dynamic – there is constant change – as one couple sits down another pair gets up to replace them. It is equilibrium – it appears to be staying the same.
7. Steady state equilibrium can be shown as a diagram. There is no net change in the contents of the container over time (hence equilibrium) but that is only because water is being added and taken away at the same rate. A change in one direction is balanced by a change in another direction.

   This differs from chemical equilibrium where there is also no net change in the contents of a system over time, but in this case that is because a reaction is taking place in both forward and backward directions at the same rate.
8. (a) Open. (b) Reversible.

2 Equilibrium

1. (a) A reversible reaction is a reaction which proceeds in both directions at the same time.
   (b) Various. Macroscopic properties include state (solid/liquid/gas), colour, temperature and pressure. For example, you could observe the colour – when the colour stays constant (there are no longer any visible changes taking place) then the system is at equilibrium.
   (c) Although the macroscopic properties stay constant at equilibrium, there is continual change happening at a submicroscopic level as both the forward and reverse reactions continue to occur. A static equilibrium can be found in physical systems, e.g. riding a bike – where being in equilibrium means that you do not fall off because opposing forces are balanced.
2. (a) Static equilibrium – no changes are taking place.
   (b) Steady state (chemical system) – matter and energy are entering and leaving the system at a constant rate.
   (c) Steady state (physical) system.
   (d) Dynamic chemical system.
3. (a) A saturated solution contains as much of a solute (in this case nickel chloride) dissolved in the solute (water) as is possible at that temperature.
   (b) Ions in the solution are in constant motion with frequent collisions. Some of the nickel and chloride ions are dissolving – they are moving away from the solid at the bottom and into the solution. At the same time, other nickel and chloride ions are colliding and precipitating out to form more solid nickel chloride which sinks to the base of the beaker. Eventually both of these reactions – dissolving and precipitating – will occur at the same rate and the system will then be in equilibrium.
   (c) Equilibrium is reached when the macroscopic properties stay constant – the colour of the solution will stay the same and the amount of solid will also stay the same. When there is no visible change taking place, the system will be in equilibrium.
   (d) $Ni^{2+}(aq) + 2Cl^{-}(aq) \rightleftharpoons NiCl_2(s)$
4. The characteristics of a system at equilibrium are:
   - It is a closed system – no matter or energy enters or leaves the system.
   - It involves a reversible reaction and the rate of the forward reaction equals the rate of the reverse reaction.
   - The macroscopic properties (ones you can observe) stay constant – there is no change in state, colour, temperature or pressure.
   - Concentrations of all reactants and all products stay constant.
   - Continuous changes occur at the atomic level, with products forming and breaking up at equal rates, but we cannot see this.
5. As reactants are used up, products are replacing the reactants. Both reactions, the forward and reverse reactions, occur at the same rate, so there is no change in the concentrations of either the reactants or the products.
6. (a) The concentration of reactants decreases, rapidly at first and then less rapidly as reactants are used up. The concentration of products is initially zero, but then product forms increasingly rapidly. Eventually the rates of the two reactions become the same – the rate of the forward reaction equals the rate of the reverse reaction. At this stage – shown by the dotted vertical line on the graph – the system has reached equilibrium. Once a system is at equilibrium, the concentrations of all reactants and products stay constant – they do not change. On the graph, the concentrations while the system is at equilibrium are shown as horizontal lines – indicating that each has a constant value.
   (b) In Figure 2.2, the same straight line at the end of each graph indicates that the rate of the forward reaction is the same as the rate of the reverse reaction, and both are staying constant – they are not changing. This occurs when a system is in equilibrium.
7. If you place a liquid such as ethanol in a closed container, both evaporation and condensation reactions will occur at the same time. Ethanol (l) $\rightleftharpoons$ ethanol(g). Eventually the forward and the reverse reaction will occur at the same rate. When that happens we have a closed system, in equilibrium.
8. Equilibrium was reached at 30 seconds. At 30 seconds both graphs became flat indicating that both the concentration of reactants and also the concentrations of product were then constant – so, by that stage, the forward reaction was occurring at the same rate as the reverse reaction.
9. Various. You should name the chemicals you used and the quantities of each and include an equation for any reaction studied.
10. (a) Graph X − Concentrations of reactants and products stay constant while the system is at equilibrium.
    Graph Y − At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction.

(b) Graph Z shows a situation in which the concentration of reactants and products not only stays constant – but they are also equal to each other. This can occur, but it is not a characteristic of all systems at equilibrium. It is the rate of reaction which must be equal for both reactions. Concentrations need only to be constant, not necessarily equal.

11. (a) The system reaches equilibrium at stage 3 because the concentration of both reactant and product stays constant throughout stages 3, 4 and 5.

(b) Chemical equilibrium – a new substance is being produced so this is a chemical equilibrium.

12. (a) Concentration of reactants, concentration of products, reaction rate of reactants, reaction rate of products.

(b) Reaction rate for forward reaction must equal the reaction rate for reverse reaction.

3 Explaining Equilibrium

1. (a) When there appears to be no change occurring – colour, state, temperature and pressure stay the same – then the system is at equilibrium.

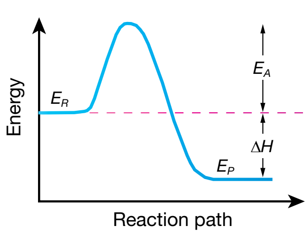
(b) The position of an equilibrium reaction tells us whether the forward or reverse reaction is favoured. If the equilibrium is referred to as to the left, or to the reactants, then the reverse reaction is favoured. If the equilibrium is to the right, or to the products, then the forward reaction is favoured.

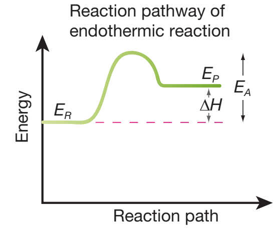
2. In a reversible reaction A + B $\rightleftharpoons$ C + D, particles A and B have enough energy to react (activation energy E_A for the forward reaction is reached). And at the same time, particles C and D also have enough energy to react (activation energy E_A for the reverse reaction is also reached). The reaction can proceed in both directions, so we say it is reversible.
Reversible reactions usually have similar sized activation energies for their forward and reverse reactions – one of which will be exothermic and the other endothermic. The activation energy for the exothermic reaction is less than the activation energy for the endothermic reaction, but the difference is small for reversible reactions.

3 (a)

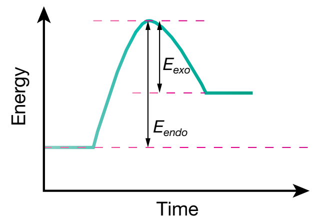
Exothermic reactions	Endothermic reactions
Reactions that release heat.	Reactions that absorb heat from the surroundings.
$\Delta H < 0$	$\Delta H > 0$
The energy released by forming bonds is greater than the energy absorbed when bonds break.	The energy released by forming bonds is less than the energy absorbed by breaking bonds.
The products have less energy in their bonds than the reactants had, so we say that the energy of the system has decreased.	The products have more energy in their bonds than the reactants had, so we say that the total energy of the system has increased.
Examples are all combustion reactions, neutralisation reactions, respiration and some dissolution reactions.	Examples are photosynthesis, thermal decomposition and some dissolution reactions.

(b) In the two following energy profiles:
E_R = energy of reactants
E_P = energy of products
E_A = activation energy
(the energy needed to start the reaction)
ΔH = change in enthalpy
Reaction pathway of exothermic reaction



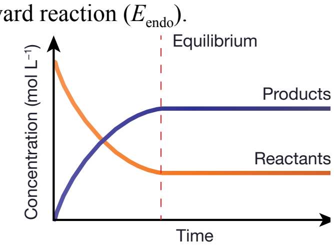


(c) Energy profile for a reversible reaction with an endothermic forward reaction.



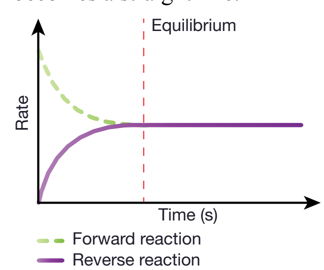
Activation energy for the reverse reaction (E_{exo}) < activation for forward reaction (E_{endo}).

4 (a)



Equilibrium is reached when the concentration of reactants is constant and the concentration of products is constant. On a graph of concentration versus time this would be represented by a straight line. So equilibrium is reached when the graph becomes a straight line.

(b)



Equilibrium is reached when the rate of the forward reaction equals the rate of the reverse reaction. The rate of each reaction then stays the same unless reaction conditions are changed. The point where the reaction rates become equal is marked on the graph.

5. (a) Graph (i) shows zero concentration of product (ammonia) and only reactants are present initially. (The reaction starts with nitrogen and hydrogen reacting to form ammonia, some of which then decomposes.)
Graph (ii) shows only ammonia is present initially – there is no hydrogen or nitrogen. (The reaction starts with the decomposition of ammonia to form nitrogen and hydrogen, some of which then react to re-form ammonia.)

(b) Graph (i): $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Graph (ii): $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(c) The concentrations of each gas are the same at equilibrium – the same amount of hydrogen is present, the same amount of nitrogen is present and the same amount of ammonia is present in the two experiments. It does not matter whether you start with ammonia or with nitrogen and hydrogen in the ratio of 1 : 3, the equilibrium concentrations will be identical. The equilibrium composition is independent of the direction from which it is approached, but is only dependent on the number of moles of each species present.