SURFING

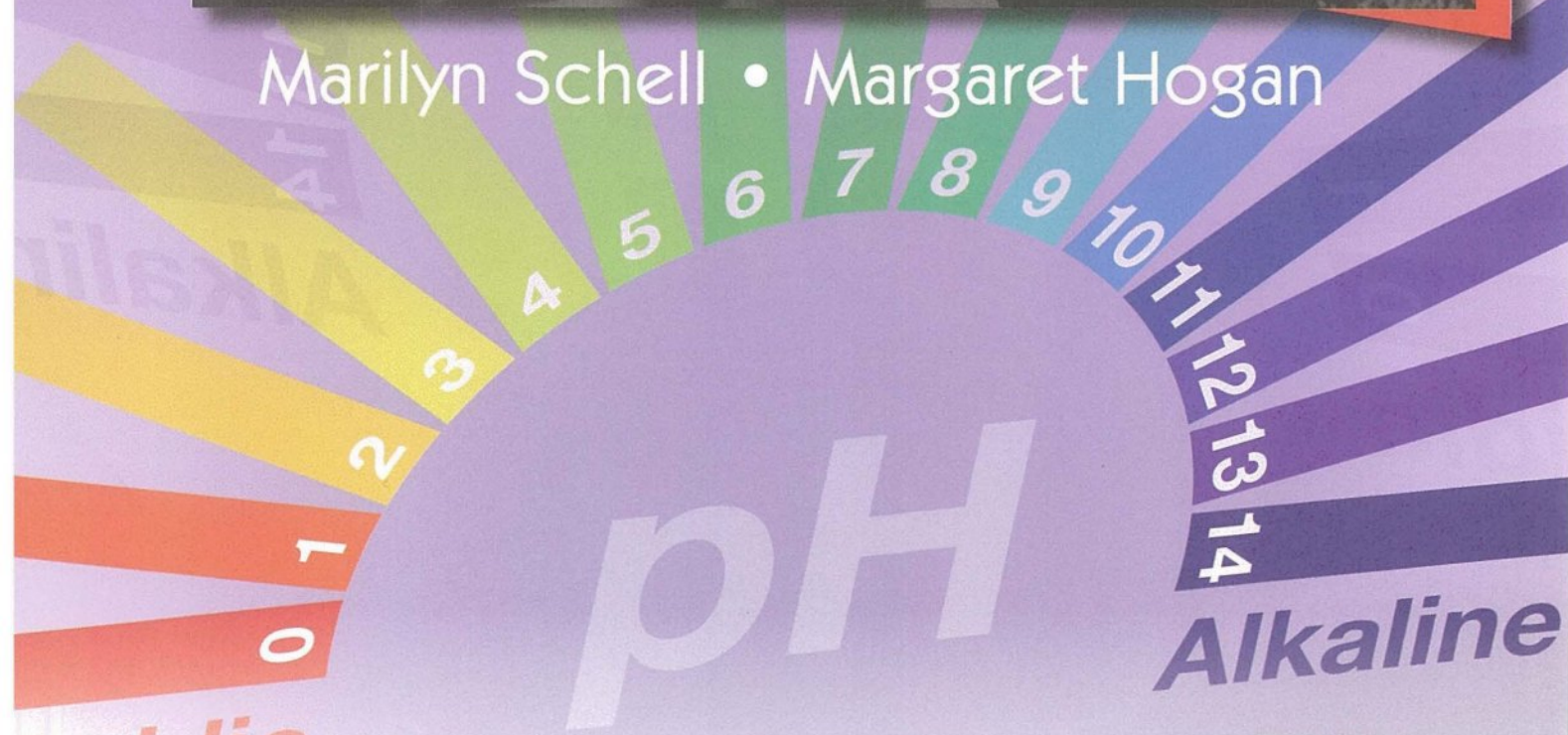# NSW CHEMISTRY 5&6

Module 5 Equilibrium and Acid Reactions
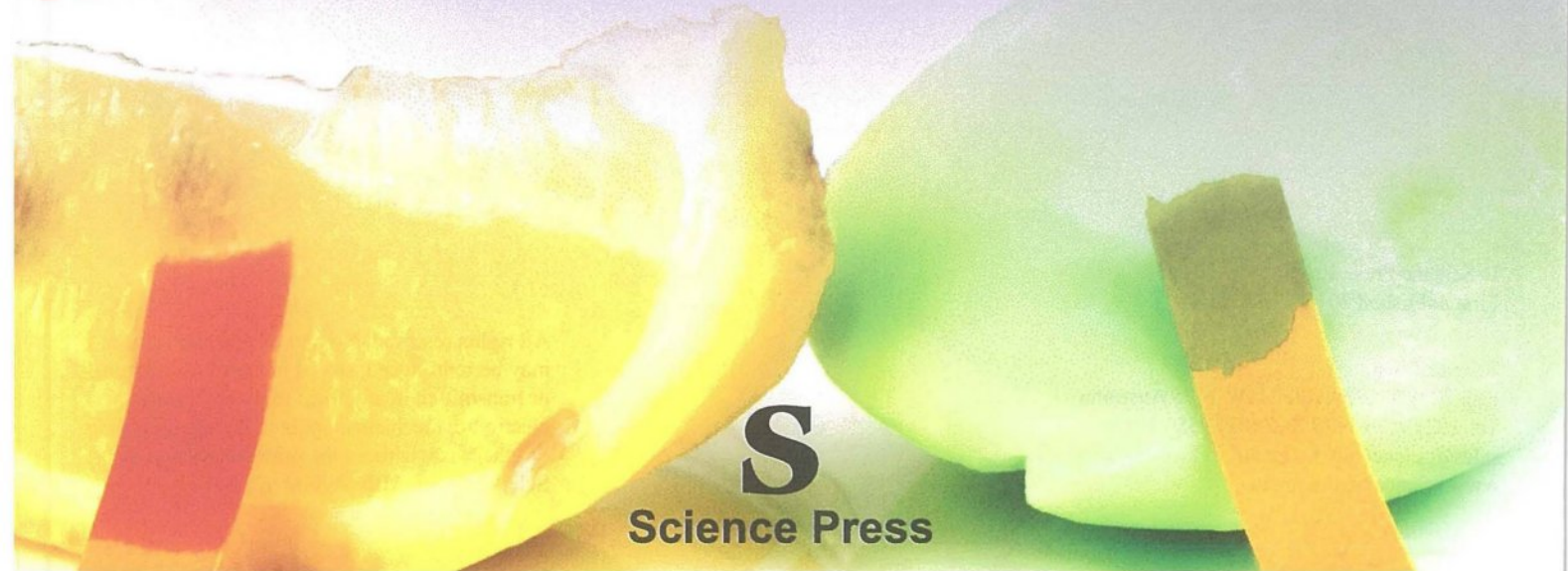**Module 6** Acid/Base Reactions

Marilyn Schell • Margaret Hogan

pH

Acidic

Alkaline

Contents

Module 5 Equilibrium and Acid Reactions

Static and Dynamic Equilibrium

INQUIRY QUESTION

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

Factors That Affect Equilibrium

INQUIRY QUESTION

What factors affect equilibrium and how?

Calculating the Equilibrium Constant

INQUIRY QUESTION

How can the position of equilibrium be described and what does the equilibrium constant represent?

Solution Equilibria

INQUIRY QUESTION

How does solubility relate to chemical equilibrium?

Module 6 Acid/Base Reactions

Properties Of Acids and Bases

INQUIRY QUESTION

What is an acid and what is a base?

Using Brönsted-Lowry Theory

INQUIRY QUESTION

What is the role of water in solutions of acids and bases?

Quantitative Analysis

INQUIRY QUESTION

How are solutions of acids and bases analysed?

Introduction

This book covers the Chemistry content specified in the NSW Chemistry Stage 6 Syllabus. Sample data has been included for suggested experiments to give you practice to reinforce practical work in class.

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.

NSW CHEMISTRY 5&6

Module 5

EQUILIBRIUM AND ACID REACTIONS

CONTENT FOCUS

In this module you will:

- Understand that chemical systems can be open or closed and can include physical changes and chemical reactions.

- Describe the characteristics of a closed system at equilibrium.

- Investigate the effects of changes in temperature, concentration of chemicals and pressure on equilibrium systems.

- Learn how to predict these changes using Le Châtelier's principle.

- Analyse quantitative relationships between reactants and products in equilibrium reactions to determine the value of the equilibrium constant.

- Use equilibrium constant values to predict the equilibrium position and determine whether or not a precipitate will form; calculate the concentrations of ions in a saturated solution at equilibrium and calculate the solubility of an ionic compound.

- Focus on processing data to determine patterns and trends and thus solve problems.

- Be able to communicate scientific understanding of ideas about equilibrium.
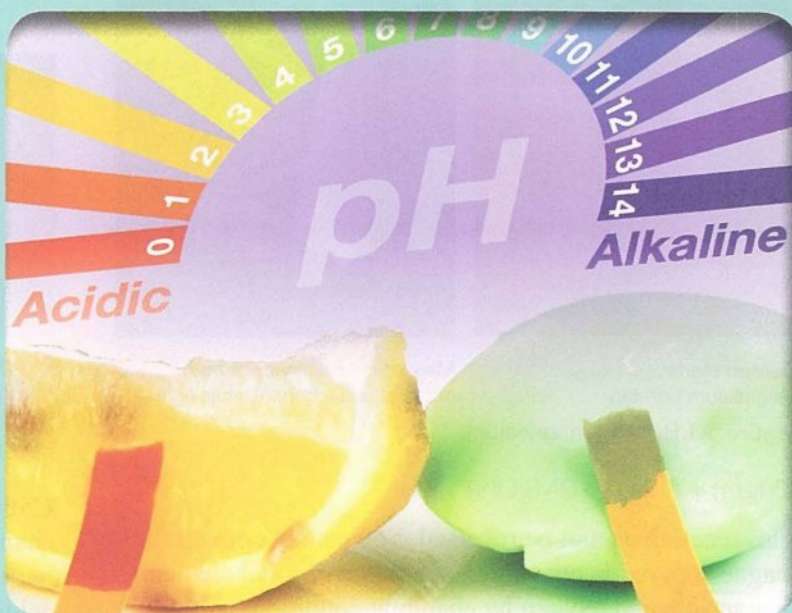
1 Investigating Reversibility Of Chemical Reactions

In the laboratory you have already seen many chemical reactions that go to completion, some very rapidly and others more slowly.

In this topic you will have a chance to carry out reactions that are reversible – reactions that can proceed in either direction depending on prevailing conditions. You will learn to predict the direction in which a reaction will proceed by evaluating the conditions such as temperature, concentration and pressure to see if they favour the formation of reactants or products.

Irreversible reactions

One of the irreversible reactions you have already seen is the combustion of **magnesium** ribbon. You know that energy is needed to start this reaction, and once started it continues with no more energy input as this is a highly exothermic reaction.
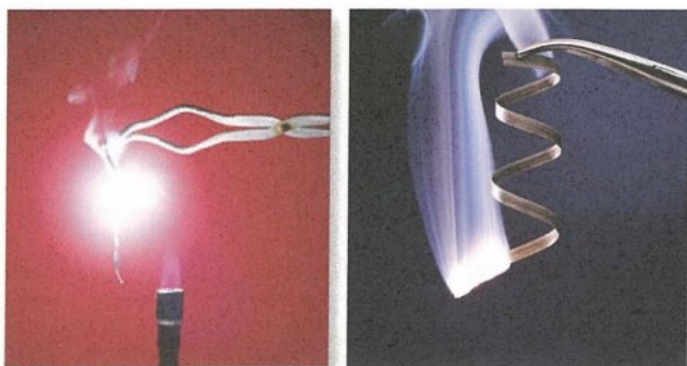
Bunsen starts magnesium burning

Magnesium continues to burn, giving out heat and a brilliant white light

Figure 1.1 Burning magnesium.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
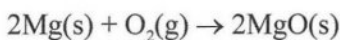
This reaction cannot be reversed. You cannot convert the magnesium oxide produced back to the original elements magnesium and oxygen by changing conditions such as temperature – it is an irreversible reaction.

Steel wool is another substance that can be burnt in the laboratory in a non-reversible reaction. In the presence of oxygen, the thin pieces of steel burn to produce iron oxide. In pure oxygen, the reaction is much faster and more vigorous.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$
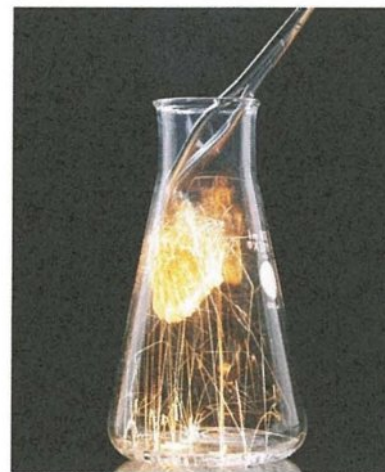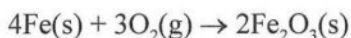
Figure 1.2 Burning steel wool in oxygen.

Reversible reactions

Many transition metals form coloured salts, and their colour can vary as their oxidation state or degree of dehydration changes.

Copper chloride and iron chloride are examples as you can see in Figure 1.2.
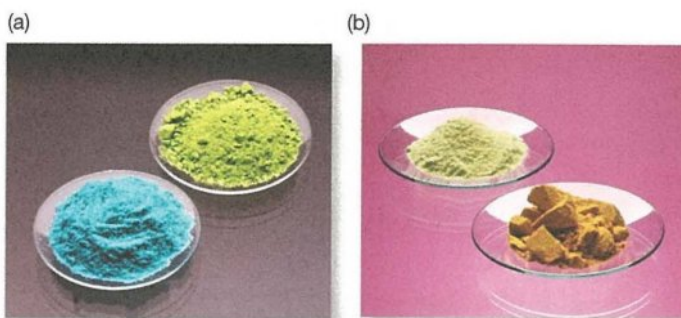
Figure 1.2 (a) Copper(I) chloride (CuCl) is green and copper(II) chloride is blue. (b) Crystals of iron(II) chloride tetrahydrate ($FeCl_2.4H_2O$) are green and crystals of iron(III) chloride hexahydrate ($FeCl_3.6H_2O$) are mustard yellow.

Cobalt chloride is another transition metal salt that changes colour. When hydrated its crystals are pink/purple ($CoCl_2.6H_2O$), when dehydrated it becomes anhydrous (without water) and is blue in colour. Cobalt chloride can be dried by heating the crystals to evaporate the water or by placing it in a desiccator. (If you are unfamiliar with a desiccator, see Question 3.)
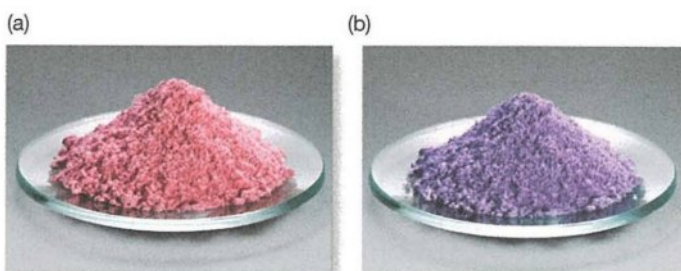
Figure 1.3 (a) Hydrated cobalt(II) chloride is pink/purple. (b) Anhydrous cobalt(II) chloride ($CoCl_2$) is blue.

Cobalt chloride paper

Strips of paper can be soaked in cobalt chloride solution to form cobalt chloride paper. This is blue when dried and it can be stored in a dry place such as a desiccator. It can be used to test for water leaks from tiny cracks – if the paper is applied and goes pink, then water is present.
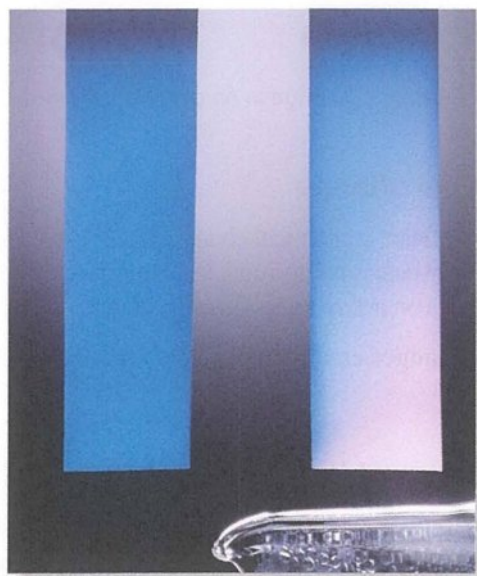
Figure 1.4 Cobalt chloride paper goes pink in the presence of water.

Simple weather indicators can be made by soaking blotting paper in cobalt chloride and cutting it into interesting shapes such as the petals of a flower. It changes colour as the atmospheric humidity changes.

Another reversible reaction you will carry out involves **iron(III) nitrate and potassium thiocyanate**. When solutions of these ionic compounds are mixed, they react to form a blood-red complex called iron(III) thiocyanate. This is sometimes used as fake blood.

The nitrate ions and potassium ions are spectator ions and do not take part in the reaction, so the reaction is:

$Fe^{3+}(aq)$ + $SCN^-(aq)$ $\rightleftharpoons$ $[FeSCN]^{2+}$
Pale yellow   colourless   brown/red
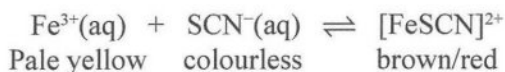
This is a reversible reaction as both the forward and reverse reactions are occurring at the same time. The reactants do not all get used up. At any instant all species (reactants and products) are present in the reaction vessel.

Adding extra iron ions or thiocyanate ions separately, makes the colour a deeper red, as they react with ions that have not been used up.

$Fe^{3+}(aq)$ + $SCN^-(aq)$ $\rightarrow$ $[FeSCN]^{2+}$
Pale yellow   colourless   brown/red
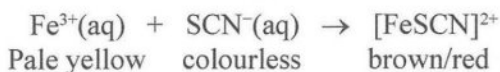
Adding extra iron thiocyanate to the mixture produces a lighter colour as the reaction is pushed in the reverse direction.

$[FeSCN]^{2+}$ $\rightarrow$ $Fe^{3+}(aq)$ + $SCN^-(aq)$
Brown/red   pale yellow   colourless
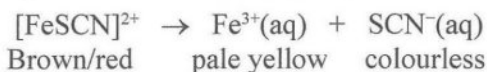
These changes could only happen if the reaction had not gone to conclusion – the reaction vessel must contain some reactants and also some product as both the forward and reverse reactions are happening simultaneously.

QUESTIONS

1. Describe the safety precautions you used when carrying out experiments involving:
    (a) The combustion of substances such as magnesium and steel wool.
    (b) The use of chemicals such as salts of transition elements.
2. (a) Describe how you made cobalt chloride change colour in the laboratory.
    (b) What happens to blue copper sulfate crystals when they are heated in a crucible above a Bunsen burner. Can this change be reversed?
    (c) Research uses of cobalt chloride paper.
3. The diagram illustrates a desiccator found in most school laboratories. What is a desiccator and what is it used for?

4. (a) In the reaction between iron nitrate and potassium thiocyanate, how could you determine which ions are spectator ions?
    (b) Research why iron thiocyanate can have a colour similar to blood.
5. Some students made up aqueous solutions of Fe^{3+} and SCN^- ions. They added these solutions and formed deep red iron(III) thiocyanate.
    Explain the following observations as they continued their investigation.
    (a) They added more of the solution containing Fe^{3+}, and the colour went a deeper red.
    (b) They also added more SCN^- and again the colour went a deeper red.
    (c) Extra $[FeSCN]^{2+}$ was added, and the mixture became lighter in colour.

2   Open and Closed 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. When a reaction reaches equilibrium, no energy enters or leaves the system either. (If you are also studying physics, note that this definition is different in physics.)
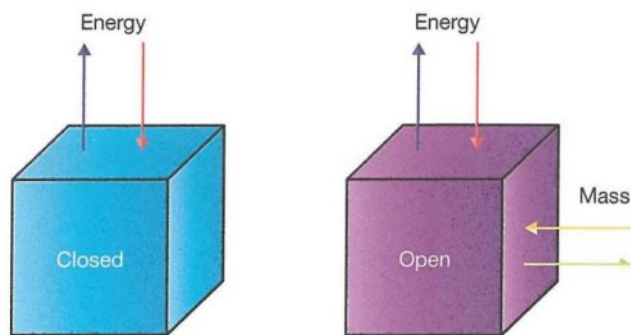
Figure 2.1 Open and closed systems.

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 container.

Figure 2.2 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 and Irreversible reactions

Sometimes, when a physical or a chemical change occurs in a closed system, the products will recombine and re-form 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:

$$H_2O(l) \rightarrow H_2O(g)$$
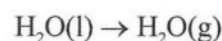
At the same time water vapour will condense:

$$H_2O(g) \rightarrow H_2O(l)$$
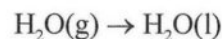
This is a reversible physical change, so we can show it by using arrows going in both directions.

$$H_2O(l) \rightleftharpoons H_2O(g)$$
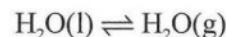
Reversible and irreversible chemical reactions

Many chemical reactions that you have seen in the laboratory **go to completion and cannot be reversed – we describe these reactions as irreversible**. 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.

Steady state

A steady state condition such as that illustrated in Figure 3.2 is *not* an example of equilibrium. It is mentioned here because conditions are stable within the system – there is no net change over time (just like in equilibrium), so students sometimes mistake it for a type of equilibrium or a model of equilibrium.

Figure 3.3 Steady state.

This is a physical system, in which matter and energy are entering and leaving the system at a constant rate so that conditions have become stable within the system. Water is flowing in and out of the container at the same rate, so the water level (and the volume) stays the same – it becomes stable, and the system is said to be in steady state. However, this is not a case of forward and reverse reactions occurring at the same rate.

We can summarise the main differences as follows.

Table 3.1 Dynamic equilibrium versus steady state.

Dynamic equilibrium	Steady state
Net free energy does not enter or leave the system.	Free energy is continuously put into the system.
Any difference in entropy between the system and the external environment tends to disappear.	The system is being maintained in a higher state of order and entropy than its surroundings.
System is closed.	System is open.

Steady state is not an example of equilibrium and cannot be used as a model of equilibrium.

1. Distinguish between static and dynamic equilibrium.
2. 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.
3. What is meant by steady state, and why is this not an example of equilibrium?
4. Each of the following situations would have constant macroscopic properties. Classify each as being in either a dynamic equilibrium, a static equilibrium or a steady state,
   (a) A chemical reaction in which a limiting reagent has been used up.
   (b) A Bunsen burner which is burning steadily at the same rate.
   (c) A chemical reaction represented by $A \rightleftharpoons B$ in which the forward reaction rate is equal to the reverse reaction rate and there is no observable change taking place.
   (d) A bath with a constant water level. There is no plug and the tap is turned on so that water is continually entering and leaving the bath at the same rate.
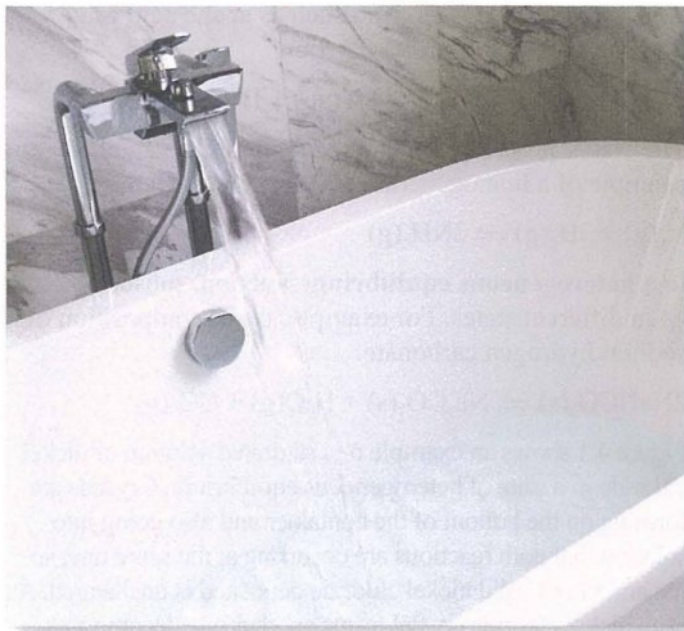
4   Characteristics Of Equilibrium

You have seen that some reactions can proceed in both a forward and reverse direction at the same time. If such a reaction occurs in a **closed system** and the **forward and reverse reactions occur at the same rate**, then the reaction is said to be at **equilibrium**.

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

If you look at a system in equilibrium, it will seem that nothing is happening. You will not see any changes taking place. There will be no change in the state (solid, liquid or gas) of the reactants or products. Also the pH, colour, temperature and pressure of the reactants and products will stay the same. Properties such as these that we can see are called macroscopic properties, so we say that at equilibrium the **macroscopic properties are constant**. This situation will continue unchanged as long as the external conditions, such as temperature, do not change and the system remains closed.

However, if you could see the tiny particles – the atoms and molecules – inside the container, you would see that there is constant change happening all the time. Reactions are continuously taking place at a microscopic level. We do not see these changes with our eyes because both the forward and reverse reactions are occurring at the same rate, so there is **no net change**.

Homogeneous and heterogeneous equilibrium

The term **homogeneous equilibrium** refers to a state of equilibrium in which all the involved species (reactants and products) are in the same state/phase. For example, the ionisation of a weak acid such as acetic acid is a homogeneous equilibrium reaction.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

The Haber process used to make ammonia is another example of a homogeneous equilibrium reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
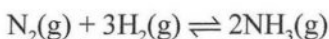
In a **heterogeneous equilibrium** reaction, substances can be in different states. For example, the decomposition of sodium hydrogen carbonate.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$
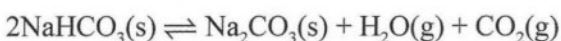
Figure 4.1 shows an example of a saturated solution of nickel chloride in a state of heterogeneous equilibrium. Crystals are forming on the bottom of the container and also going into solution, but both reactions are occurring at the same rate, so the amount of solid nickel chloride deposited is unchanged. As each nickel chloride crystal forms another one decomposes.

$$NiCl_2(s) \rightleftharpoons Ni^{2+}(aq) + 2Cl^-(aq)$$
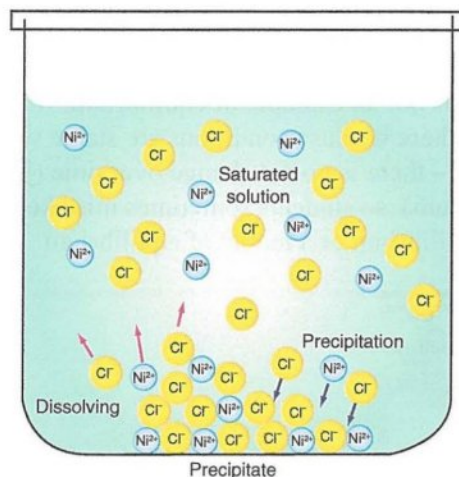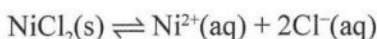
Figure 4.1 Saturated solution of nickel(II) chloride solution in equilibrium.

Characteristics of equilibrium systems

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.
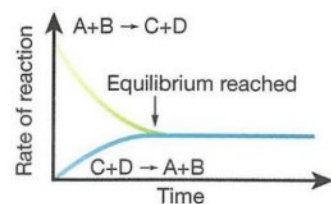
Figure 4.2 Equilibrium and rate of reaction.

3.   The **macroscopic properties** (ones you can see) **stay constant** – there is no change in pH, 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.
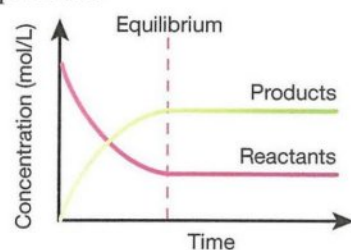
Figure 4.3 Concentration and equilibrium.

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).

6. The equilibrium can be approached **from either direction**. For example, in the equilibrium reaction, $A + B \rightleftharpoons C + D$, you can start with the chemicals A and B or with C and D.

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.
2. Explain why chemical equilibrium systems are described as being dynamic rather than static.
3. Outline the six characteristics of an equilibrium system.
4. Explain how the concentration of reactants can stay constant at equilibrium even though the reaction is still proceeding.
5. (a) Outline trends occurring in the concentration/time graphs in Figure 4.3.
   (b) Explain why both graphs in Figure 4.2 finish as the same straight line.
6. 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.

   Concentration and equilibrium
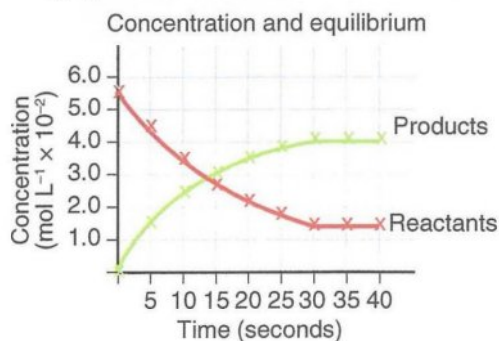
   Identify the time at which equilibrium was reached and justify your answer.
7. Describe an equilibrium system that you observed in the science laboratory.

8. The graphs below illustrate two characteristics of systems at equilibrium.

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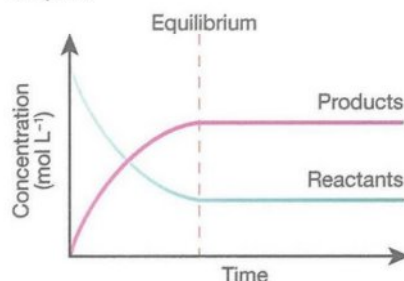
   Graph Y
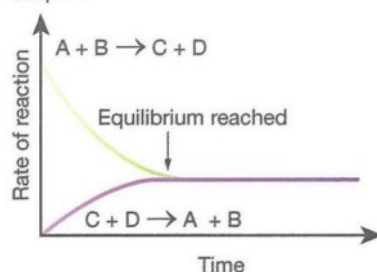
   (a) Outline the characteristic illustrated by each graph.
   (b) Compare graphs X and Y above with graph Z below.

   Graph Z
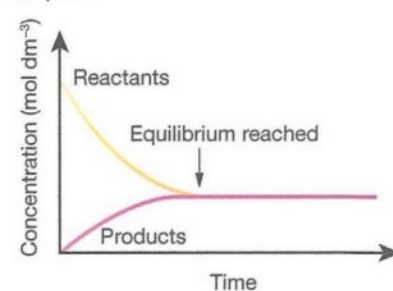
   Does graph Z represent a characteristic of all systems at equilibrium? Justify your answer.
9. In the following series of diagrams, molecules of $NO_2(g)$ (shown as O) are reacting to produce $N_2O_4(g)$ (shown as X). Eventually the two gases reach equilibrium.
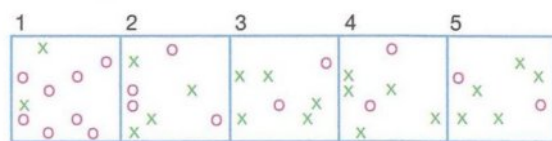
   (a) At which stage is equilibrium reached? Justify your answer.
   (b) Is this a physical or a chemical equilibrium? Explain.
10. Check your knowledge with this quick quiz.
    (a) What conditions must be constant for a system to reach a stable equilibrium?
    (b) At equilibrium, what becomes constant?
    (c) At equilibrium, what must be equal?

5   Revising Enthalpy and Entropy

You will recall from your year 11 studies that enthalpy and entropy are driving forces of chemical reactions and they are related to energy changes taking place. Chemical reactions progress in the direction from higher to lower energy. We need to revise those concepts and determine their importance in equilibrium reactions.

In chemical reactions, bonds of reactants need to be broken so they can be rearranged and form bonds in the products. Breaking bonds uses energy and making bonds releases energy, so the net energy of a reaction depends on the difference between the energy absorbed and released.

The initial rate at which products form in a reaction depends on the initial concentrations of the reactants. Some product particles will react and re-form reactants. So the reaction can proceed in both directions.

As the forward reaction proceeds, the concentration of product increases. This causes an increase in the rate of the reverse reaction. Eventually the rates of the forward and reverse reactions may become equal. At this stage the concentration of reactants becomes stable and the concentration of products becomes stable, and the reaction is described as being in equilibrium.

Looking at the energy of a chemical reaction can help us to predict the direction of a chemical reaction and to determine whether it will achieve equilibrium or proceed to completion.

Enthalpy (H) is the total energy in a system. This cannot be measured, but often we can measure the change in enthalpy (ΔH) of a reaction – the difference between the energy of reactants and products. Exothermic reactions have negative enthalpy changes, endothermic reactions have positive enthalpy changes.

Entropy (S) is a measure of the possible ways in which energy can be distributed in a system of molecules. The more spread out the energy, the higher the entropy will be, and the more likely the reaction will occur spontaneously.

Table 5.1 Comparing enthalpy and entropy.

Enthalpy (H)	Entropy (S)
The total energy content of a process or closed system.	The ways energy can be distributed in a system of molecules.
Energy decrease favours a reaction.	Entropy increase (dispersion of energy) favours a reaction.
Measured in joules kg⁻¹.	Measured in joules mol⁻¹ K⁻¹.
Energy is conserved.	Entropy is not conserved.

Combustion and photosynthesis

You have seen that enthalpy and entropy are important when we consider **non-equilibrium systems** such as combustion and photosynthesis.

Combustion reactions involve the combining of a substance with oxygen and they are irreversible reactions – a combustion reaction cannot be reversed.

Figure 5.1 Combustion

It does not form an equilibrium reaction. Irreversible reactions such as combustion can only proceed in one direction, their products cannot reverse back into reactants, so they can never be at equilibrium. All combustion reactions are exothermic. Enthalpy of combustion reactions is always negative, as energy is released to the environment. Most combustion reactions occur spontaneously, although this does depend on the temperature and the relative sizes of ΔH and ΔS_{system}. If the entropy of an exothermic reaction is increasing (positive) then the reaction will definitely occur spontaneously.

Photosynthesis takes place in green plants and in some bacteria. It is the process by which sugars are produced from carbon dioxide and water. Photosynthesis consists of a series of reaction steps, but the overall reaction can be shown by the equation:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

Sunlight

Carbon dioxide

Oxygen

Sugars

Water

Process of photosynthesis
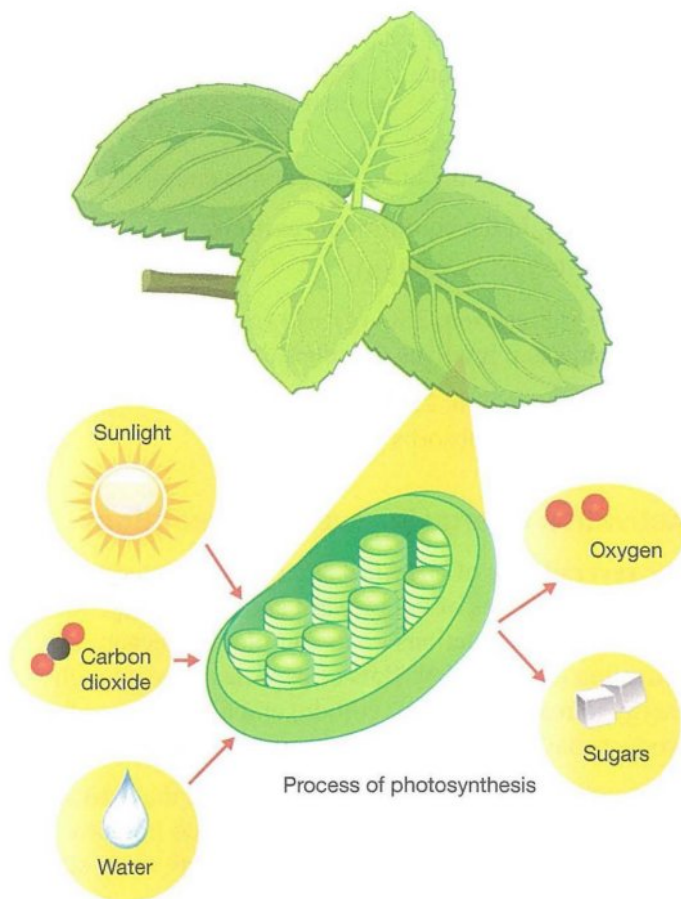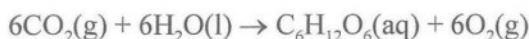
Figure 5.2 Photosynthesis takes place in tiny structures called chloroplasts that occur in the cells of green plants.

This is an irreversible endothermic reaction; the enthalpy of reaction for photosynthesis is positive. This is not a spontaneous reaction as the energy of the products is greater than the energy of the reactants, and energy is needed for this reaction to occur. Very little of the reactants would be changed to products without the input of energy into the system. Green plants are able to carry out photosynthesis because they contain the green pigment chlorophyll which acts as a catalyst and can absorb a range of energy wavelengths (mostly blue and red) from sunlight.

Note: $C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ the respiration reaction, looks like the reverse of photosynthesis. However, these are just reaction summaries for two very different processes with different numbers of steps in each. Photosynthesis and respiration are not reversible reactions. They each go to completion and do not reach an equilibrium.

Enthalpy and entropy in equilibrium

Entropy and enthalpy are both drivers of reactions such as photosynthesis and combustion, and you will recall that Gibbs free energy reflects the balance between entropy and enthalpy as drivers of any chemical reaction.

$$\Delta G° = \Delta H - T\Delta S$$

Where:

$\Delta G°$ = the standard state free energy of reaction

ΔH = change in enthalpy of the system

$T\Delta S$ = change in the entropy of the system when temperature is constant

ΔG tells us how far the standard state is from equilibrium. The smaller the value of ΔG, the closer the reaction is to equilibrium.

In the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$,

as the reaction shifts to the right, the value of ΔG decreases until it reaches zero, and then there is no further change in free energy.

When $\Delta G = 0$, the system is at equilibrium.

Neither the forward nor the reverse reaction is favoured. Therefore, in a system at equilibrium, enthalpy and entropy no longer need to be considered as driving forces.

QUESTIONS

1. Distinguish between enthalpy and entropy.
2. Which direction of change in enthalpy and entropy favours a non-equilibrium chemical reaction?
3. Explain why equilibrium cannot be reached during combustion reactions.
4. Some people claim that respiration is the reverse reaction of photosynthesis. Does this mean that photosynthesis is reversible?
5. Check your knowledge with this short quiz.
   (a) The total energy of a system is called its

   ....
   (b) Identify two driving forces of chemical reactions.
   (c) If the energy distributed through a system becomes more spread out, the entropy of the system will (increase/decrease).
   (d) Photosynthesis and respiration are reversible reactions – true or false?
   (e) What is the value of $\Delta G°$ for a reaction at equilibrium.
   (f) Combustion is always a(n) (reversible/irreversible) chemical reaction.

6   More About Equilibrium

In year 11 you learned about the collision theory which provides a possible explanation about how chemicals react to form products. This would be a good time to revise collision theory, activation energy and reaction rates as they are all important concepts in understanding equilibrium reactions.

Collision theory

All particles are seen as constantly moving and they react with other particles when they collide with the correct orientation and with enough energy to overcome activation energy. **Activation energy** is the energy needed to get a chemical reaction started. The kinetic energy levels of reacting particles must be high enough to break bonds so that atoms become free to make new bonds as they rearrange in a chemical reaction.

(a)   Exothermic reaction.
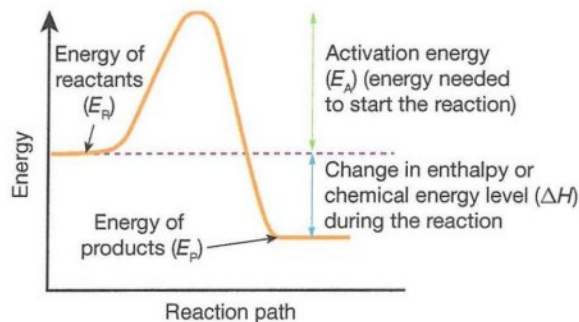
(b)   Endothermic reaction.
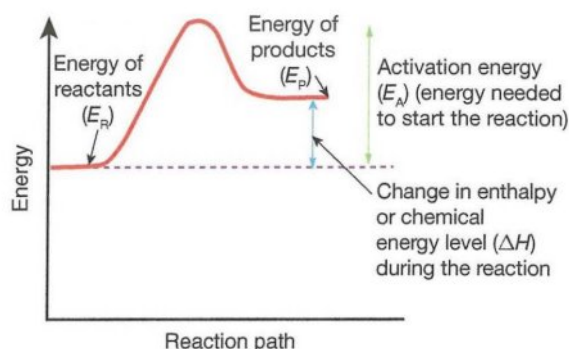
Figure 6.1 Energy profiles showing activation energy for exothermic and endothermic reactions.

At any instant, particles present will vary in their levels of kinetic energy. Most will not have enough energy to react when they collide, but some can react as they have energy levels equal to or greater than the activation energy for that reaction – the energy needed to get a chemical reaction started. The Maxwell-Boltzmann distribution illustrates this.

The large yellow area represents the majority of particles present. These do not have enough energy to react; they have not reached activation energy.

The small red area represents the particles which do have enough energy to react when they collide – these particles have reached activation energy levels for this reaction.
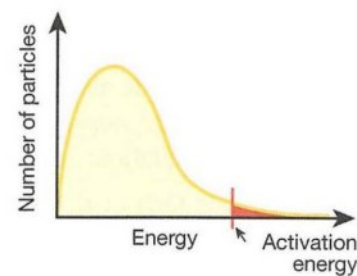
Figure 6.2 The Maxwell-Boltzmann distribution.

In a reversible reaction, the reaction in one direction is exothermic and the reaction in the other direction is endothermic.

For example, in the equilibrium reaction:
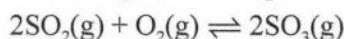
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

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

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

Activation energy in reversible reactions

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.

A reversible reaction which is exothermic in the forward direction will be endothermic in the reverse direction and vice versa.
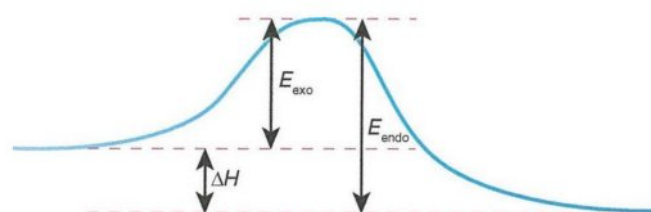
E_{exo} = activation energy for the forward reaction

E_{endo} = activation energy for the reverse reaction

ΔH = the difference between the activation energies

Figure 6.3 Energy profile for a reversible reaction.

The activation energy is usually supplied by thermal energy, for example through intermolecular collisions. However, other sources of activation energy are possible, for example the absorption of light and electrochemical activation.

The energy profile describes the mechanism of the reaction, illustrates the concept of activation energy and shows changes in potential energy between reactants and products during a chemical reaction.

Reaction rates

Reaction rate is the speed at which a chemical reaction occurs – the speed at which reactants are used and products are formed. Reaction rates depend on the rate and force of collisions between particles of reactants, (which may be atoms, ions or molecules). This depends on how fast they are travelling, the nature of the reactants, e.g. their state and any existing bonds that need to be broken. You will recall that reaction rates can also be influenced by the following.

- The concentration of reactants. The higher the concentration of reactants, the faster the reaction rate.
- Temperature of the surroundings. The higher the temperature, the greater the number of particles moving fast enough to overcome activation energy and thus the faster the reaction rate.
- Structure of reacting particles, e.g. their size. The smaller the size of reacting particles, the greater their surface area, and the faster their reaction rate.
- The pressure (if gases are involved). The higher the pressure (or smaller the volume of the reaction vessel) the faster the reaction rate.
- The presence or absence of a catalyst. The presence of a catalyst can increase reaction rate by providing an alternative pathway with lower activation energy for the reaction.

These factors apply to equilibrium reactions as they do to reactions that go to completion. The only difference with equilibrium reactions is that you have to consider their effects on both the forward and reverse reactions.

Equilibrium position

The reaction rate is not the same as the extent or position of a reaction.

For a rapid reaction which is not reversible we will see all the reactants converted to products (as long as they are mixed in stoichiometric proportions).

However, in a reversible reaction, this refers to how much of the reactants have been converted to products, and how much of the products have been re-converted to reactants. Even in a fast, reversible reaction, we will never see all the reactants converted to products.

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.

$$SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
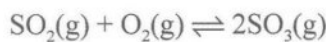
If this reaction is taking place in a sealed container, under constant conditions, it will eventually reach equilibrium. It does not matter whether you start with sulfur dioxide and oxygen or with sulfur trioxide in your container, as long as the conditions such as temperature are identical, you will 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 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 then more sulfur trioxide is present in the container at equilibrium.

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.

QUESTIONS

1. What is the collision theory?
2. What is the activation energy of a chemical reaction?
3. (a) Define reaction rate.
   (b) Identify factors that can affect reaction rate.
4. (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?
5. Explain the reversibility of chemical reactions in terms of activation energies of the forward and reverse reactions.
6. 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.

7. On each of the graphs below, mark the position when equilibrium is reached. Justify your answer.

(a)

(b)
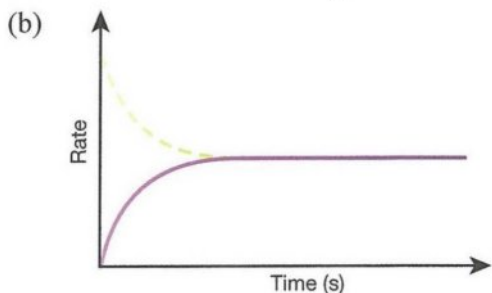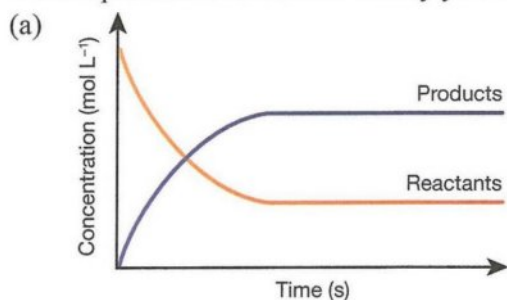
8. Nitrogen and hydrogen react to form ammonia which decomposes to form hydrogen and nitrogen gas. In a closed container, under constant conditions, this mixture will reach equilibrium.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
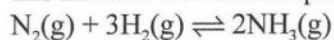
The graphs show equilibrium being achieved from different initial concentrations of gases.

(i)

(ii)
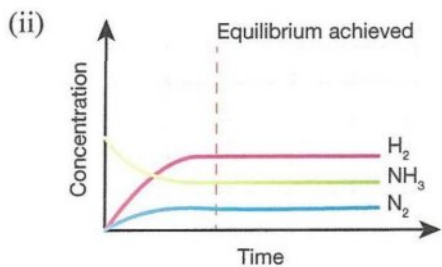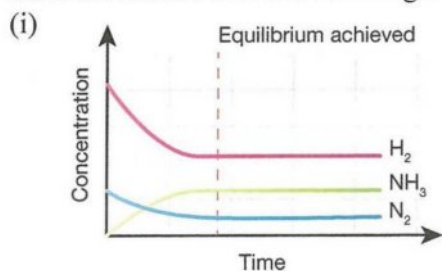
(a) Compare the initial concentrations of hydrogen, nitrogen and ammonia illustrated in graphs (i) and (ii).
(b) Write the forward reaction for each graph.
(c) Compare the final concentrations of gases in graphs (i) and (ii).

9. 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)
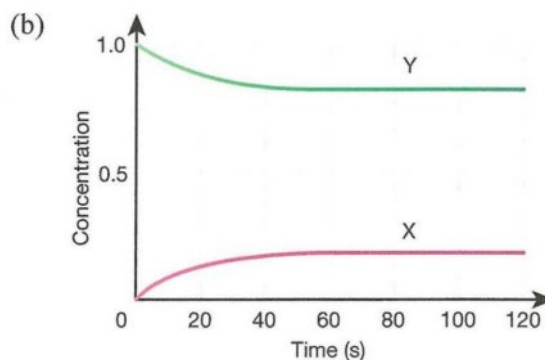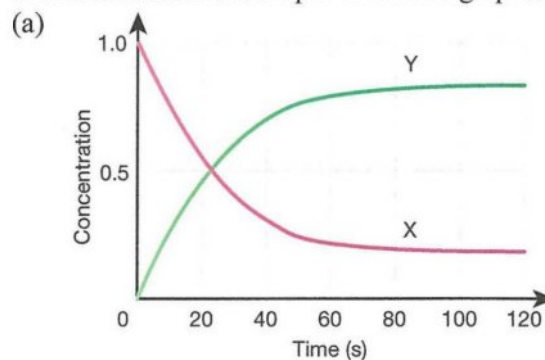
10. Make a list of as many things you can think of that you have so far learned about reversible reactions and equilibrium.

11. State whether each of the following statements is true or false and justify your decision.
    (a) The statement, 'The reactions are at equilibrium', means that the reaction is finished, it is stable and it will not react any more unless something is added.
    (b) When a system is in chemical equilibrium, no more change takes place.

12. 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?

7 Investigating Changes In Equilibrium

There are many experiments that you could carry out in the laboratory to investigate how the equilibrium position can change when an equilibrium is disturbed.

For each of the examples below, you should try to predict the changes that will occur and then check your predictions in the laboratory.

The cobalt chloride equilibrium

Cobalt forms ions which are both pink and blue. In an aqueous solution of cobalt(II) and chloride ions, the pink $Co(H_2O)_6^{2+}$ ions form an equilibrium with blue $CoCl_4^{2+}$ ions.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2+}(aq) + 6H_2O(l)$$

    Pink   colourless   blue

Some changes you can make to this equilibrium reaction include:

- The chloride ion concentration can be increased, e.g. by adding dilute hydrochloric acid.
- Ethanol can be added to remove water from the equilibrium. Predict the colour change.
- The reaction mixture can be heated or cooled. At higher temperatures the mixture becomes a deeper blue, and at lower temperatures it becomes more pink. Can you work out which direction is exothermic?

NO_2 and N_2O_4 equilibrium

Your teacher can react copper metal with concentrated nitric acid in a fume cupboard to form nitrogen dioxide.

$$4HNO_3(l) + Cu(s) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

Alternatively sealed tubes of NO_2 can be purchased to use. *Caution:* Nitrogen dioxide is a poisonous, choking gas and nitric acid is very corrosive.

Nitrogen dioxide immediately forms an equilibrium mixture.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2 \text{ kJ mol}^{-1} N_2O_4$$

Brown   colourless

- Sealed tubes or flasks containing nitrogen dioxide can be warmed and cooled to observe changes in equilibrium position. Predict the effects on the equilibrium position caused by heating and cooling the mixture.

The chromate-dichromate mixture

$$2CrO_4^{2+}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O$$

  Yellow   orange

In this experiment, as the colours are similar, you need to be careful that you can distinguish between a colour change that is just due to dilution and a change that indicates a new equilibrium is being reached.

- What could you add to the mixture to move the equilibrium to the right?
- How could you move the equilibrium left?

The ferrocyanate equilibrium

In aqueous solution, iron(III) ions react with thiocyanate ions to form an iron cyanate complex which is blood red:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}$$

Yellow colourless blood-red

This can be made by mixing iron(III) nitrate and potassium thiocyanate. Nitrate ions (NO_3^-) and potassium ions will be present in the mixture as spectator ions.

This is a useful reaction to investigate because of the vivid colour changes. If a change makes the reaction move to the right, the mixture will go more red. If the reaction moves left the red will go lighter in colour.

Some changes you can make to this equilibrium include:

- Warming or cooling the reaction mix changes the equilibrium position. If the reaction as written above is exothermic in the forward direction, predict the effect of suspending the mixture in a hot water bath and in an iced water bath.
- Adding a dilute solution of iron(III) chloride. This is soluble and will dissolve in the equilibrium mixture, increasing the concentration of Fe^{3+} ions. Predict the colour change.
- Adding KSCN increases the concentration of SCN^-. Predict the colour change.
- Adding KCl causes a reaction between the Cl^- ions and Fe^{3+} ions to form $FeCl_3$. This reduces the $[Fe^{3+}]$. Predict the colour change.
- Add a drop of 6 mol L^{-1} hydrochloric acid. Will the chloride ions present in HCl have the same effect as adding KCl?
- Adding silver nitrate – this reacts with the $(FeSCN)^{2+}$, forming a white precipitate of silver thiocyanate, and thus removing it from the mixture, so the concentration of the complex is reduced.

You need to add varying concentrations of these chemicals to the ferrocyanate equilibrium and observe any changes carefully to see how the equilibrium shifts when it is disturbed.

QUESTIONS

1. Describe the experiments that you carried out to investigate the following equilibrium systems. In your answer include the safety precautions needed for each experiment.
   (a) The cobalt chloride equilibrium.
   (b) The interaction between nitrogen dioxide and dinitrogen tetroxide.
   (c) The chromate-dichromate equilibrium.
   (d) The ferrocyanate equilibrium.

8 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 8.1 shows a system which reaches equilibrium and this is then disrupted by the addition of more reactant.
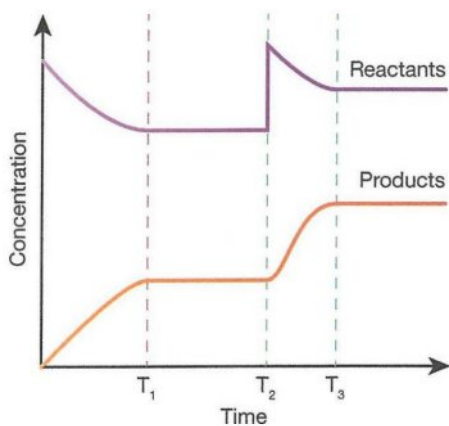

Figure 8.1 Effect on equilibrium system when equilibrium is disturbed by changing concentration.

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 reactants and products have both increased, but products have increased more than reactants. 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 8.2 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.
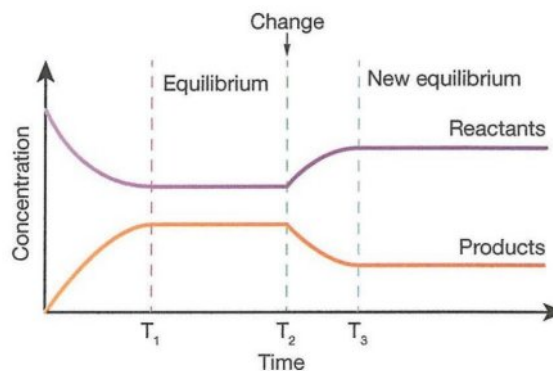
Figure 8.2 Effect on an equilibrium system when temperature is changed.

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 8.2.
   (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.

9   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
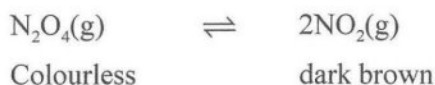
This reaction, carried out in a sealed tube, will soon reach equilibrium and there will be no further visible change – as long as the temperature is kept constant.
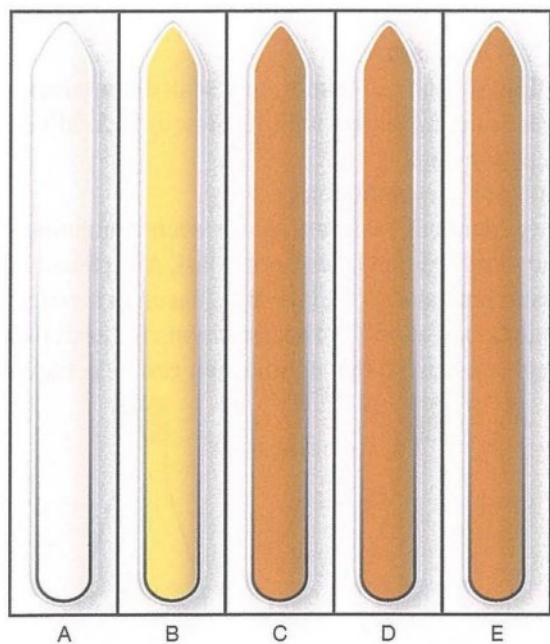

Figure 9.1 Successive images of a mixture of N_2O_4 and NO_2 as equilibrium is reached.

If you **increase the temperature** of the surroundings, for example by putting the tube 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.

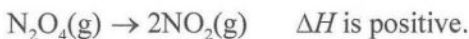## Explaining effects of temperature on equilibrium position

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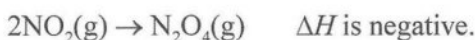
Conversely, decreasing the temperature favours the exothermic reaction which has the lower activation energy.

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.

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad \Delta H \text{ is positive.}$$

The reverse reaction is exothermic.

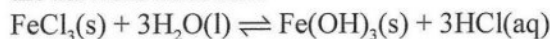$$2NO_2(g) \rightarrow N_2O_4(g) \qquad \Delta H \text{ is negative.}$$

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) $A + B \rightleftharpoons C + D + \text{heat}$
    (b) $A + B + \text{heat} \rightleftharpoons C + D$
    (c) $A + B \rightleftharpoons C + D$, $\Delta H = \text{negative}$
    (d) $A + B \rightleftharpoons C + D$, $\Delta H = \text{positive}$
3. Describe the effect of the following changes on the equilibrium reaction, $A + B \rightleftharpoons C + D + \text{heat}$.
    (a) Decrease the reaction temperature.
    (b) Increase the reaction temperature.
4. Consider the equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.
    (a) Figure 9.1 shows a series of images 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 100°C, 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)
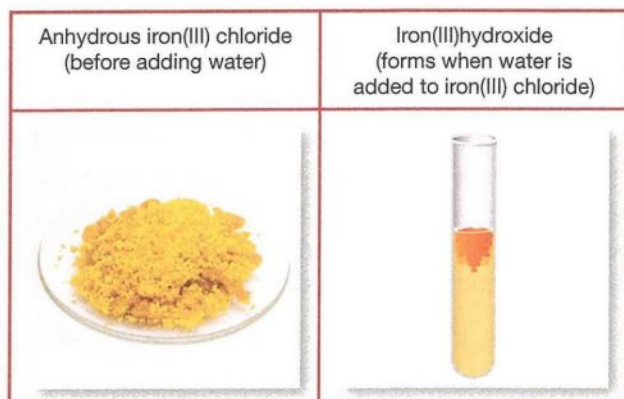
(a) Predict any colour change you would expect to occur when the reaction temperature is changed.
(b) Describe the effect of increasing the reaction temperature on the equilibrium position of this reaction.

6. In Chapter 8 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.
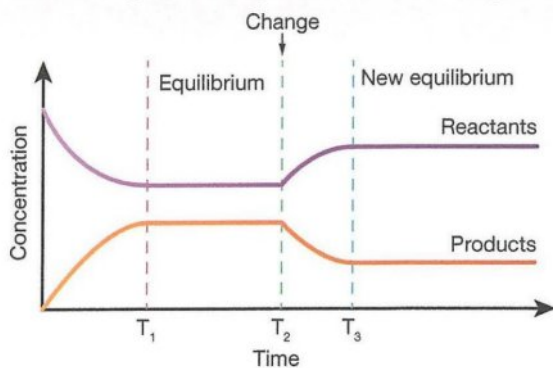

(a) Compare the equilibrium concentrations, as shown by this graph, at a lower and a higher temperature.
(b) Based on this information, deduce whether the forward reaction is endothermic or exothermic.

7. Cobalt(II) chloride hexahydrate changes colour from pink/purple to blue when heated as represented by the equation: $CoCl_2.6H_2O \rightleftharpoons CoCl_2(aq) + 6H_2O(l)$
     Pink/purple   blue
Account for this change using collision theory.

8. Hydrogen and iodine react to form hydrogen iodide. In a sealed container, under stable conditions, this system will reach equilibrium.
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \; \Delta H = -51 \; kJ$
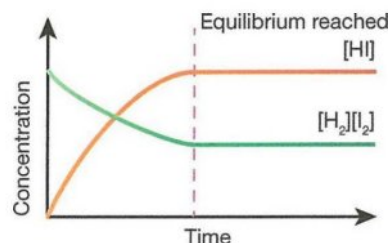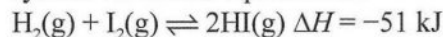
(a) Is this reaction endothermic or exothermic in the forward direction?
(b) If this reaction is carried out at a lower temperature, at the new equilibrium position the concentration of hydrogen iodide will be (larger/smaller) because the equilibrium will have shifted to the (left/right).
(c) Sketch what the above graph would look like if this reaction were carried out at a lower temperature.

9. 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.
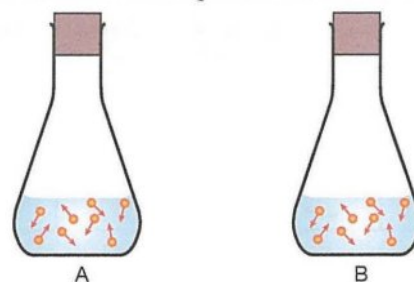
(a) Copy the diagram to show what is happening in each flask at equilibrium.
(b) How do the flask B contents compare with the contents of flask A?

10. 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?
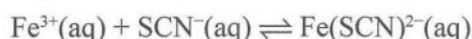
10 Equilibrium and Concentration

A chemical system at equilibrium will be affected by changes in concentration and the system will find a new equilibrium position.

Effects of changing concentration

If the concentration of a species (chemical) in an equilibrium system is **increased**, the reaction moves toward the other side, using up some of the added chemical and finding a new equilibrium position.

If the concentration of a species is **reduced**, the equilibrium shifts towards its side of the equation – thus increasing the concentration again.

For example, you have already seen that, if aqueous thiocyanate ions are added to an aqueous solution of an iron(III) salt, a red colour is produced as an iron thiocyanate complex forms. In a stable environment, an equilibrium position will be reached.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2-}(aq)$$
Light brown   red

If you **increase the concentration** of either iron ions (Fe^{3+}) or thiocyanate ions (SCN^-), the colour becomes a deeper red. A new equilibrium position is established favouring the forward reaction as the system uses up the added ions. The equilibrium position moves to the right.

If you **decrease the concentration** of either iron ions (Fe^{3+}) or thiocyanate ions (SCN^-), the colour becomes less red. The reverse reaction is favoured as the system tries to make more iron ions or thiocyanate ions to replace those removed. The new equilibrium position moves to the left.

Adding and removing chemicals

Adding chemicals to increase concentration is relatively easy. Removing them may not be so easy. We talk about removing chemicals as if you could just reach into the mixture and pull them out. Of course, that is not the case. To remove a chemical from a mixture of reactants and products, another substance may be added to react with it. For example, to remove carbon dioxide, you could use solid sodium hydroxide or calcium hydroxide.

In the thiocyanate equilibrium, if you add chloride ions or fluoride ions to the mixture they react with the Fe^{3+}, forming a stable substance and thus removing the Fe^{3+} from the reaction. This will decrease the concentration of Fe^{3+} ions.

The mixture will lose its red colour and become light brown. A new equilibrium position is established favouring the reverse reaction. The equilibrium position has moved to the left.

## Explaining effects of changing concentration

This shift in equilibrium can be explained by applying collision theory to the forward and reverse reactions.

For example, in the iron thiocyanate reaction, when the concentration of Fe^{3+} ions increases, having more particles present will increase the frequency of collisions and some of these colliding particles will have energy levels equal to or higher than the activation energy allowing them to react. In other words, the rate of the forward reaction will increase. The change will favour the forward reaction.

The new equilibrium position is eventually established, with the equilibrium mixture having an increased percentage of the product, $Fe(SCN)^{2-}$ ions. The equilibrium position has moved to the right.

1. Chlorine gas reacts with liquid iodine chloride to produce solid, yellow iodine trichloride and, in a closed system, this reaction will reach equilibrium.
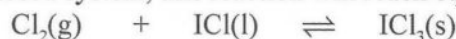
$$Cl_2(g) \quad + \quad ICl(l) \quad \rightleftharpoons \quad ICl_3(s)$$
Pale green   brown   yellow

Describe and explain the effect of the following changes on this equilibrium system.
(a) Adding more chlorine.
(b) Removing chlorine.

2. The following reversible reaction will reach equilibrium. Its colour will then stay constant as long as conditions are unchanged. The colour of the mixture will change when the concentration of reactants or products is altered.

Chromate + hydrogen $\rightleftharpoons$ dichromate + water
   ions   ions   ions
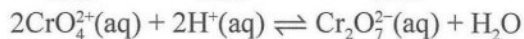
$$2CrO_4^{2+}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O$$
Yellow   orange

(a) Predict the colour change when dilute hydrochloric acid is added to this system at equilibrium.
(b) Predict the colour change when sodium hydroxide is added to this system at equilibrium.

11 Equilibrium and Pressure/Volume

Changing the pressure on an equilibrium system will have an effect whenever there are any gases involved in the reaction. Just what effect it will have depends on the number of moles of gases on each side of the equation.

For example, ammonia is produced commercially by reacting nitrogen and hydrogen gases, a reversible reaction which reaches equilibrium under constant conditions. These conditions must be carefully controlled to maximise the yield of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$

Notice that there are 4 moles of gas on the left and only 2 moles of gas on the right side of the equation.
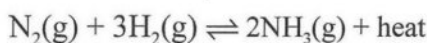
Increasing the pressure on this system will favour the forward reaction – so the equilibrium position will move to the right and the yield of ammonia will increase.

Reducing the pressure on this equilibrium system will favour the reverse reaction. The equilibrium position will shift to the side with the most moles of gas – in this case, to the left. This results in more moles of gas being produced, increasing the pressure again. The reverse reaction is favoured and less ammonia is produced.

Explaining effects of changing pressure/volume

Changing the pressure on a closed system can be achieved by changing the volume or concentration. To **increase pressure** the system can be compressed to occupy a smaller volume. Alternatively, more of a gas involved in the reaction can be added. Each of these changes will result in pushing particles closer together and causing more collisions. When you increase the pressure on a gas, you increase its concentration and thus the collision rate.

For the forward reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, **increasing pressure** means more collisions between nitrogen and hydrogen molecules that have enough energy to react – increasing the rate of this reaction, and pushing the equilibrium position to the right. This increases the yield of ammonia.

Conversely, decreasing pressure favours the reverse reaction, so more gas moles are made, helping the pressure to increase again.

Sometimes changing pressure has no effect

Notice that changing the pressure will have **no effect on an equilibrium** system in which the following occurs.

- The number of moles of gas on the left and right sides of the equation is the same (each side will be affected equally by pressure changes and so there will be no net change, e.g. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

- There are no gases present,
  e.g. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2-}(aq)$

QUESTIONS

1. Suggest ways in which the pressure on an equilibrium system could be altered.

2. The following equilibrium is set up.
   $$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
   Explain the effect on the equilibrium position if the pressure decreases.

3. In a closed system, methane and steam react to form an equilibrium system.
   $$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$
   The yield of carbon monoxide and hydrogen can be increased by decreasing the pressure on this system. Explain in terms of collision theory.

4. One step in the production of sulfuric acid involves converting sulfur dioxide to sulfur trioxide.
   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
   Identify any effect on this system that would be caused by an increase in pressure.

5. (a) Research the equilibrium that occurs in a bottle of soft drink due to carbon dioxide being dissolved in the aqueous solution that makes up the drink.

   (b) Research any effect on an equilibrium system of adding an inert gas (one not involved in the reaction).

6. In the last three chapters you have learned how changes in temperature, concentration and pressure can affect a closed system at equilibrium. Answer the following quick quiz to check your knowledge.

   (a) A reaction that proceeds in both directions at the same time is said to be ....

   (b) At equilibrium the concentration of reactants and products is ....

   (c) Increasing the number of reactant gas particles in a sealed container will (increase/decrease) the concentration and pressure.

   (d) Removing a product as it forms from an equilibrium vessel will (increase/decrease) the yield of products.

   (e) Changing the pressure on an equilibrium system will only affect the system when a .... is present.

   (f) The effect of changes in concentration and pressure on equilibrium can be explained by applying .... theory.

12 Le Châtelier's Principle

Henri Louis Le Châtelier (1850-1936) was a French chemist and engineer.

Figure 12.1 Henri Louis Le Châtelier.

In 1885 he presented his ideas on chemical equilibrium which are known as Le Châtelier's principle. His principle does not explain why changes occur in equilibrium systems, but it is very useful for predicting the changes that will occur in an equilibrium system when the conditions such as temperature, pressure and concentration are changed.

Le Châtelier's principle states that if a system is in equilibrium, and it is disturbed or changed in any way, then the system will adjust itself to minimise the amount of change.

This happens for changes in:

- **Concentration** of the reactants or products.
- **Pressure and volume** (*if* gas(es) is/are involved).
- **Temperature** (different effects for exothermic and endothermic directions of the reversible reaction).

This means that if we have a system in equilibrium, and we change the concentration, pressure or temperature of the reaction, then the equilibrium will be disrupted. Eventually a new equilibrium system will be established, but the equilibrium position will have moved in such a way that the effects of the change will be minimised as much as possible.

We will look at the effects of each of these changes, using three different equilibrium systems.

Changes in temperature

Consider the following reaction (in which ΔH of the forward reaction is negative).

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

Le Châtelier's principle says that when an equilibrium system is disturbed, the system will adjust to minimise the change. So if it is cooled, it will react to increase the temperature – to raise it towards its original value, thus minimising the change. An exothermic reaction will give out heat and increase temperature, so cooling the reaction will lead to an increase in the forward reaction. Using Le Châtelier's principle we can predict that the equilibrium position will move right, producing more $N_2O_4(g)$.

Increasing the temperature favours the endothermic direction of an equilibrium and decreasing the temperature favours the exothermic direction.

Changes in concentration

$$Cl_2(g) \quad + \quad ICl(l) \rightleftharpoons ICl_3(s)$$

Pale green   brown   yellow

If more chlorine is added to this equilibrium system it will be disturbed by the change in concentration. Le Châtelier's principle says that when an equilibrium system is disturbed, the system will adjust to minimise the change. So we can predict that, if the Cl_2 concentration is increased, the forward reaction will be favoured in order to use up the added Cl_2. This decreases its concentration again – back towards its original value.

Changes in pressure for reactions involving gas

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

There are gases present in this equilibrium system, so changing the pressure will have an effect. If this equilibrium system is placed under increased pressure, then according to Le Châtelier's principle, the system will adjust by reducing the pressure to minimise the change. There are fewer moles of gas on the left side (2 moles) than on the right side (4 moles), so we can predict that the reverse reaction will be favoured by increasing pressure and the equilibrium position will move towards the left – the side with fewer gas molecules (the presence of fewer gas molecules means lower pressure).
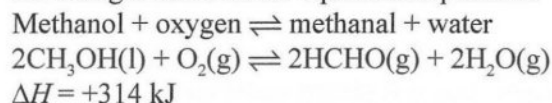
QUESTIONS

1. Recall the meaning of the following terms.
   (a) Reversible reaction.
   (b) Macroscopic properties.
   (c) Activation energy.
2. (a) Recall five properties of an equilibrium system.
   (b) State Le Châtelier's principle.
   (c) Identify three changes that can affect an equilibrium system.

3. The thermal decomposition of calcium carbonate in a closed container can form an equilibrium system.
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
   (a) Explain the meaning of thermal decomposition.
   (b) Would this system still be in equilibrium if the reaction were carried out in an open container? Explain.
   (c) Use Le Châtelier's principle to predict any effect on the equilibrium position for this reaction if some carbon dioxide were removed.
   (d) Name a chemical that could be used to absorb the carbon dioxide.
   (e) Use Le Châtelier's principle to predict any effect on the equilibrium when the pressure on the system is increased.

4. For the equilibrium reaction:
$A(g) + B(g) \rightleftharpoons C(aq) + D(g)$, the reaction in the forward direction as written is exothermic. Use Le Châtelier's principle to predict the effect of the following changes on the equilibrium position.
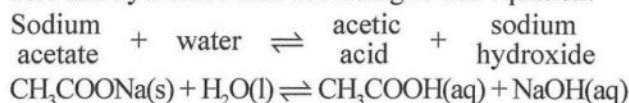   (a) Increase the concentration of A.
   (b) Increase the concentration of D.
   (c) Remove D as it forms.
   (d) Increase the pressure.
   (e) Add a catalyst.
   (f) Increase the temperature.

5. The following reaction shows the production of methanal (HCHO) from methanol (CH_3OH). Complete the table below, explaining how you would use Le Châtelier's principle to predict the effects of the changes listed on the equilibrium position.
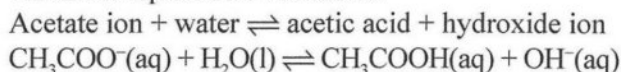Methanol + oxygen $\rightleftharpoons$ methanal + water
$2CH_3OH(l) + O_2(g) \rightleftharpoons 2HCHO(g) + 2H_2O(g)$
$\Delta H = +314$ kJ

Change to system	Predicted effect on equilibrium position
Temperature increase	
Pressure increase	
Volume increase	
Increase concentration of methanol	

6. Some salts such as sodium acetate (CH_3COONa) react with water when they are dissolved forming a weak acid and hydroxide ions according to this equation:

| Sodium acetate | + | water | $\rightleftharpoons$ | acetic acid | + | sodium hydroxide |

$CH_3COONa(s) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NaOH(aq)$
The ionic equation is written as:
Acetate ion + water $\rightleftharpoons$ acetic acid + hydroxide ion
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
Copy and complete the table to show the effects of adding chemicals to this equilibrium system.

Factor	Effect	Equilibrium moves
Adding hydrochloric acid	Hydrogen ions from the acid react with the .... and remove them as water.	
Adding sodium acetate	Ionises, forming more .... ions.	

7. (a) For the following reaction, list ways in which you could increase the yield of D.
$A(aq) + B(aq) \rightleftharpoons C(aq) + D(aq) + heat$
   (b) Consider the following equilibrium reaction which is exothermic in the forward direction.
$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$
Identify four changes that would increase the yield of chlorine gas.

8. Solid carbon reacts with water vapour when heated to form water gas which is a flammable mixture of carbon monoxide gas and hydrogen gas. The reaction is reversible and the forward reaction is endothermic.
   (a) Write the equation for this reaction at equilibrium.
   (b) Use Le Châtelier's principle to predict any effects on the equilibrium of the following changes.
      (i) Removing carbon monoxide.
      (ii) Increasing the temperature of the system.
      (iii) Adding more of the carbon.

9. Decide whether each of the following statements is true or false and justify each decision.
   (a) All chemical reactions can reach equilibrium.
   (b) Le Châtelier's principle explains the effects of changes in equilibrium systems.
   (c) Adding more of a chemical to a closed system always increases the pressure.

10. A can of soft drink contains dissolved carbon dioxide in an equilibrium situation.
$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ ΔH is negative.
Predict the effect on the equilibrium if the conditions change as follows:
   (a) The can is cooled. (b) The can is opened.

11. Check your knowledge with this quick quiz.
   (a) Heating an exothermic equilibrium reaction favours the (products/reactants).
   (b) Removing a product as it is formed pushes the equilibrium to the (left/right).
   (c) If a system is in equilibrium, and it is disturbed or changed in any way, the system will adjust itself to minimise the amount of change. This statement is referred to as ....
   (d) An exothermic reaction (absorbs/releases) heat and has a (positive/negative) heat of reaction.
   (e) Could Le Châtelier's principle be applied to the reaction that occurs when hydrogen burns?
   (f) Increasing the number of reacting gas particles in a sealed container will (increase/decrease) the pressure.

13 Equilibrium Graphs

The effects of changes in equilibrium conditions are often illustrated graphically using concentration/time graphs. The following graphs show reactions at equilibrium and the effects on the concentration of reactants and products when there are changes in temperature, concentration and pressure. In each case the graph shows the system initially at equilibrium and a change occurs at the time indicated by the dotted line.

Changes in temperature

In Figure 13.1 the temperature of the equilibrium system is increased. In this example, **the forward reaction is exothermic**: reactants $\rightleftharpoons$ products + heat

So an increase in the temperature pushes the reaction left, favouring the reactants.
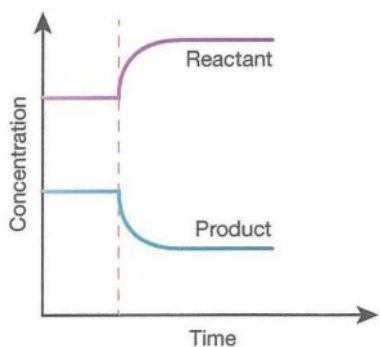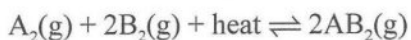

Figure 13.1 Increased temperature with exothermic forward reaction.

In Figure 13.2 the temperature of the equilibrium system is increased again, but in this case the **forward reaction is endothermic**. The reaction can be written as:

$$A_2(g) + 2B_2(g) + heat \rightleftharpoons 2AB_2(g)$$

Increasing the temperature pushes the equilibrium position to the right, to use up some of the added heat, favouring the product.
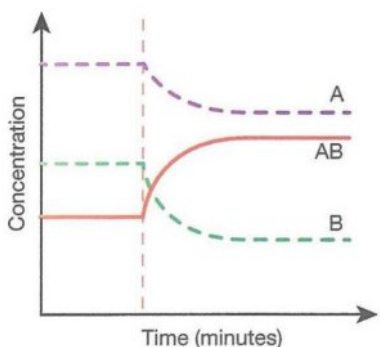

Figure 13.2 Increased temperature with endothermic forward reaction.

Changes in concentration

Figure 13.3 illustrates the effect on a system at equilibrium when the **concentration of a reactant is increased**. The added reactant is gradually used up to minimise the change, producing more product. The equilibrium position moves towards the right (the change favours the product).
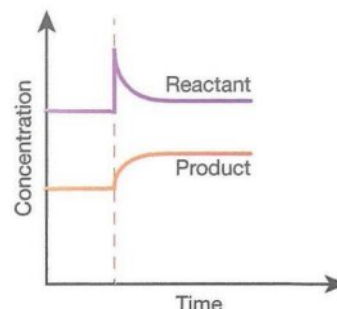
Figure 13.3 Concentration of the reactant is increased.

In Figure 13.4, the reaction is $2C \rightleftharpoons 2A + B$. When the **concentration of A is decreased**, the equilibrium moves to the right, to make more of A and minimise the change.
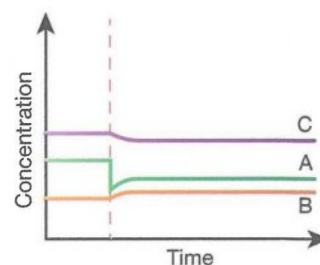
Figure 13.4 Concentration of a product is decreased.

Notice that when you add or remove a substance, this causes a peak in the graph and then it gradually returns towards its original position.

Change in pressure

In this example $A(g) \rightleftharpoons 2B(g)$, the **pressure is increased**. The concentrations of reactant and product both increase, but the reactant increases more than the product – the equilibrium moves left, favouring the reactant.
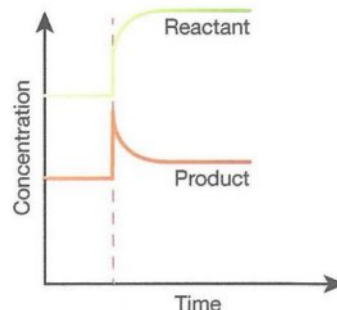
Figure 13.5 Effect of an increase in pressure on a system at equilibrium.

1. The graph shows concentrations of reactants and products for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The system is initially at equilibrium, but is then disturbed so that all the concentrations change.

    (a) Suggest a change that could have disrupted the equilibrium as shown. Justify your answer.
    (b) In which direction has the equilibrium moved?

2. The equilibrium system,
    $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \quad \Delta H$ is positive
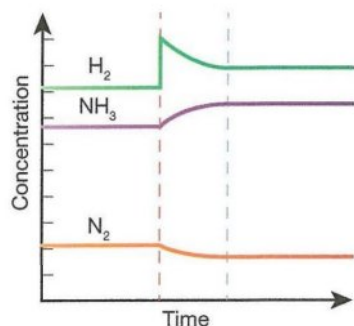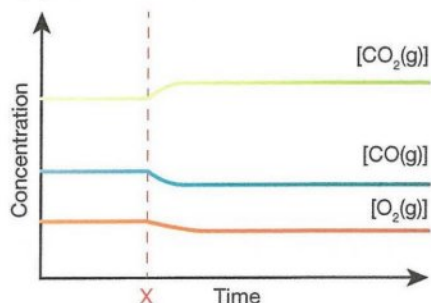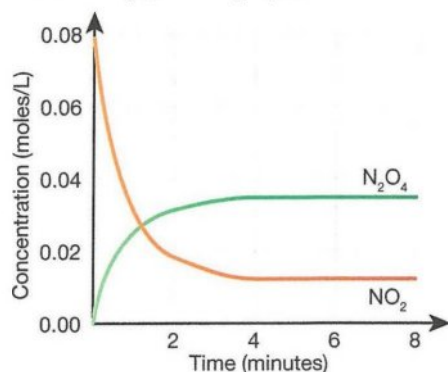   is disturbed at time X by a change in temperature. Deduce whether the temperature of the system has been increased or decreased to cause this disturbance and justify your answer.

3. The graph shows changes in concentrations of nitrogen dioxide and dinitrogen tetroxide in a closed system over time. The forward reaction is exothermic: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

    (a) Which gas(es) was/were present initially?
    (b) At what time did the reaction reach equilibrium?
    (c) Sketch changes that would occur if the temperature were increased at time 5 minutes.

4. The equilibrium system, $2NO_2(g) \rightleftharpoons N_2O_4(g)$ is disturbed and changes as shown in the graph.
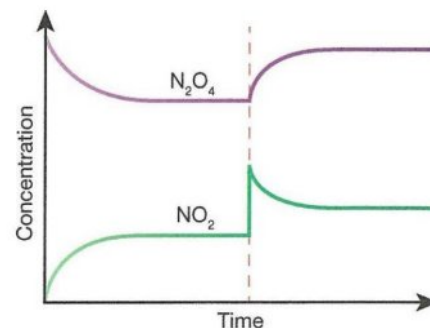
    (a) Explain what could have caused this change.
    (b) Compare the concentrations of reactant and product at the equilibrium positions before and after the change.

5. The following graph shows a system at equilibrium, a change occurring that disrupts the initial equilibrium, and a new equilibrium position eventually being reached. The reaction involved is the production of ammonia, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$.
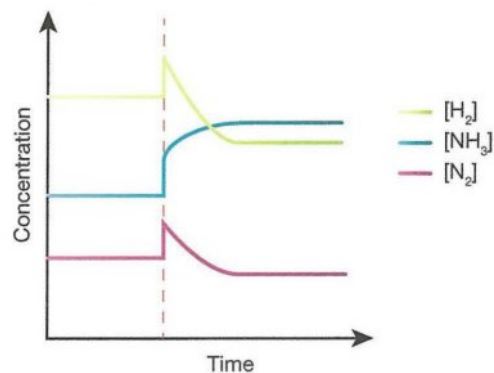
    (a) Identify the change which disrupted the equilibrium position.
    (b) In which direction has the equilibrium moved? Justify your answer.

6. The graph below shows a change in an equilibrium system for the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
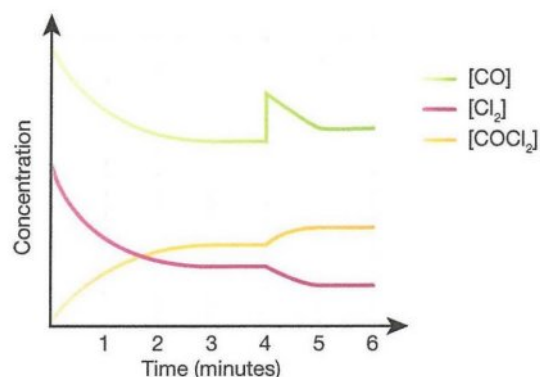
    (a) What could have caused the changes in the equilibrium system at time 4 minutes?
    (b) Explain the changes observed for each species.

14 Modelling Equilibrium Changes

There are many ways to model an equilibrium reaction.

Here are two examples – one using beads, and one comparing the reaction to the movement of people between cities.

Bead model

Collect some objects, e.g. balls, beads or buttons with four different colours, patterns or shapes.

Let's say that we have black and white beads. We will call these the reactants in a reaction. We also have spotted and striped beads; these will be our products.

If this were a **reaction that went to completion**, we would start with black and white beads and every time a black reacted with a white we would take out a black bead and a white bead and replace them with a spotted bead and a striped bead. Eventually we would end up with only spotted and striped beads.

Black bead + white bead → spotted bead + striped bead

If this were a **reversible reaction**, then the reaction would be going in both directions and we would write the equation as:

Black bead + white bead ⇌ spotted bead + striped bead

To model this reversible reaction we have to show two different reactions taking place at the same time.

Forward reaction

Black bead + white bead → spotted bead + striped bead

Reverse reaction

Spotted bead + striped bead → black bead + white bead
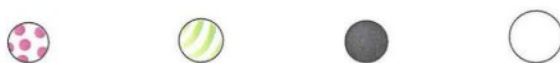
Work in pairs.

- In a container, place a few of each colour bead. Let's say we put into the container:
  8 black beads   10 white beads
  7 spotted beads   9 striped beads

- One person models the forward reaction – takes out 1 black bead and 1 white bead and replaces them with 1 spotted bead and 1 striped bead.

- The other person in your group models the reverse reaction – takes out 1 spotted bead and 1 striped bead and replaces them with 1 black bead and 1 white bead.

- Both keep removing and replacing beads at any speed you like – you are modelling a reversible reaction.

- Then try to both remove and replace the beads at the same rate. Now you are modelling a reaction at equilibrium. The rate of the forward reaction equals the rate of the reverse reaction. You will then notice the number of each colour of bead (the concentration) staying the same. The concentration will be constant.

Of course, you do not have to use black, white, spotted and striped beads for this model – any other objects, in colours or patterns will do.

Figure 14.1 Bead model of equilibrium.

Cities model

Imagine two cities, let's call them Emerald and Rubiad. Emerald has 120 000 people and Rubiad has 86 000 people. The only method of entering or leaving the cities is by train.
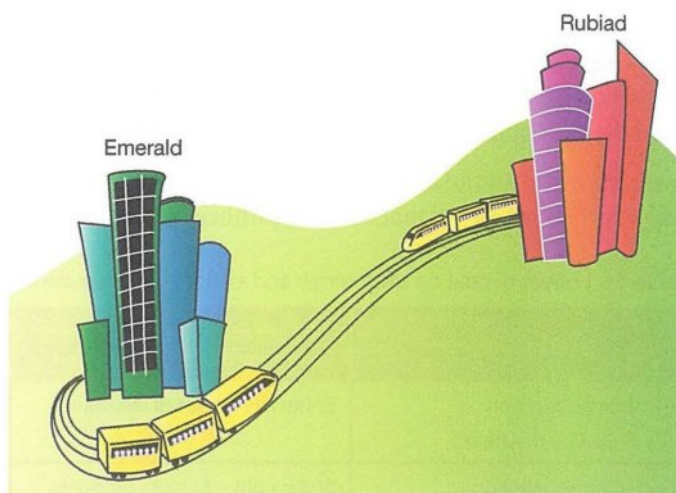
Figure 14.2 Cities and train model.

One day, 30 people in Emerald decide they would rather live in Rubiad so they get on the train and move to Rubiad. At the same time, 20 people in Rubiad decide they would like to move to Emerald. The next day 10 people move from Emerald to Rubiad and 35 people move from Rubiad to Emerald. You are modelling a reversible reaction.

If the same number of people leaves Rubiad and Emerald each day (reaction rate is the same) then this becomes a model of equilibrium. The two cities will stay in equilibrium as long as conditions stay the same so that the rate of change in each direction stays the same.

Modelling Le Châtelier's principle

To revise what has been covered so far on equilibrium reactions, it is a good idea to look at changes in temperature, concentration and pressure in the same equilibrium system and use Le Châtelier's principle to predict what will happen to the system if it is at equilibrium and the conditions are changed. You can model these effects by drawing diagrams, using people to represent chemicals, or by making physical models.

When carbon dioxide dissolves in water to form carbonic acid, in a closed system, the following equilibrium can form.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ ΔH is negative.
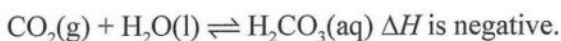
We can alter the equilibrium position of this system by changing temperature, concentration or pressure.

Changing temperature

The forward reaction is exothermic, so we can rewrite the equation as:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + heat$
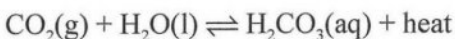
If this equilibrium system is heated, the equilibrium position will change so as to use up the added heat and thus minimise the change (as predicted by Le Châtelier's principle). The equilibrium will move to the left, more carbonic acid will decompose, using up the added heat, and less carbon dioxide will dissolve, producing less heat.

Table 14.1 shows the effect of heat on exothermic and endothermic reactions that are in equilibrium.

Table 14.1 Effect of heat on exothermic and endothermic reactions.

Reaction	Effect on equilibrium when temperature is increased
Exothermic reaction $A + B \rightleftharpoons C + D + heat$	Shifts left – favours reactants.
Endothermic reaction $P + Q + heat \rightleftharpoons X + Y$	Shifts right – favours products.

The opposite effect happens when these reactions in equilibrium are cooled.

Changing concentration

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
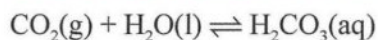
We can change the concentration of species in this equilibrium system in a number of ways. Here are some examples.

If **more carbon dioxide is added** to this equilibrium system, then the concentration of carbon dioxide will increase. As predicted by Le Châtelier's principle, the system will move to use up this added carbon dioxide. To do this it shifts to the right – more carbon dioxide dissolves in water – we say that the forward reaction is favoured.

Adding more carbonic acid to the equilibrium system has the opposite effect. The equilibrium shifts left to use it up.

Removing a reaction chemical has the opposite effect to adding more of it. For example, if carbon dioxide is removed (perhaps by absorbing it in sodium hydroxide), the equilibrium moves left to make more carbon dioxide and replace some of the gas removed.

Changing pressure

We will look at the effect of changing pressure on the same equilibrium system. There is a gas involved in this reaction (CO_2), so any changes in pressure will have an effect on this equilibrium system.

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$
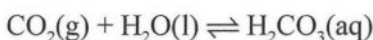
As predicted by Le Châtelier's principle, if we **increase the pressure** on the system (e.g. by compressing it), it will respond by moving the equilibrium in whichever direction will reduce the pressure again – minimising the change. Reducing the number of gas particles present in the system will reduce the pressure. It can only do this by getting rid of some carbon dioxide gas, as that is the only gas present.

To reduce carbon dioxide concentration, the equilibrium must move to the right – the forward reaction is favoured. More carbon dioxide will dissolve, forming carbonic acid. This reduces the number of gas particles present, which reduces the pressure.

Decreasing the pressure will have the opposite effect, the equilibrium moves to the left to increase the concentration of carbon dioxide gas again.

As predicted by Le Châtelier, when there is a change to a system at equilibrium, the system moves to minimise the change and a new equilibrium position is established. It will not move the equilibrium back to exactly where it was before the change, but it will move in that direction.

Adding a catalyst

Another change we could make is to add a catalyst. However, adding a catalyst to a system at equilibrium will have no effect on the system.

If a catalyst is added to chemicals which form a reversible reaction *before* they reach a state of equilibrium, then it will have an effect – the system will **reach equilibrium faster** than without the catalyst. This is because the catalyst provides alternative pathways, reducing activation energy, so that both the forward and reverse reactions will occur at a faster rate.
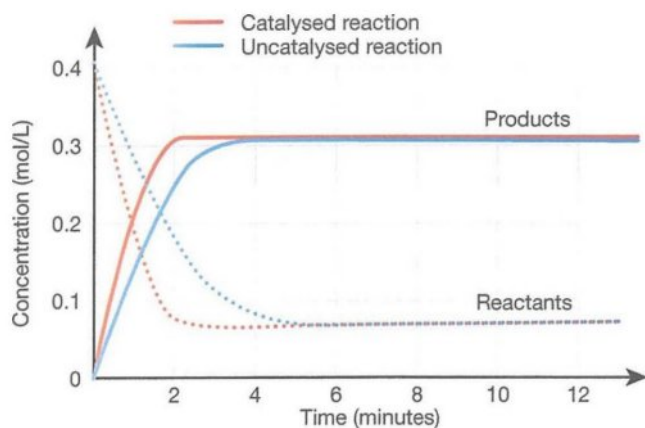

Figure 14.3 Adding a catalyst at the start of reaction. Reaction rate increases, the slope is steeper for both reactants and products so equilibrium is reached sooner.

But notice that, even if a catalyst is added before equilibrium is reached, it will not affect the position of the equilibrium because it will speed up or slow down both the forward and reverse reactions equally.

Le Châtelier's principle does not apply to adding a catalyst.
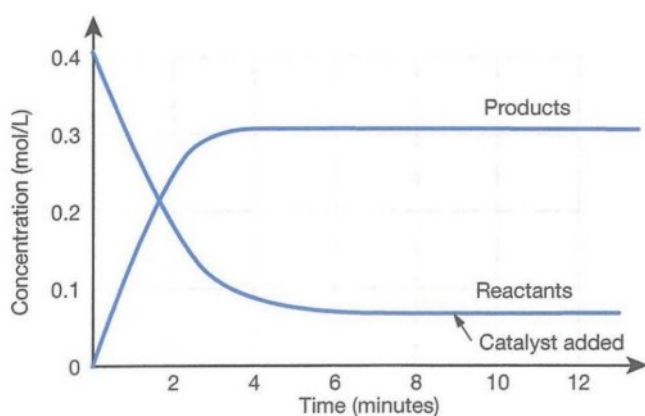
Figure 14.4 Adding a catalyst after equilibrium is reached has no effect.

In Chapter 61 we will look at how reaction conditions are changed to increase yields for an industrial production process that uses an equilibrium reaction.

QUESTIONS

1. During your chemistry studies, you have studied a number of concepts by means of models.
   (a) What is a model?
   (b) Outline some advantages and limitations of using models in chemistry.
2. (a) State Le Châtelier's principle.
   (b) Choose a model – you could use the bead or cities models described above, or make up your own. Use your chosen model to demonstrate Le Châtelier's principle.
3. Carbon dioxide dissolving in water in a closed system can form an equilibrium mixture. The forward reaction is exothermic.
   (a) Write an equation to show this.
   (b) Copy and complete the table to show the effects on this equilibrium, of changing the conditions as listed.

Change	Effect on equilibrium	Effect on concentration of product
Increasing concentration of $CO_2(g)$		
Cooling the container		
Decreasing the size of the container		

4. You have already seen that methane reacts with water to form carbon monoxide and hydrogen gas. This reaction reaches equilibrium in a closed system.
   (a) Write an equation for this reaction.
   (b) Use Le Châtelier's principle to predict the effects on the equilibrium position of the following changes. Justify your predictions.
      (i) Hydrogen concentration is increased.
      (ii) Carbon monoxide is removed.
      (iii) The pressure is increased.
5. Identify whether each of the following statements is true or false.
   (a) A representation of reality is called a model.
   (b) A model provides us with true facts.
   (c) A model can help us visualise or understand an idea.
   (d) Increasing the temperature of a system at equilibrium always shifts the equilibrium to the left.
   (e) $[CO_2(g)]\uparrow$ means the concentration of carbon dioxide gas increased.
   (f) In the equilibrium reaction:
      $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$,
      Le Châtelier's principle would predict that decreasing pressure would push the equilibrium to the right.

15 Modelling Equilibrium using Measuring Cylinders

A group of students set out to model equilibrium using two identical 100 mL measuring cylinders, which they labelled A and B, a 10 mL graduated pipette and a 2 mL graduated pipette.

This is the method they followed.

Method

- Pour 100 mL of water into measuring cylinder A.
- Place the 10 mL pipette upside down into measuring cylinder A so it rests on the bottom of the cylinder and fills with water.
- Put a finger over the end of the pipette. Lift the pipette with water to transfer the water to measuring cylinder B.
- This is the forward process: Water A → Water B
- Put the 2 mL pipette upside down into measuring cylinder B.
- Put your finger over the top and transfer water back to measuring cylinder A.
- This is the reverse process: Water B → Water A
- This completes one transfer cycle:
- Water A ⇌ Water B
- Measure and record the volume of water in each measuring cylinder at the end of the cycle.
- Carry out more transfer cycles, measuring and recording the volumes after each cycle.
- Here are some of the students' results.

Transfer cycle	Volume in A (mL)	Volume in B (mL)
0	100	0
1	90	10
2	81	20
3	73	27
4	66	34
5	61	39
6	56	45

- The students carried out 30 cycles in this manner and then plotted their results in a graph.

Results

The students' results are illustrated in the following line of best fit graph.
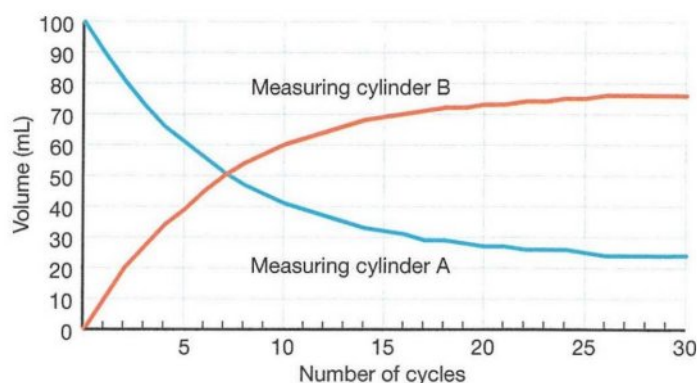
QUESTIONS

1. Describe the trend in the change in volume in:
   (a) Measuring cylinder A.
   (b) Measuring cylinder B.
2. Why did the volume of water in each measuring cylinder stay constant after cycle 26?
3. Considering this as a model of dynamic equilibrium, at what stage did equilibrium occur? Mark this on the graph.
4. Compare this process using measuring cylinders to a reversible reaction coming to equilibrium.
5. If possible, carry out the experiment yourself. Then try to take the analogy further to see if you can cause a 'disturbance in the equilibrium' (e.g. by adding extra water to measuring cylinder A) and then determine if the system reaches a new equilibrium position. Complete 20 transfer cycles to see how the system responds to the 'disturbance'. Did it respond in a way that reverses the change you made as you would expect of a chemical equilibrium reaction, eventually arriving at a new equilibrium position?
6. For each of your two equilibrium positions, calculate the ratio of the volume of water in measuring cylinders A and B at equilibrium, Water B : Water A. Did this ratio stay constant while the system was at equilibrium?
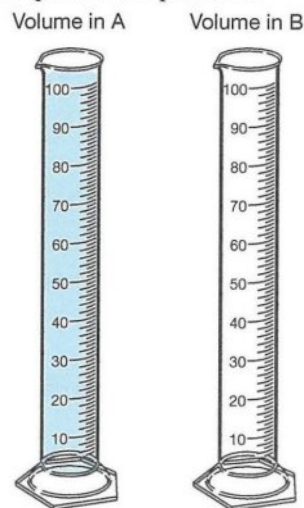
However, there are also many chemical reactions that are **reversible in a closed system**; both the forward and the reverse reactions can occur at the same time.

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 learned about in year 11 when you studied acids, is the **ionisation of water** to form hydrogen ions and hydroxide ions.

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

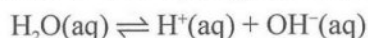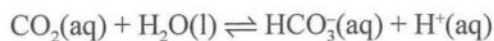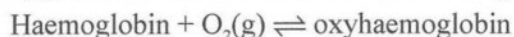- Many reversible reactions occur in **living organisms**, for example, reactions involved in the transport of oxygen and carbon dioxide around the body in blood.

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

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

- We also make use of some reversible reactions. For example, some eyeglasses have **photochromatic (transition) 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.

Calcium carbonate

Test tube

Lime water
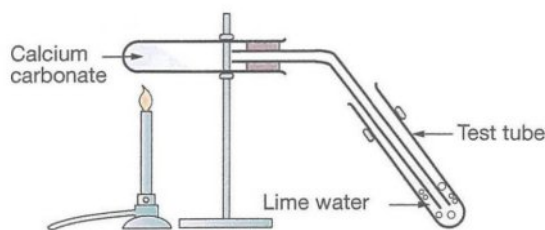
Figure 2.3 Decomposing calcium carbonate.

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.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$
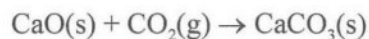
Both forward and reverse reactions would be taking place at the same time, and we would have a reversible reaction in a closed system.

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

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

3   Static Versus Dynamic Equilibrium

Equilibrium in chemistry refers to a situation where no changes can be seen happening in a chemical system. Usually a mention of equilibrium in chemistry refers to dynamic equilibrium, but you need to make sure that you can distinguish dynamic from static equilibrium.

Static equilibrium

Static equilibrium occurs when nothing is happening in a reaction. The forward and reverse reaction rates are both zero. This is the equilibrium of a system at rest.

An example is the conversion between the two allotropes of carbon – diamond and graphite. Theoretically the reaction is: $C(diamond) \rightleftharpoons C(graphite)$

But at room temperature, you are not going to see either reaction taking place, so this could be considered a static equilibrium situation.

Another example is a reaction in which there is a limiting reagent. Once the limiting reagent has been used up, neither forward nor reverse reaction will occur, so a static equilibrium exists.
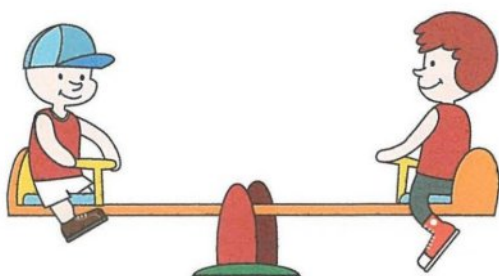
Figure 3.1 Static equilibrium. The seesaw is balanced and not moving.

Dynamic equilibrium

Dynamic equilibrium refers to a system in which the forward and reverse reactions are occurring at the same time and at the same rate, so that there is no *net* change.

You might like to try **modelling a reversible reaction coming to a state of dynamic equilibrium** with your friends by dancing.

In reversible reactions the forward and reverse reactions both occur at the same time and we can model this using a dance.

People getting up to dance, represent the reactants coming together. Couples breaking up and sitting down, represent the product breaking up and reactants re-forming again. There are always some couples forming and others breaking up, just as in a reversible reaction there are always particles combining and others breaking up.

If the dance goes on for a long time, you could eventually reach a state of dynamic equilibrium – the number of couples getting up at any instant could be the same as the number of couples sitting down.

If you just glanced at the dancing couples, you might think there was no change happening – there might always seem to be the same number of couples on the floor dancing. But looking more closely, you would see that although the number of people dancing stays the same, it is not always the same people dancing.

The dance is then in dynamic equilibrium. It is in equilibrium because it seems to be staying the same. It is dynamic because there is constant change happening.

The same thing happens when a chemical reaction is at dynamic equilibrium. There may seem to be no observable change taking place, but the forward and reverse reactions are occurring at the same rate and there is constant change at an atomic level.

Figure 3.2 Modelling a reversible reaction and dynamic equilibrium.

16 Revision Of Equilibrium and Factors That Affect Equilibrium

Use the following questions to help you revise equilibrium. Multiple choice questions can be very helpful in finding out whether or not the concept you have developed about a topic is the same as the scientific concept. Answer the questions like a test. If you make any errors, and you do not understand why your answers are not correct, you should discuss the questions with your teacher.

1. Of the following reactions, which one is not a reversible reaction?
   (A) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   (B) $CuSO_4(s) + 5H_2O(l) \rightleftharpoons CuSO_4.5H_2O(s)$
   (C) $SO_2(g) + O_2(g) \rightleftharpoons SO_2(g)$
   (D) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

2. For which of the following reactions would decreasing the pressure cause an increase in the yield of product?
   (A) $A(g) + B(g) \rightleftharpoons C(g) + D(g)$
   (B) $A(aq) + B(aq) \rightleftharpoons C(aq) + D(aq)$
   (C) $A(aq) + B(g) \rightleftharpoons C(g) + D(g)$
   (D) $A(g) + B(g) \rightleftharpoons C(g) + D(aq)$

3. In a system at equilibrium:
   (A) The rate of the forward reaction equals the rate of the reverse reaction.
   (B) The concentration of reactants equals the concentration of products.
   (C) All concentrations are equal.
   (D) The addition of a catalyst increases the yield of a product.

4. Consider the four energy profiles shown below. Identify the one that is exothermic and most likely to go to completion.

   (A)

   (B)

   (C)

   (D)
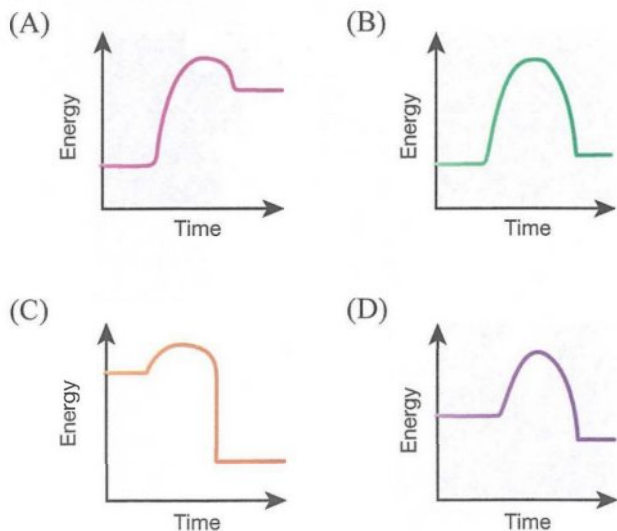
5. The rates of many chemical reactions are initially fast and then slow down as reactants are used up. Which graph best illustrates this?

   (A)

   (B)

   (C)

   (D)
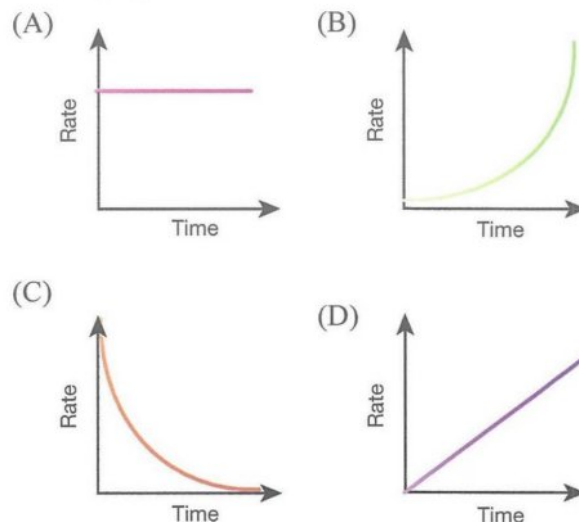
6. Which of the following represents a system at equilibrium?
   (A) A sealed can of soft drink.
   (B) Year 12 in the playground at lunch time.
   (C) The Earth's water cycle.
   (D) An open can of soft drink.

7. An equilibrium will not be established if:
   (A) Water forms.
   (B) A gas escapes.
   (C) A precipitate forms.
   (D) Temperature is kept constant.

8. When catalysts are used in a reversible reaction:
   (A) More product is formed.
   (B) The forward reaction rate increases.
   (C) Equilibrium is reached sooner.
   (D) There is no change.

9. A reaction can be seen to be at equilibrium when:
   (A) There is no macroscopic change.
   (B) No gas is produced.
   (C) No precipitate forms.
   (D) The catalyst has been used up.

10. Consider the reaction:
    $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
    Which one of the following statements is correct about this system when it has reached equilibrium?
    (A) The concentration of reactants equals the concentration of products.
    (B) The concentrations of all reactants and products remain constant.
    (C) The concentrations of all reactants and products are equal.
    (D) The concentrations of carbon monoxide and water are equal but different from the concentrations of carbon dioxide and hydrogen.

11. The concentrations of reactants and products in a system at equilibrium depend on:
    (A) The initial concentrations.
    (B) The equilibrium position.
    (C) The relative chemical energies of the reactants and products.
    (D) All of the above.

12. The following reaction is at equilibrium at 1000°C.
    $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\Delta H = -566$ kJ
    Of the following changes, which one will not produce a larger yield of carbon dioxide?
    (A) Reducing the volume of the reaction vessel.
    (B) Adding a catalyst.
    (C) Adding more CO(g).
    (D) Decreasing the temperature.

13. For the equilibrium reaction:
    $A(g) + B(g) \rightleftharpoons C(aq) + D(g)$
    the reaction in the forward direction (as written) is exothermic. Which of the following changes would cause the equilibrium position to move to the left?
    (A) Increase the concentration of A.
    (B) Increase the concentration of D.
    (C) Remove D as it forms.
    (D) Increase the pressure.

14. Which of the following does not alter the equilibrium position of a system at equilibrium?
    (A) Changing the temperature of the system.
    (B) Adding more of one reaction species.
    (C) Adding a catalyst to the system.
    (D) Increasing pressure by decreasing volume.

15. Cobalt chloride exists as two different complex ions, $[Co(H_2O)_6]^{2+}$ which is pink and $[CoCl_4]^{2-}$ which is blue.
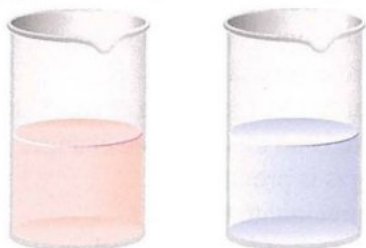
    In solution, both cobalt chloride complexes exist together in equilibrium. The forward reaction is endothermic.
    $[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$
          Pink   blue
    This equilibrium can be disturbed by changing the temperature or the chloride ion concentration.
    To turn the colour blue you would:
    (A) Add dilute hydrochloric acid or place the container in a hot water bath.
    (B) Dilute the solution by adding water and place the container in an ice water bath.
    (C) Place the container in the refrigerator.
    (D) Add a chemical which will react with cobalt chloride to form a blue salt.
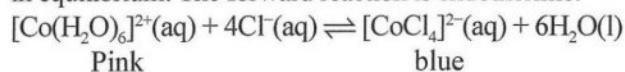
16. Phosgene gas, carbon monoxide and chlorine form an equilibrium mixture in a sealed container. The reversible reaction taking place is:
    $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ $\Delta H = -108$ kJ mol L^{-1}
    The graph shows equilibrium being reached, then disturbed and finally a new equilibrium position being reached.
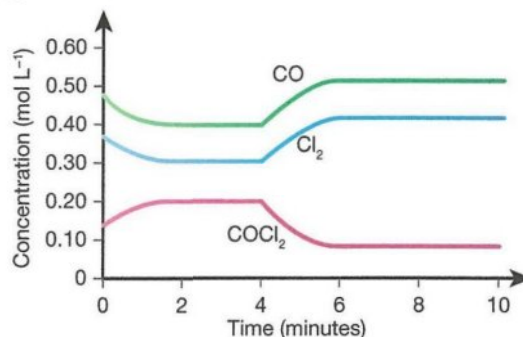
    At time 4 minutes, the equilibrium system was disturbed by:
    (A) Extracting some $COCl_2$.
    (B) Adding more CO and Cl_2.
    (C) Adding a catalyst.
    (D) Heating the system.

    INQUIRY QUESTION
    1. What happens when chemical reactions do not go to completion?
    2. What are the characteristics of a system at equilibrium?
    3. Summarise which factors affect equilibrium and how.
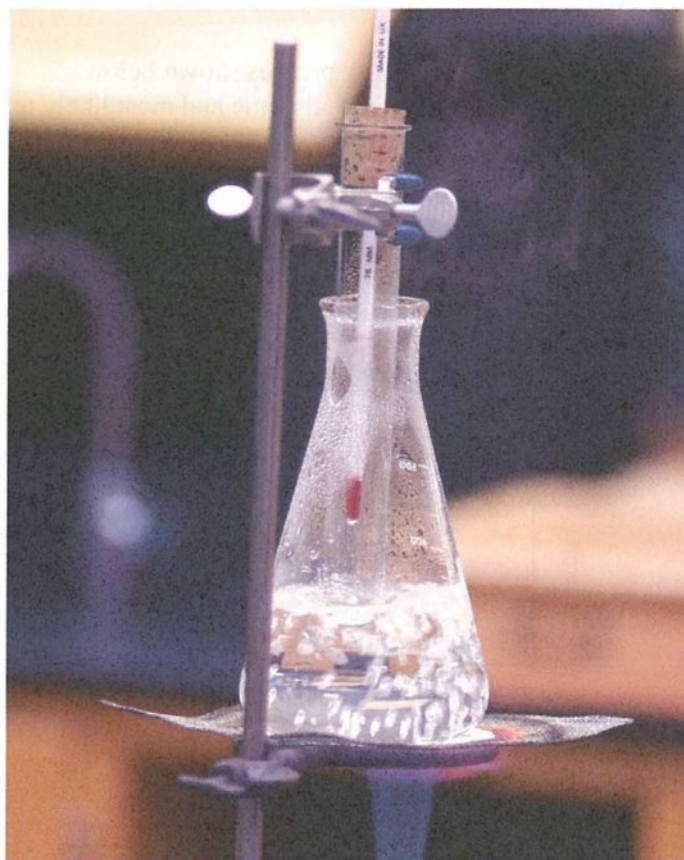
17 The Equilibrium Expression and Constant

We can write a general equilibrium equation as:

$$aA + bB \rightleftharpoons cC + dD$$

Where a, b, c, d are the number of moles of substances A, B, C and D that are present at equilibrium.

Using the concentrations of each substance, in a system at equilibrium, it is possible to calculate a value called the **equilibrium constant** (K_{eq}). The equilibrium constant is defined as the product of the concentrations of products, present at equilibrium, each raised to the power of their coefficients, to the product of the concentrations of reactants, present at equilibrium, each raised to the power of their coefficients.

K_{eq} values can be calculated.

The equilibrium constant $K_{eq} = \dfrac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$

Where [ ] means the concentration (in moles L^{-1}) of each substance that is present **at equilibrium**.

This is called the **equilibrium constant expression**. Here are two examples.

For the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
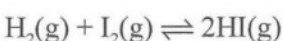
The equilibrium constant expression would be:

$$K_{eq} = \frac{[HI(g)]^2}{[H_2(g)] \times [I_2(g)]}$$

For the reaction:

$$CH_4(g) + 2H_2O(g) \rightleftharpoons 4H_2(g) + CO_2(g)$$

The equilibrium constant expression would be:

$$K_{eq} = \frac{[H_2(g)]^4 \times [CO_2(g)]}{[CH_4(g)] \times [H_2O(g)]^2}$$

Here are some things that you need to understand about equilibrium constants (K_{eq} values).

1. The **concentration** values used to calculate K_{eq} are not the concentrations you started with. They are the concentrations of the chemicals that are present **when equilibrium is reached**.

2. The concentrations of **solids and pure liquids** are not changed by adding them to or removing them from an equilibrium system, so they are consi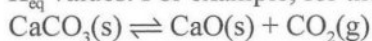dered to have a concentration of 1. Thus they do not affect the value of K_{eq} and can be ignored when looking at K_{eq} values. For example, for the reaction:

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

   $$K_{eq} = \frac{[CaO(s)] \times [CO_2(g)]}{[CaCO_3(s)]}$$

The value for each of the solids CaO and $CaCO_3$ is 1, so the value of K_{eq} becomes: $K_{eq} = [CO_2(g)]$.

3. The equilibrium constant (K_{eq} value) **stays the same for a particular equilibrium regardless of the concentrations you start with**. You can start the reaction with chemicals A and B or with C and D, and you can start with any concentration you like of A, B, C and D, and the equilibrium constant will still be the same – The *ratio* of the concentrations of products to reactants will stay the same, despite the fact that individual concentrations vary.

For example, look at the following figures for two experiments involving the production of ammonia, where the concentrations of reactants were different in each case.

Table 17.1 K_{eq} values are constant despite starting concentrations being different.

Initial concentrations (mol L^{-1})	Concentrations at equilibrium (mol L^{-1})	Calculated value of K_{eq}
Nitrogen = 1.0 Hydrogen = 1.0 Ammonia = 0	Nitrogen = 0.92 Hydrogen = 0.76 Ammonia = 0.16	6.0×10^{-2}
Nitrogen = 0 Hydrogen = 0 Ammonia = 1.0	Nitrogen = 0.40 Hydrogen = 1.20 Ammonia = 0.20	6.0×10^{-2}

4. The value of K_{eq} is *not* affected by:
   - **Changes in concentration or pressure** – these only change the position of the equilibrium.
   - **The addition of a catalyst**. Adding a catalyst only speeds up the forward and the reverse reaction and therefore reduces the time needed to reach equilibrium. It does not change the equilibrium position and has no effect once equilibrium is reached.

5. The **effect of temperature on K_{eq}**.
   The K_{eq} value (equilibrium constant) of an equilibrium system is **affected by changes in temperature**. In fact, temperature change is the only change which can affect K_{eq} values. When temperature changes, the effect on K_{eq} **depends on whether the reaction is endothermic or exothermic**.
   If the **reaction is exothermic** in the forward direction, an increase in temperature pushes the reaction to the left, as we have already seen. This favours the formation of reactants, so [A] and [B] increase while [C] and [D] decrease causing K_{eq} to decrease.
   For an **endothermic reaction**, an increase in temperature favours the formation of products so [C] and [D] increase, while [A] and [B] decrease and K_{eq} increases.

In summary, when temperature increases, the K_{eq} value:

- **decreases for exothermic reactions**
- **increases for endothermic reactions.**

Relevance and uses of K_{eq} values

If K_{eq} is large (e.g. $> 10^3$), there is more of the products present in the equilibrium mixture than reactants. In other words, the equilibrium lies to the right. This means the reaction has gone almost to completion.

If K_{eq} is small ($< 10^{-3}$), there is more of the reactants present in the equilibrium mixture than products. The equilibrium lies to the left. This means that the reverse reaction is favoured.

If K_{eq} is between 1000 (10^3) and 0.001 (10^{-3}) there will be significant amounts of both reactants and products present in the equilibrium mixture.

For example, under different conditions of temperature and pressure, we could represent the reaction, $A + B \rightleftharpoons C$ as follows. The size of the print represents the relative concentrations of each species.

Large K_{eq}	$A + B \rightleftharpoons C$ (When conditions cause a high yield of product, K is large.)
Medium K_{eq}	$A + B \rightleftharpoons C$
Small K_{eq}	$A + B \rightleftharpoons C$ (When conditions produce a small yield of product, K values are small.)

Uses of equilibrium constant values include comparing the relative strengths of acids and bases and comparing the solubility of ionic compounds.

QUESTIONS

1. (a) Define equilibrium constant and write the equilibrium constant expression.
    (b) Use the equilibrium expression to describe the relative proportions of products to reactants.
2. Write equilibrium constant expressions for each of the following chemical systems in dynamic equilibrium.
    (a) $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
    (b) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(l)$
    (c) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$
    (d) $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$

3. Describe the effects of an increase in temperature on the equilibrium constant when reactions are:
    (a) Exothermic. (b) Endothermic.
4. In the Haber process for the production of ammonia, the reaction of nitrogen with hydrogen is exothermic. The equilibrium constant for this reaction varies with temperature as follows.

Temperature (°C)	Equilibrium constant (K_{eq})
327	4.3×10^{-3}
427	4.5×10^{-5}
527	5.4×10^{-6}

    (a) Write an equation for this reaction.
    (b) Write the equilibrium constant expression for this reaction.
    (c) Describe the trend in K_{eq} value with temperature change. Explain this trend.
5. From the following list, circle the factor(s) that has/have the potential to change the K_{eq} value of an equilibrium system.
    (i) Increase pressure.
    (ii) Decrease pressure.
    (iii) Increase temperature.
    (iv) Decrease temperature.
    (v) Increase volume.
    (vi) Decrease volume.
    (vii) Increase concentration of reactants.
    (viii) Increase concentration of products.
    (ix) Decrease concentration of reactants.
    (x) Decrease concentration of products.
    (xi) Add a catalyst.
6. Check your knowledge with this quick quiz.
    (a) For an exothermic reaction, if the temperature increases, the value of K_{eq} ....
    (b) The only factor that can change the K_{eq} value of an equilibrium reaction is ....
    (c) State the general equation used to calculate the equilibrium constant for a reaction at a particular temperature.
    (d) When the K_{eq} value for a reaction is small, the equilibrium lies to the (left/right) because it favours the (reactants/products).
    (e) The value of the equilibrium constant will (increase/decrease/stay the same) when the concentration of reactants is increased.
    (f) When a catalyst is added to an equilibrium system the position of equilibrium will (move left/move right/stay the same).

18 Calculating Equilibrium Constants

Some tips to remember when calculating equilibrium constant values are as follows.

- Concentration must be in moles per litre.
- In all other mole calculations you use the number of moles actually involved in the reaction for your calculations. However, when you calculate K_{eq} values, you must use the concentration (moles/L) present at equilibrium.
- You are not required to give units for K_{eq} values.
- Size of the container is important. If you are told there are 10 moles of a gas in a 5 litre container, then the concentration of that gas is 2 moles per litre.
- If temperature changes, the equilibrium will be disturbed and the value of K_{eq} will change. The effect on K_{eq} of changing temperature will depend on whether the reaction is endothermic or exothermic.

	Temperature increases	Effect on a system at equilibrium
Exothermic reactions A + B ⇌ C + D + heat	K_{eq} decreases	Moves left – favours reactants
Endothermic reactions X + Y + heat ⇌ P + Q	K_{eq} increases	Moves right – favours products

Types of calculations

1. **You could be given concentrations at equilibrium and asked to calculate K_{eq}.**

   Example:
   The following equilibrium reaction occurs as follows.

   $$A + 2B \rightleftharpoons C + 3D$$
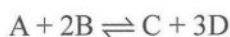
   At equilibrium, the concentrations of the reactants and products are as follows.

   $[A] = 5$ mol L^{-1} $[B] = 2$ mol L^{-1}

   $[C] = 3$ mol L^{-1} $[D] = 4$ mol L^{-1}

   Calculate the equilibrium constant K_{eq}.

   Answer:
   The equilibrium constant $K_{eq} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

   $$K_{eq} = \frac{3 \times 4^3}{5 \times 2^2} = 9.6$$

The most common error in calculating K_{eq} values is to forget that you must use the concentrations measured at equilibrium. To do this you should construct an ICE table – ICE stands for **I**nitial, **C**hange and **E**quilibrium. You can see this in Example 2.

2. **You could be asked to work out the concentrations at equilibrium so you can calculate K_{eq}.**

   Example:
   A and B react to form C and D as shown in the following equation.

   $$A + B \rightleftharpoons C + D$$

   Complete the following table to show concentrations (in mol L^{-1}) of the reactants and products and then calculate the value of K_{eq}.

	[A]	[B]	[C]	[D]
Initial concentration	0.6	0.6	0	0
Change in concentration				
Equilibrium concentration			0.5	

   Answer:
   [C] has changed from 0 to 0.5, it has increased by +0.5 mol L^{-1}.

   From the equation:
   If [C] has changed from 0 to 0.5, then [D] will have changed the same (1 : 1 ratio) and 0.5 mol L^{-1} of A and B will have been used.

	[A]	[B]	[C]	[D]
Initial concentration	0.6	0.6	0	0
Change in concentration	–0.5	–0.5	+0.5	+0.5
Equilibrium concentration	0.1	0.1	0.5	0.5

   The equilibrium constant $K_{eq} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

   $$= \frac{0.5 \times 0.5}{0.1 \times 0.1} = 25$$

3. **You could be asked to find the concentrations at equilibrium from a graph.**

   The following equilibrium reaction occurs.

   $$A + B \rightleftharpoons 3C$$

   The changes in concentration are illustrated in the following graph. Use this graph to complete the table below and calculate the value of K_{eq}.
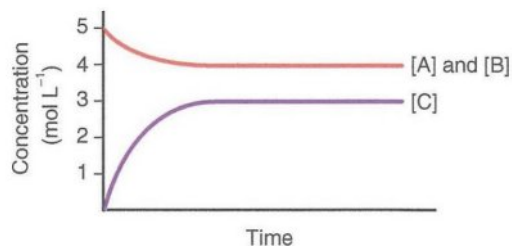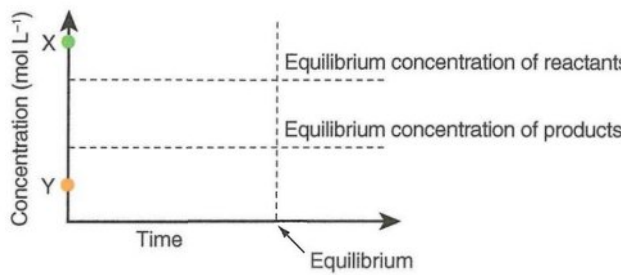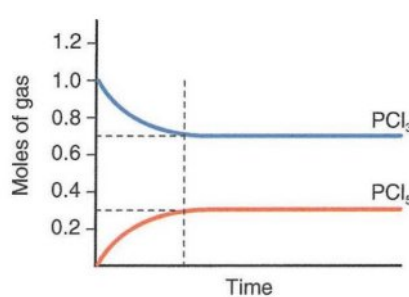

Figure 61.1 Equilibrium reaction A + B ⇌ 3C.

Using this graph you could draw up the following table.

	[A]	[B]	[C]
Initial concentration	5	5	0
Change in concentration	−1	−1	+3
Final equilibrium concentration	4	4	3

$$K_{eq} = \frac{3^3}{4 \times 4} = 0.6$$

QUESTIONS

1. In the reaction:
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
The equilibrium concentrations were found to be 1.6 mol L^{-1} H$_2$, 1.8 mol L^{-1} I$_2$ and 1.2 mol L^{-1} HI at a particular temperature.
   (a) Write the equilibrium constant expression for this reaction.
   (b) Calculate the value of K_{eq}.

2. The value of the equilibrium constant, at 25°C, is 5.5×10^{-3} for the reaction:
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
   (a) State the equilibrium constant expression for this reaction.
   (b) The two gases are at equilibrium in a 1 litre container at 25°C. The concentration of N$_2$O$_4$ is 0.10 mol L^{-1}. Calculate the concentration of NO$_2$.

3. An equilibrium system can be represented by the following equation.
$$P(g) + Q(g) \rightleftharpoons R(g) + S(g)$$
The reaction is carried out in a 2 litre container. At equilibrium the following amounts of gases are found.
P = 0.250 mol   Q = 0.500 mol
R = 0.250 mol   S = 1.000 mol
   (a) Write the equilibrium constant expression for this reaction.
   (b) Calculate the value of K_{eq}.

4. Find the equilibrium constant for the following reaction, carried out in a 2 L container at 250°C.
$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
At equilibrium there was:
0.035 moles of PCl$_5$ and
0.053 moles each of PCl$_3$ and Cl$_2$.

5. Methanol is produced synthetically as a gas by the following reaction.
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
Calculate the equilibrium concentration of methanol if the equilibrium constant for this reaction is 0.60 and the equilibrium concentrations are:
Carbon monoxide = 3.76×10^{-3} mol L^{-1}
Hydrogen gas = 4.30×10^{-3} mol L^{-1}

6. An experiment gave the following data for the equilibrium.
$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$
Equilibrium concentrations were found to be:
[COCl$_2$] = 4.5×10^{-5} mol L^{-1}
[CO] = 1.96×10^{-3} mol L^{-1}
[Cl$_2$] = 1.96×10^{-3} mol L^{-1}
Calculate the equilibrium constant for this reaction at this temperature.

7. Sulfur dioxide and oxygen react to form sulfur trioxide as follows.
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
1 mole of sulfur dioxide is mixed with 0.5 moles of oxygen gas in a 1 L container. There is 0.9 mol of SO$_3$ at equilibrium. Calculate the following.
   (a) Equilibrium concentrations of sulfur dioxide and oxygen.
   (b) Equilibrium constant for this reaction.

8. Sketch curves on the following axes to show how the concentration of reactants and products is likely to change as a system approaches equilibrium. Point X shows the original concentration of reactants and point Y shows the original concentration of products.

9. One mole of phosphorus trichloride gas is mixed with 1 mole of chlorine gas in a 1 litre container and maintained at a constant temperature. The two gases react as shown by the following equation.
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$
Use the information in the following graph to calculate the equilibrium constant for this reaction at this temperature.

19 Investigating Equilibrium Constants

In the laboratory you will investigate some equilibrium constants and also the effect of temperature on the value of the equilibrium constant (K_{eq}).

Determining the equilibrium constant for a chemical equilibrium system

Some students set out to determine the equilibrium constant for the reaction:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$
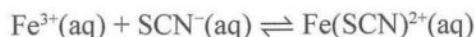
Iron(III) thiocyanate is a blood-red complex ion which is stable in aqueous solution.
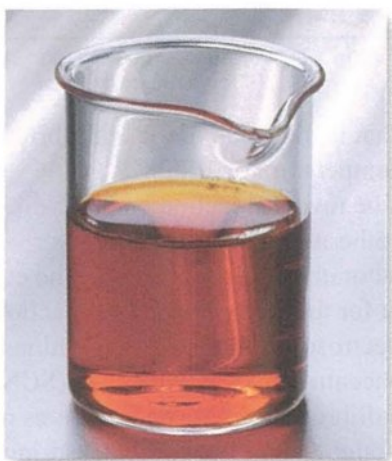

Figure 19.1 Iron thiocyanate is often described as blood-red or brick red.

Solutions were made up containing Fe^{3+} and SCN^- ions of known concentration. These solutions were mixed and allowed to reach equilibrium. The experiment was maintained at a constant temperature.

The equilibrium constant expression is:

$$K_{eq} = \frac{Fe(SCN)^{2+}(aq)}{[Fe^{3+}(aq)]\,[SCN^-(aq)]}$$

To calculate the equilibrium constant, the students needed to know the concentration of the three species present in the mixture **at equilibrium**.

A spectrometer was used to determine the concentration of the product $Fe(SCN)^{2+}$ present at equilibrium. A spectrometer passes light of a particular wavelength through the mixture – a wavelength which is maximally absorbed by $Fe(SCN)^{2+}$. The amount of light absorbed is measured to find the concentration of $Fe(SCN)^{2+}$ in the mixture at equilibrium. The higher the amount of light absorbed, the more concentrated is the solution.

Concentrations at equilibrium of the other ions present (Fe^{3+} and SCN^-) were calculated as shown in the ICE table below.

Results

Initial concentration of Fe^{3+} = 0.001 mol L^{-1}
Initial concentration of SCN^- = 0.0002 mol L^{-1}
Equilibrium concentration of $Fe(SCN)^{2+}(aq)$ = 0000195 mol L^{-1}

Calculations

The reaction starts with only reactants, $[Fe(SCN)^{2+}] = 0$. If 1.95×10^{-4} mol L^{-1} is gained on the product side, it must be lost from the reactant side as shown in the ICE table.

ICE Table (Initial/Change/Equilibrium)

Concentration	[Fe³⁺]	[SCN⁻]	[Fe(SCN)²⁺]
Initial	0.0010	0.0002	0
Change	−0.0000195	−0.0000195	+0.0000195
Equilibrium	0.0009805	0.0001805	0.0000195

$$K_{eq} = \frac{Fe(SCN)^{2+}(aq)}{[Fe^{3+}(aq)]\,[SCN^-(aq)]}$$
$$= \frac{0.0000195}{(0.0009805)(0.0001805)} = 110$$

The equilibrium constant was found to be 110 at the temperature at which the experiment was carried out.

Note: You are not required to give units for K_{eq} values.

Effect of temperature on K_{eq}

The equilibrium constant changes with temperature.

As temperature changes, K_{eq} can increase or decrease depending on whether a reaction is exothermic or endothermic.

According to Le Châtelier's principle, if the temperature increases in an equilibrium system for which the forward reaction is exothermic,
$$A + B \rightleftharpoons C + D + heat$$
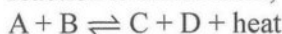
Then the system will try to lower the temperature by absorbing heat and moving the reaction to the left. This results in the value of K_{eq} becoming lower.

Changes in other factors such as concentration and pressure will change the position of the equilibrium, but not the equilibrium constant. The equilibrium constant for a reaction only changes with temperature.

Consider the following example.

Example:
The information in the table was obtained for the reaction:
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H = -88 \text{ kJ mol}^{-1}$$

Temperature (K)	Equilibrium constant	Time to produce 1 mole of PCl5
298	7.6 × 10⁷	4 hours
400	1.2 × 10⁴	10 minutes
500	75	20 seconds
600	2.5	0.5 seconds
700	0.3	0.05 seconds

(a) Describe the relationship between the temperature at which the reaction took place and the size of the equilibrium constant.

(b) A chemist wanted to produce a large volume of PCl_5 quickly and decided to use a temperature of 400 K. Why did she use this temperature?

Answer:

(a) At low temperatures the equilibrium constant was very large. At high temperatures the equilibrium constant became much smaller. As temperature of reaction increases, the value of the K_{eq} value decreases.

(b) Using a higher temperature would produce the gas faster, but the yield would be very low. The reaction is exothermic so at high temperatures it would move left and favour the reactants (as described in Le Châtelier's principle), giving a low yield.

At low temperatures the products are favoured – the reaction moves right because the reaction is exothermic (Le Châtelier), but the reaction is very slow at low temperatures.

Using a temperature of 400 K is a compromise producing a reasonable yield and a reasonable rate of forward reaction.

QUESTIONS

1. A series of three experiments, carried out at 425.3°C, for the equilibrium reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ produced the following measured concentrations of chemicals at equilibrium.

$[H_2(g)]$ mol L^{-1}	$[I_2(g)]$ mol L^{-1}	$[HI(g)]$ mol L^{-1}
4.789×10^{-4}	4.789×10^{-4}	3.531×10^{-3}
1.1409×10^{-3}	1.1409×10^{-3}	8.410×10^{-3}
4.953×10^{-4}	4.953×10^{-4}	3.655×10^{-3}

(a) State the equilibrium constant expression for this reaction.

(b) Calculate the value of the equilibrium constant for each of the three sets of data in the table and comment on the values obtained.

2. Nitric oxide (NO) reacts with oxygen to form nitrogen dioxide.
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
The table provides values of the equilibrium constant for this reaction at different temperatures.

Temperature (K)	750	1000	1500	2000
K_{eq}	112	1.60	0.024	0.00064

(a) State the equilibrium constant expression for this reaction.

(b) Outline any trend apparent in the values of the equilibrium constant for this reaction.

(c) Deduce whether the forward reaction as written is exothermic or endothermic. Justify your deduction.

(d) At 1000 K the reaction vessel contains the following mixture of gases:
0.04 mol L^{-1} O_2
0.09 mol L^{-1} NO
0.02 mol L^{-1} NO_2
Determine if the reaction has reached equilibrium.

3. The graph shows K_{eq} values, at different temperatures, for the reversible reaction:
$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$
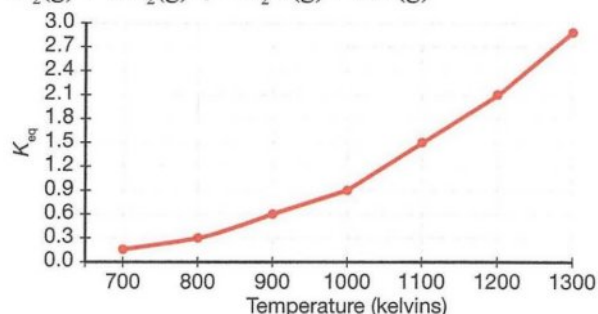
(a) What is the value of the equilibrium constant at a temperature of 1000 K?

(b) Is the reverse reaction endothermic or exothermic? Justify your answer.

4. In the laboratory determination of the equilibrium constant for the ferrothiocyanate reaction:
(a) Spectroscopy is used to determine the concentration of blood-red $Fe(SCN)^{2+}$ in an equilibrium mixture and involves passing light through the mixture and measuring the amount of light absorbed. Research the wavelength of light that is absorbed.

(b) Identify two safety precautions that need to be observed while carrying out experiments with these chemicals.

5. A group of students repeated the experiment described in the text above to determine the equilibrium constant for the equation:
$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$
The data they obtained were:
Initial concentration of $Fe^{3+}(aq) = 9.76 \times 10^{-4}$ mol L^{-1}
Initial concentration of $SCN^-(aq) = 1.78 \times 10^{-4}$ mol L^{-1}
Equilibrium concentration of $Fe(SCN)^{2+}(aq)$ $= 1.96 \times 10^{-5}$ mol L^{-1}

(a) Use these figures to calculate their experimental value for the equilibrium constant.

(b) Would you expect any change in this value if the experiment was repeated with the following changes in conditions? (The forward reaction is exothermic.)
(i) A lower temperature.
(ii) A catalyst is added.
(iii) Using different concentrations of Fe^{3+} ions and SCN^- ions.

20 Equilibrium Dissociation Constants

Equilibrium constants can be calculated and used for different types of chemical reactions. Here are some examples.

Dissociation of ionic solutions

You will recall from your work in year 11 that a dissociation reaction is one in which a compound breaks up into two or more parts.

You have already studied dissociation of ionic substances as they dissolve in water to form solutions. You have seen that ionic compounds dissociate when the attraction between polar water molecules and the ions 'pulls apart' the ionic crystal. You investigated molar heats of solution, and determined that some were exothermic, e.g. $CaCl_2$ and others were endothermic, e.g. NH_4NO_3.

The general formula for a dissociation reaction can be written as:
$$AB \rightarrow A^+ + B^-$$
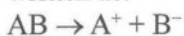
However, dissociation reactions are usually reversible reactions, they can reach equilibrium and an equilibrium constant can be determined for these reactions.
$$AB \rightleftharpoons A^+ + B^-$$
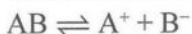
$$K_{eq} = \frac{[A^+][B^-]}{[AB]}$$

Like all equilibria, as the equilibrium constant approaches zero, the reaction tends to form 100% reactants. As an equilibrium constant approaches infinity, the reaction approaches the formation of 100% products. You will learn more about the dissociation of ionic solutions in the next section when we look at solubility.

Dissociation of acids

Acids form hydrogen ions (H^+) in aqueous solution. They are the only polar molecular compounds that dissociate into ions when they dissolve.

The equilibrium constant for the dissociation of acids is called the acidity constant, or **acid dissociation constant** (K_a) and it is a quantitative measure of the strength of an acid in solution.

Strong acids such as hydrochloric acid and sulfuric acid dissociate completely in aqueous solution, the reaction goes to completion, so this is not an equilibrium reaction.

A K_a value for HCl would be very large because of its 100% dissociation.
$$HCl(l) \rightarrow H^+(aq) + Cl^-(aq)$$
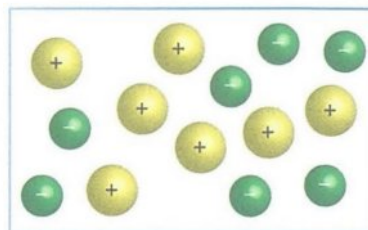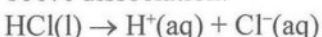
Figure 20.1 Complete dissociation of a strong acid such as hydrochloric acid.

Sulfuric acid is diprotic, it produces two hydrogen ions (protons) when it dissociates.
$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

This occurs in two steps. The first step is:
$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
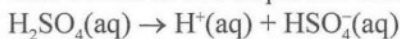
In this first dissociation, sulfuric acid acts as a strong acid, with each molecule releasing a hydrogen ion.
$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$
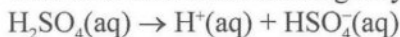
K_a for this dissociation is very large. A great deal of energy is released in this exothermic dissociation so sulfuric acid should be used with caution. When diluting concentrated acid it is essential to add the acid to the water very slowly, and stir as you add.

In the second dissociation, the hydrogen sulfate ion (HSO_4^-) acts as a weak acid and only partly dissociates.
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$
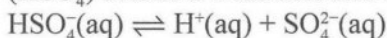
Only about 27% of the ions dissociate and release a hydrogen ion, so K_a for this dissociation is very small.

Most acids do not dissociate completely when they dissolve, they form an equilibrium and these are called weak acids.

Weak acids, such as carbonic acid and acetic acid, do not fully dissociate in solution, their ions form an equilibrium with the acid. The weaker the acid, the less it will dissociate.

The dissociation of weak acids can be shown as:
$$HA \rightleftharpoons H^+ + A^-$$
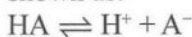
Where A^- represents the anion such as the carbonate ion in carbonic acid.
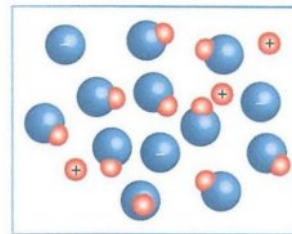
Figure 20.2 Incomplete dissociation of a weak acid such as acetic acid.

Acetic acid (CH_3COOH) is a weak acid, it partially dissociates and forms an equilibrium.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Notice that the concentrations of the hydrogen ions and acetate ions are equal as they are both produced and used up in a 1 : 1 molar relationship.

Carbonic acid (H_2CO_3) is also a weak acid; very few carbonic acid molecules ionise and an equilibrium is reached. The equilibrium lies to the left and the acid dissociation constant (K_a) is small.

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

$$K_a = \frac{[H^+]^2\,[CO_3^{2-}]}{[H_2CO_3]}$$

The value of K_a **varies from acid to acid**. At the same temperature, carbonic acid has a K_a value of 4.2×10^{-7} and acetic acid has a value for its K_a of 1.7×10^{-5}.

The K_a for acetic acid > the K_a for carbonic acid, so acetic acid is a stronger acid than carbonic acid.

Note: Don't let the numbers trick you here – 10^{-7} is smaller than 10^{-5}, 0.00000042 is smaller than 0.000017.

The less the acid dissociates, the smaller the K_a value, and the weaker the acid will be.

The more an acid dissociates, the higher the K_a value, and the stronger the acid will be.

So you can see that one use of equilibrium constants is to **compare the relative strength of acids**.

As with other K values, **the acid dissociation constant K_a also varies with temperature**. For example, if the dissociation reaction is exothermic, then the value of the K_a will decrease with increasing temperature.

Dissociation of bases

Bases also dissociate in water to form an equilibrium mixture, and they also have an equilibrium constant called the **base dissociation constant K_b**.

Strong bases include the hydroxides of group 1 and 2 metals, for example potassium hydroxide, sodium hydroxide, lithium hydroxide, barium hydroxide and calcium hydroxide. These strong bases ionise almost completely in solution, so their K_b would be very high.

Weak bases only partly dissociate in water. They react incompletely with water to form hydroxide ions. The reaction can be written as:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}$$

Water can be ignored in equations of dissociation constants as its value would be 1.

The base dissociation constant measures the strength of a base dissolved in water.

Ammonia is a typical weak base. It does not contain hydroxide ions but it reacts with water to form hydroxide ions as follows:

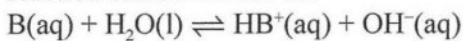$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
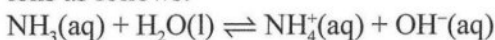
The base equilibrium constant expression for this reaction is:

$$K_b = \frac{[NH_4^+(aq)]\,[OH^-(aq)]}{[NH_3(aq)]}$$

The equilibrium lies far to the left, so very few hydroxide ions are produced and ammonium hydroxide is a weak base.

Later this year, when you have learned more about acids and bases, you will find that there is a relationship between the K_a of an acid and the K_b of a base that is called its conjugate base. $K_a \times K_b = [H^+]\,[OH^-]$.

When you have learned more about pH and how to calculate it, you will be better prepared to understand calculations of K_a and K_b.

Ionic product of water (K_w)

Another type of constant is the ionic product of water (K_w). This is the equilibrium constant for the expression,

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

$$K_{eq} = \frac{[H^+(aq)]\,[OH^-(aq)]}{[H_2O(l)]}$$

So little water is ionised at any time, that its concentration virtually remains unchanged and $[H_2O(l)]$ can be regarded as a constant.

$K_{eq}\,[H_2O(l)] = [H^+(aq)]\,[OH^-(aq)]$

K_{eq} and $[H_2O(l)]$ are both constants, so they can be replaced with a new constant – which is called K_w, **the ionic product of water**.

$$K_w = [H^+(aq)]\,[OH^-(aq)]$$

If we multiply together the concentrations of hydrogen ions and hydroxide ions present in water or any aqueous solution, we end up with a constant value – and this value is what we call the ionic product of water or K_w.

As happens with other equilibrium constant values, the value of K_w varies with temperature.

In pure water, at room temperature, $K_w = 1 \times 10^{-14}$
And $[H^+] = [OH^-] = 10^{-7}$

You will learn more about the ionic product of water when you study acids and bases in Module 6.

Solubility product K_{sp}

K_{sp} **is called the solubility product constant**. It is a special type of equilibrium constant for solutions of sparingly (slightly) soluble salts which partly dissociate in water, forming ions surrounded by water molecules within the solution. As the name suggests, this K value is associated with the solubility of a salt. You will be learning more about the solubility product constant later in this topic.

The best yield is achieved in this process, by taking into consideration the following factors.

- Increasing the **temperature** increases the reaction rate in both directions. However, the forward reaction is exothermic, so as the temperature increases, the reaction moves left minimising the change. This response decreases the yield – not what you want at all. A compromise is reached by using a temperature of 400°C to 500°C. This is high enough for a fast reaction rate, but low enough to still get a good yield.

- High **pressure** (approximately 300 atmospheres) is used to shift the equilibrium to the right and increase the yield of ammonia. By Le Châtelier's principle, increasing pressure increases the forward reaction. This works because there are fewer particles on the right side of the equation than on the left.

- Using a **catalyst** such as iron oxide (Fe_3O_4) will increase the reaction rates of both the forward and reverse reactions by lowering the activation energy. This allows equilibrium to be reached more rapidly.

- Ammonia is **liquefied and constantly removed** as it is formed. This change moves the reaction to the right as the system tries to replace the ammonia removed.

- Nitrogen and hydrogen are added in a ratio of 1 : 3 so they are present in **stoichiometric proportions**.

QUESTIONS

1. (a) Identify three properties of ammonia.
   (b) Research four uses of ammonia.
2. Identify the raw materials used in the manufacture of ammonia and their sources.
3. Identify the conditions used in the manufacture of ammonia by the Haber-Bosch process to ensure optimal yield.
4. (a) Write the reversible equation to show the reaction of nitrogen and hydrogen to produce ammonia.
   (b) Copy and complete the following table to show how Le Châtelier's principle can be used to predict changes in this equilibrium system when the production conditions are changed.

Change	Effect on equilibrium	Effect on yield
Increase concentration of a reactant.		
Decrease concentration of the product – remove NH_3.		
Increase pressure on the system (or reduce volume).		
Increase the temperature of the system.		

5. Explain why the reaction to synthesise ammonia from its component gases is referred to as:
   (a) A reversible reaction.
   (b) An exothermic reaction.
   (c) An equilibrium system.
6. Figure 21.4 shows the percentage yield of ammonia at different temperatures and pressures. Use the graph to answer the following questions.
   (a) State the relationship between percentage yield and pressure.
   (b) Determine the percentage yield of ammonia when the reaction is carried out under the following conditions.
       (i) 400°C and 300 atmospheres pressure.
       (ii) 700°C and 300 atmospheres pressure.
       (iii) 400°C and 800 atmospheres pressure.
7. (a) Calculate the theoretical mass of ammonia produced when 2.5 kg of nitrogen reacts with hydrogen.
   (b) If the yield obtained is only 30%, how much ammonia will actually be produced?
8. Answer these quick quiz questions on the Haber-Bosch process.
   (a) Name the main product of the Haber-Bosch process.
   (b) Describe this substance.
   (c) Identify a chemical fertiliser made from ammonia.
   (d) Name the two raw materials used in the Haber-Bosch process.
   (e) Name the chemist who was the first to make ammonia from hydrogen and nitrogen.
   (f) Name the engineer who developed this reaction into an industrial process.
   (g) Write formulas for the two substances that were reacted to make the hydrogen for this process.
   (h) The reaction between nitrogen and hydrogen is an exothermic process, producing 92 kJ mol^{-1}. Write an equation to show this.
   (i) The Haber-Bosch process is exothermic. Would an increase or decrease in temperature move the equilibrium to the right?
   (j) Would the rate of reaction be increased by increasing or decreasing the temperature?
   (k) Name a catalyst used in the Haber-Bosch process.
   (l) Which would favour an increased yield of ammonia, increasing or decreasing pressure?
   (m) Which chemical would you constantly remove from the reaction vessel to increase the yield of ammonia?
   (n) Identify three types of substances made from ammonia.

9. The development of the Haber-Bosch process illustrates the effect of social and economic contexts on the development of chemistry. It also provides an example of how the development of technology can lead to changes in techniques and world practices. Read the following passage and answer the questions at the end.

For centuries people used animal waste for fertiliser without knowing the chemistry behind this practice. With the Industrial Revolution and increasing population of Europe, the demand for food increased and with it the demand for fertiliser and thus nitrates to make them. Nitrates were also needed for the production of synthetic dyes and for the developing explosives industry. Explosives were needed for mining and warfare. Three common explosives are ammonium nitrate, trinitrotoluene (TNT) and nitroglycerine (dynamite).

The main source of nitrates was saltpetre (sodium nitrate) from Chile, with some also being obtained mainly from guano. This was not sustainable as the supplies could not meet demands forever – they would eventually run out.

Early in World War I, the powerful British navy prevented saltpetre being shipped to Germany. Germany then turned to the Haber-Bosch process to make ammonia from atmospheric nitrogen. A process called the Ostwald process was used to convert the ammonia into nitric acid and nitrates. Not having to rely on a foreign source of chemicals to make explosives allowed Germany to continue the war.

Fritz Haber was a German chemist. Just prior to WWI, while researching ways to produce nitrogen based explosives, Haber made ammonia from hydrogen gas and atmospheric nitrogen in the laboratory. Initially the process was very slow and not feasible as an industrial process. After hundreds of experiments, Haber found that iron filings could be used as a catalyst suitable for increasing the speed of the reaction. However, he could still only produce small amounts of ammonia with the apparatus available to him. Haber later received the Nobel Prize for Chemistry (1918) for this achievement.

In 1913, Carl Bosch developed Haber's ideas into an industrial process called the Haber-Bosch process. Bosch received a Nobel Prize in 1931 for large scale chemical synthesis and the development of the high pressure technology needed to make such plants work.

During the war, Britain and America were also trying to develop this process, but they did not have the catalysts or high pressure equipment needed. Today this is a well developed industry in industrial societies and it has led to an increase in the availability and use of fertilisers. The use of artificial fertilisers has had a huge effect on the economy and made possible a vast increase in food production to feed the rapidly growing population.

Despite these beneficial effects, there is currently concern that the use of the Haber-Bosch process and our current dependence on artificial fertilisers is environmentally undesirable and is not sustainable. This is because the Haber-Bosch process uses considerable energy, producing carbon dioxide and contributing to atmospheric levels of nitrogen dioxide and thus adding to pollution and global warming.

Research is underway aimed at producing a process requiring less energy and also looking for other ways to increase nitrogen fixation within the soil.

(a) Underline key words in the passage.
(b) Define guano.
(c) What contribution did Fritz Haber make?
(d) Identify the chemicals produced by the:
   (i) Haber-Bosch process.
   (ii) Ostwald process.
(e) Before 1914, Germany was making fertiliser as well as explosives and ammunition from nitrates obtained from saltpetre which was mined in Chile and transported by sea.
   (i) Explain why this became impossible after 1914.
   (ii) Identify factors that may have led to an increase in the demand for ammonia.
(f) Describe how Germany made fertilisers and explosives after its supplies of saltpetre were cut off.
(g) Explain the significance of the Haber-Bosch and Ostwald processes to Germany during World War I.
(h) Carl Bosch was largely responsible for making the synthetic production of ammonia economically viable. Outline two technological developments that were necessary to allow large-scale industrial use of the Haber process.
(i) Identify two undesirable effects of the Haber-Bosch process.

22 Equilibrium Around Us

Reversible reactions and equilibria occur in many chemical systems that operate in different areas and at different scales. Here are some examples.

The ocean and atmosphere

The levels of carbon dioxide in the atmosphere influence global systems. Atmospheric carbon dioxide is formed naturally (e.g. from oceans, respiration of plants and animals, decomposition of organic matter and released by volcanoes) and also made by humans (anthropogenic sources, e.g. burning fossil fuels). Carbon dioxide levels affect surface temperatures, ocean currents and the direction and strength of winds.

As we burn increasing amounts of fossil fuels, we produce more carbon dioxide and its concentration in the atmosphere increases. More carbon dioxide then dissolves to balance the oceanic and atmospheric gas pressures.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
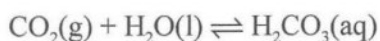
The oceans and their algae, vegetation and coral absorb a considerable amount of carbon dioxide emissions from the combustion of fossil fuels. Estimates of the actual amount absorbed vary from about 40% to 93%.

Dissolved carbon dioxide makes the oceans more acidic as the carbonic acid dissociates and releases hydrogen ions.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
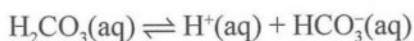
The pH has already dropped from 8.2 to 8.1, which doesn't sound much, but represents about a 25% increase in acidity. It has not become an acid, but it is less basic.

This has harmful effects on ecosystems. For example, organisms such as coral, crustaceans and molluscs have structures made of calcium carbonate which are at risk as the pH drops. Hopefully the United Nations Kyoto Protocol and the International Panel on Climate Change can persuade governments to commit to achieving a significant reduction in greenhouse gas emissions.

Foods and drinks

The production of foods and drinks depends on chemists successfully controlling a number of reversible reactions to produce the desired products. Weak acids are commonly added to food and drinks. They have a sour taste and are important for flavour in some foods such as sweet and sour sauces and salad dressing. Dilute acids are also used as preservatives, e.g. dilute acetic acid in the form of vinegar.

The wine industry

Wines contain many chemicals including proteins, sugars, minerals, dissolved gases such as carbon dioxide and sulfur dioxide, weak acids and volatile substances including esters.

Some weak acids such as tartaric, lactic and acetic acids, occur naturally in wines, and ascorbic acid may be added during production.

Weak acids in wines undergo reversible dissociation, as they do in other situations. The equilibrium position of these weak acids may be affected by the presence of other components such as sugar and alcohol and this affects the pH of the wine.
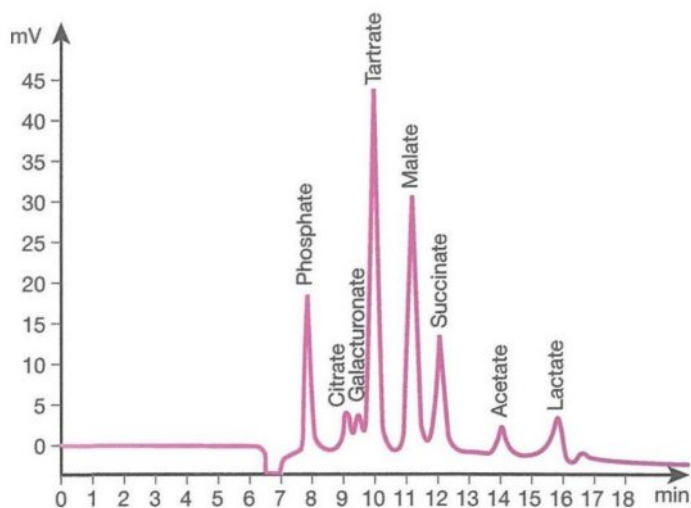
Figure 22.1 A chromatogram showing anions of some organic acids in a white wine.

The wine maker has to identify how the concentrations of the various chemicals are related to each other and also how they affect the colour, taste and aroma of the final wine product.

Many chemical tests are carried out on wines these days. They are tested for pH, specific gravity, sterility, the presence of many chemicals including ethanol, sugars, and sulfur dioxide.

A technique called **auto-titration** is regularly used to determine acid concentrations in wine.

Figure 22.2 Auto-titration of wines.

Other techniques used in the wine industry include gas chromatography and spectroscopy (colorimetry).

Gas chromatography and **mass spectrometry** are used in wine making to determine volatile chemicals present, e.g. fruity aromas. Such techniques allow for the separation of over 100 compounds and determine the relative amounts of each compound in a wine. They can check for the presence of unwanted chemicals such as pesticides, sulfur compounds and industrial solvents. Wines, like other foods and drinks, can contain small amounts of pesticide residues as shown in Figure 22.3.
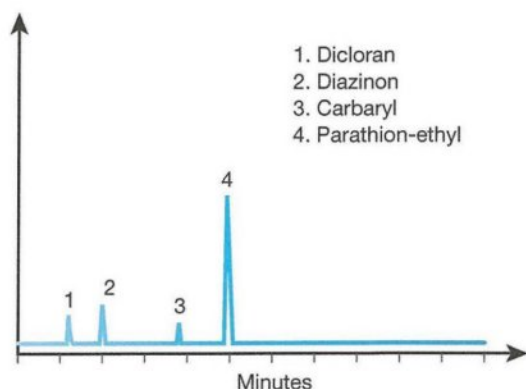
Figure 22.3 A chromatogram showing some pesticides found in wine.

Spectroscopy is used to detect compounds such as alcohol, sugars, tannins and coloured pigments. Each wine has a spectral signature which reveals its taste and quality.
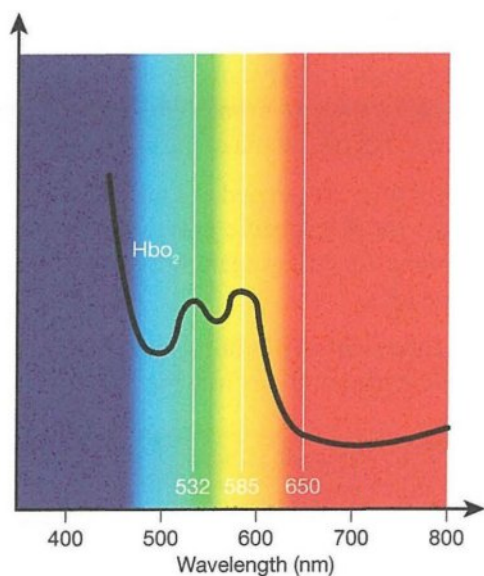
Figure 22.4 Spectral analysis of wine.

Wine makers use these and other techniques to solve problems such as unpleasant odours and tastes in wines. For example, they may find chemicals present that result from microbial action or high temperature exposure. To overcome this problem they would look to changes in their manufacturing and handling processes.

Sulfur dioxide (SO_2) is produced naturally in wines during fermentation. However, most of the sulfur dioxide in wines is added by the wine maker because sulfur dioxide is commonly used as a preservative in wines. It can be added as sulfur dioxide gas, or in the form of a powdered sulfite such as sodium sulfite, and it undergoes the following reactions.

$$H_2O(l) + SO_2(g) \rightleftharpoons H_2SO_3(aq)$$

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$
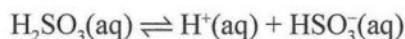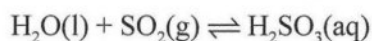
Sulfur dioxide is an antimicrobial agent, helping to stop the growth of undesirable micro-organisms. It also acts as an antioxidant, protecting the fruit from browning. Sulfur dioxide also binds with a chemical called acetaldehyde which can be produced during wine making. Acetaldehyde has an unpleasant smell, but when bound with sulfur dioxide it is odourless.

The amount of sulfur dioxide needed in wine is affected by the pH of the wine and mathematical equations (called sulfite calculators) are used to determine the amount of sulfur dioxide to be added to a particular wine. Wines labeled as 'organic' and 'preservative free' may not contain any sulfur dioxide, depending on the preferences of the wine maker.

Figure 22.5 Grapes for wine.

Carbon monoxide poisoning

The principles of equilibrium are important in the body. For example, acid-base equilibrium reactions are important in maintaining the pH of the blood, helped by chemicals called buffers. Another example of the importance of equilibrium reactions in the body is the transport of oxygen through the body.

The transport of oxygen through the body relies on the presence of a protein called haemoglobin which contains iron and is responsible for the red colour of blood. This is a chemical in red blood cells and its role is to absorb oxygen and carry it to our cells in the form of oxyhaemoglobin.

$$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$$

(a)

(b)
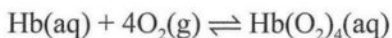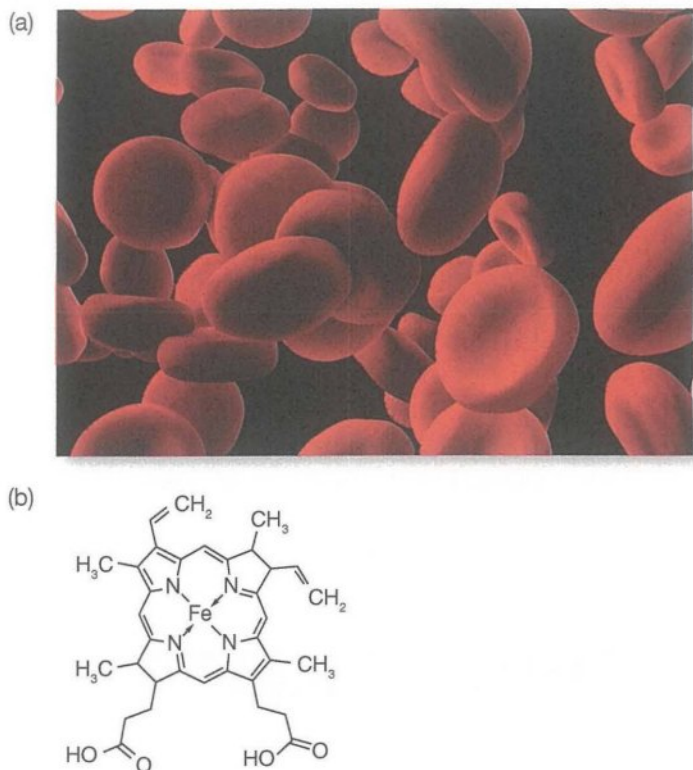
Figure 22.6 (a) Red blood cells contain haemoglobin. (b) Part of a haemoglobin molecule.

The transport of oxygen in the blood is disrupted when carbon monoxide is inhaled. Carbon monoxide is an odourless, tasteless, colourless gas produced by the incomplete combustion of fossil fuels. It is a toxic gas and results in many cases of poisoning every year. A concentration of 100 ppm will produce symptoms. These can include a flushed face, light-headedness, headaches, tiredness, confusion and shortness of breath.

When carbon monoxide is inhaled, haemoglobin in the blood combines with the carbon monoxide in preference to oxygen, forming carboxyhaemoglobin, which is even redder than oxyhaemoglobin but is not able to bind with oxygen.

$$Hb(aq) + 4CO(g) \rightleftharpoons Hb(CO)_4(aq)$$
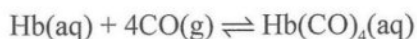
This reduces the ability of the blood to carry oxygen, leaving tissues low in oxygen. Instead carbon monoxide is carried to the cells where it can be released, and here it is toxic; it can cause serious damage. Long term or severe exposure can cause damage to organs such as the heart and brain and can even cause death.

The risk of carbon monoxide poisoning is why fossil fuels should never be burnt in an enclosed space. For instance, a car should never have the motor running in a closed garage and a barbecue should never be used in a garage, or house or even close to a doorway. Other sources of carbon monoxide poisoning include the use of poorly ventilated household appliances such as heaters. Blockages in chimneys, flues or car exhausts can also lead to a build-up of carbon monoxide.

The combined equilibrium reaction that forms when inhaling carbon monoxide leads to carbon monoxide poisoning is:

$$Hb(O_2)_4(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq) + 4O_2(aq)$$
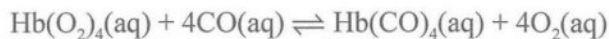
This equilibrium reaction has a large equilibrium constant – it lies to the right. The body no longer has enough oxyhaemoglobin to support life processes in its cells.

The treatment for carbon monoxide poisoning makes use of Le Châtelier's principle. It acts to disturb the equilibrium and establish a new equilibrium position in a more desirable direction.

The patient is given 100% oxygen to inhale.

This increase in $[O_2]$ pushes the equilibrium above to the left, thus decreasing the concentration of carboxyhaemoglobin $[Hb(CO)_4]$ and increasing the concentration of oxyhaemoglobin $[Hb(O_2)_4]$.

The result is that $Hb(CO)_4$ decomposes, releasing the carbon monoxide, which can then be breathed out.

QUESTIONS

1. (a) Data shows that atmospheric carbon dioxide levels are now approaching 400 ppm. Carbon dioxide dissolves in water to form the weak acid, carbonic acid. Describe the effect of increasing levels of atmospheric carbon dioxide on ocean acidity. Include equations in your answer.
    (b) The following reaction occurs in oceans, and its equilibrium lies to the left.
        $$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$
        Predict any effect that ocean acidification could have on organisms with calcium carbonate in their shells, such as molluscs, oysters and clams.
2. Outline an example of the importance of chemical equilibrium in wine.
3. Outline an example of chemical equilibrium in the home.
4. Research the names and uses of some food additives.
5. Research and evaluate the roles and effectiveness of the United Nations Kyoto Protocol or the International Panel on Climate Control.
6. Discuss an example of the importance of Le Châtelier's principle in the body.
7. Outline reasons why a gas barbecue should never be used inside a garage or house.
8. Haemoglobin in red blood cells normally absorbs inhaled oxygen forming an equilibrium reaction.
    $$Hb(aq) + 4O_2(g) \rightleftharpoons Hb(O_2)_4(aq)$$
    Deduce the effect on this equilibrium reaction in the blood for a person who travels to an area at high altitude.

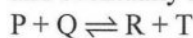# 23 Revision Of Calculating the Equilibrium Constant

As you revise this section, you should think about how the equilibrium position can be described and what the equilibrium constant represents.

Work through the multiple choice questions. If you have trouble understanding the answer to any question you should talk to your teacher.

QUESTIONS

1. Hydrogen iodide dissociates to form the gases hydrogen and iodine.
   $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
   Which one of the following statements tells us that the mixture of gases is at equilibrium?
   (A) The same number of gas molecules occurs on each side of the equation.
   (B) The number of bonds broken in the forward reaction is the same as the number of bonds formed.
   (C) The rate of the reverse reaction is the same as the rate of the forward reaction.
   (D) No water or solids are formed during this reversible reaction.

2. Equilibrium constants (K_{eq}) are useful for determining the strength of acids. Which of the following statements is correct?
   (A) A high K_{eq} value indicates an acid is weak.
   (B) Only strong acids have a K_{eq} value.
   (C) The weaker an acid, the lower the K_{eq} value.
   (D) Concentrated acids have high K_{eq} values.

3. Which alternative provides the equilibrium expression for the following reaction?
   $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

   (A) $\dfrac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

   (B) $\dfrac{HI^2(g)}{H_2(g) \times I_2(g)}$

   (C) $\dfrac{[H_2(g)][I_2(g)]}{[HI(g)]^2}$

   (D) $\dfrac{[HI(g)]}{[H_2(g)][I_2(g)]}$

4. The value of the equilibrium constant for an equilibrium system can be changed by changing the:
   (A) Temperature.
   (B) Pressure.
   (C) Concentration.
   (D) Volume.

5. Barium hydroxide ($Ba(OH)_2$) is slightly soluble in water.
   $Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$
   A sample of barium hydroxide will completely dissolve when:
   (A) More $Ba(OH)_2$ is added.
   (B) The solution is alkaline.
   (C) The solution is acidic.
   (D) Pressure is increased.

6. Reactants P and Q are mixed, each at a concentration of 0.8 mol L^{-1}. They react slowly forming R and T and eventually reach equilibrium.
   $P + Q \rightleftharpoons R + T$
   The concentration of R is measured when equilibrium is reached and found to be 0.6 mol L^{-1}. Complete the following table and use the values in the table to determine the value of the equilibrium constant for this reaction.

Factor	[P]	[Q]	[R]	[T]
Initial concentration				
Equilibrium concentration				
Change in concentration				

   The value of the equilibrium constant will be:
   (A) 0.56
   (B) 0.6
   (C) 1.8
   (D) 9

7. The reaction represented by the equation is allowed to reach equilibrium.
   $2X + 2Y \rightleftharpoons 3Z + 2G$
   The following measurements are obtained.

	X	Y	Z	G
Concentration at equilibrium (mol L^{-1})	2	3	3	1

   The value of the K_{eq} for this reaction is:
   (A) 0.75
   (B) 0.3
   (C) 0.25
   (D) 0.09

8. In the Haber-Bosch process, the reactants are:
   (A) N_2 and H_2
   (B) N_2 and NH_3
   (C) NO_3^- and NH_3
   (D) H_2 and NH_3

9. Today the main source of nitrogen for the Haber-Bosch process is:
   (A) The electrolysis of water.
   (B) Fertiliser.
   (C) Nitrates extracted from soil.
   (D) Atmospheric nitrogen.

10. In the Haber-Bosch process, represented by the equation, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, in order to increase the yield, the reaction pressure is increased to about 300 atmospheres. This works because:
    (A) There are more molecules of hydrogen than molecules of nitrogen or ammonia.
    (B) There are fewer molecules of gaseous products than gaseous reactants.
    (C) There are more molecules of gaseous products than gaseous reactants.
    (D) Increasing pressure causes more collisions with the sides of the container.

11. Which of the following is a suitable catalyst for the Haber-Bosch process?
    (A) Concentrated sulfuric acid.
    (B) Alumina silica gel.
    (C) Iron oxide.
    (D) Transition metals.

12. For maximum yield in the Haber-Bosch process:
    (A) A very low temperature is maintained, as the reaction is exothermic and a high temperature would decrease yield.
    (B) A very high temperature is maintained to increase the number of collisions and hence the reaction rate.
    (C) A moderate temperature is maintained as a compromise between A and B.
    (D) The temperature is allowed to fluctuate so Le Châtelier's principle can take effect.

13. A toxic gas which combines preferentially with haemoglobin in red blood cells is:
    (A) Carbon dioxide.
    (B) Carbon monoxide.
    (C) Nitrogen.
    (D) Nitrogen monoxide

14. The equilibrium dissociation expression for carbonic acid can be expressed as:
    (A) $K_b = \dfrac{[H^+]^2 \, [CO_3^{2-}]}{[H_2CO_3]}$

    (B) $K_a = \dfrac{[H^+]^2 \, [CO_3^{2-}]}{[H_2CO_3]}$

    (C) $K_a = \dfrac{[H_2CO_3]}{[H^+]^2 \, [CO_3^{2-}]}$

    (D) $K_a = \dfrac{[HCO_3]}{[H^+] \, [CO_3]}$

15. Acetic acid exists in aqueous equilibrium.
    $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$
    Which of the following events will occur if dilute hydrochloric acid is added?
    (A) The equilibrium constant will get larger.
    (B) The equilibrium constant will get smaller.
    (C) The acetate ion concentration will decrease.
    (D) The acetate ion concentration will increase.

INQUIRY QUESTION

1. How can the position of equilibrium be described?
2. What does the equilibrium constant represent?
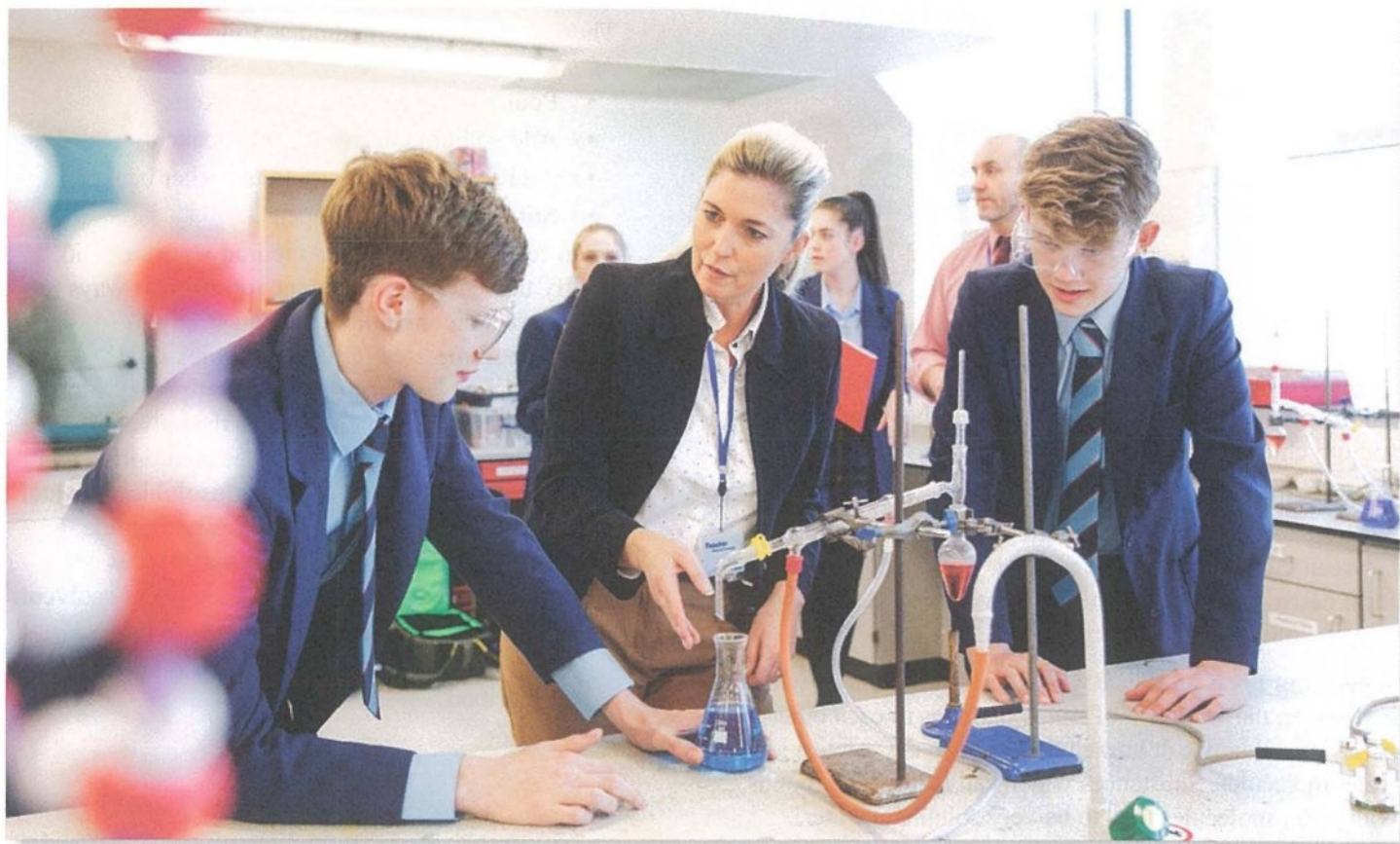
24 The Dissolution Of Ionic Compounds

When you place an ionic compound in water, the ionic lattice breaks up and its ions are dispersed throughout the water forming a solution. This process is called dissolution.

This occurs because water has polar molecules.
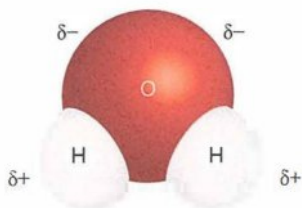
Figure 24.1 Polar water molecule showing positive and negative charges.

The dissolution of an ionic compound in water involves breaking up its ionic lattice. The positive and negative charged ends of polar water molecules attract the negative and positive ions of the ionic lattice. The ions form ion-dipole bonds with the water molecules and we describe them as being hydrated.
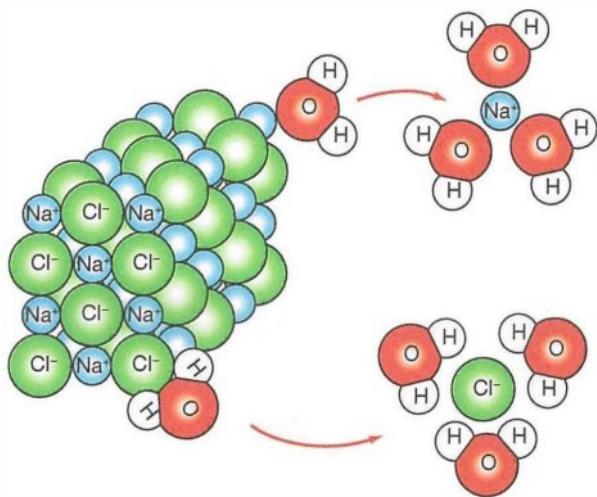
Figure 24.2 Sodium chloride dissolving in water.

Water is the **solvent**, it does the dissolving. Sodium chloride is the **solute**, it gets dissolved. The result is a sodium chloride **solution**.

When a substance dissolves, energy is used to break existing bonds between the particles of the solute and between the particles of the solvent. New bonds can then form between the solute and the solvent and the forming of new bonds releases energy.

Whether or not a substance will dissolve depends on which is stronger, the attraction of solute particles to each other in the crystal lattice or attractions between the solute and water molecules. Substances which can form strong bonds with water molecules tend to be very soluble in water.

The aqueous solution formed when a substance dissolves in water is a homogeneous mixture of two or more substances. The solute is evenly spread throughout the water.

Solutions are clear – this means that they are transparent – you can see right through them. Notice that, when you are describing solutions, clear does not mean the same as colourless. All of the following solutions are clear, only the last one is colourless. You have already seen that many salts of transition metals form coloured solutions (such as the blue solution of copper sulfate).
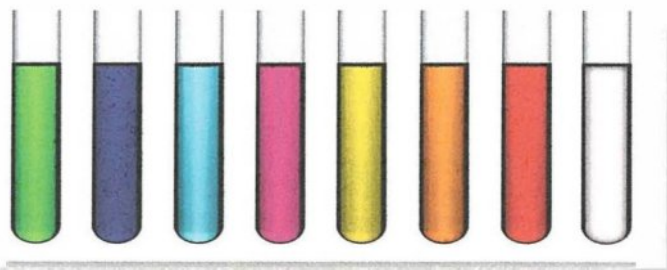
Figure 24.3 Solutions are transparent (clear) and may be coloured or colourless.

QUESTIONS

1. (a) Name five ionic compounds that are soluble in water and two that are insoluble.
   (b) Account for the ability of water to dissolve many ionic compounds.
2. A group of students set out to compare the solubility of sodium chloride and sodium carbonate in water. They wrote up their method as follows.
   Method:
   - Pour some water into two beakers.
   - Add sodium chloride to one beaker.
   - Add sodium carbonate to the other beaker.
   - Stir and see what happens.

   Their teacher said that this method was not valid. Justify the teacher's comment and suggest ways to improve on the method described.
3. Check your knowledge with this quick quiz.
   (a) Water molecules are (polar/non-polar).
   (b) A solution in which water is the solvent is referred to as an .... solution.
   (c) Sodium chloride is (soluble/insoluble) in water.
   (d) Calcium carbonate is (soluble/insoluble).
   (e) Because water dissolves so many types of substances it is called the .... solvent.
   (f) Bonds in ionic lattices are ionic. When Na^+ and Cl^- form bonds with water, how are the bonds described?

25 Water As a Solvent

The ability of water to dissolve substances is important in biological, domestic and industrial contexts.

Biological contexts

The solubility of polar and ionic substances in water is vital to the existence of life on Earth. For example:

- **Chemical reactions** within cells (known as metabolism) occur in solution. Water can also be a reactant, for example in the process of photosynthesis in plants.

- During **digestion**, most food is broken down into ions and small molecules and dissolved in water in the intestine then absorbed into the blood and lymph to circulate around the body.

- Many **metabolic wastes are removed** from the body in solution, for example in sweat and urine.

- Aqueous solutions occur in the body as lubricants for example the **synovial fluid** in joints, and the **amniotic fluid** surrounding a baby as it develops in the amniotic sac within the uterus. All the cells of the body are bathed in aqueous solution, which provides food and oxygen and removes waste products.

- Blood is 80% to 90% water and it **transports many substances around the body** in aqueous solution. Blood transports a range of dissolved substances, both ionic and molecular, for example food, vitamins, minerals and metabolic wastes such as urea and carbon dioxide. These substances pass through the walls of cells and capillaries in aqueous solution.

Maintenance of normal blood solute concentrations and pH levels is vital for our health. The normal concentrations of solutes have been studied in the blood of healthy people, and reference ranges established. Analysis of solutes in a patient's blood can be compared against these standards and any differences analysed to see if they indicate the presence of conditions such as diabetes (sugar levels) and anaemia (iron levels). Tests can be used to check for kidney, thyroid and liver function, blood clotting times, cholesterol level, the presence of antibodies and inflammation and much more.

Domestic and industrial contexts

When we **cook vegetables and fruits** in water a lot of the good vitamins and minerals in them dissolve in the water and may be drained off and wasted, which is one reason nutritionists encourage us to eat fresh fruit and vegetables.

Aqueous solutions containing ions are good electrical conductors. These are called **electrolytes** and they play an important role in applications such as the manufacture and use of batteries. Also drinks containing electrolytes are given to athletes to restore balance of ions lost in sweating.

The solvent properties of water are important in **maintaining hygiene**. Cleaning by washing in water relies on the ability of the water to dissolve a large range of substances. Soaps and detergents are used to increase cleaning ability by allowing non-polar substances to dissolve in water.

Water is also important in agriculture and its solvent properties are a key component. **Essential minerals for plant growth**, such as nitrogen and phosphorus, enter the plant from the soil in the form of nitrates and phosphates. These pass into the roots dissolved in water.

Analysis of foods, medicines and other mixtures can be carried out using a procedure called chromatography which uses the solvent properties of liquids such as water to analyse their components.

Many **waste products**, insecticides, herbicides, some toxic, are discharged into waterways dissolved in solution. Most industries use water at some stage especially the industries that produce metals, wood and paper products, glass, fabrics, gasoline and oils. Water is used in industry, not only as a solvent but also for processing, washing, cooling, transporting and cleaning. The purification of water by removing suspended and dissolved substances is a huge industry. We will discuss some of these issues later.

QUESTIONS

1. (a) Define metabolism.
   (b) Write an equation to show the use of water as a reactant in photosynthesis.
   (c) Identify three examples of aqueous solutions in the human body.
   (d) Justify the description of blood as an aqueous solution.
2. Scientific research can have useful applications. Discuss this with reference to scientific research into the composition of blood and the use of blood substitutes including plasma expanders.
3. Identify uses of water in cleaning and discuss the significance of its solvent properties to health.
4. Research and outline the importance of the solvent properties of water to plants.

26 Solubility and Cycad Toxins

The solubility of toxins in water played an important role in removing the toxins from plants called cycads so that the cycads could be used as food.

Cycads are a group of very ancient plants. Cycads have lived on Earth for about 300 million years and dominated the Earth about 200 million years ago. They were the main plants in forests that existed on Earth during the Mesozoic era even before dinosaurs roamed the Earth. Cycads were the first seed bearing plants (they existed before there were any flowering plants on Earth). They are woody stemmed plants, and some have trunks that are underground.
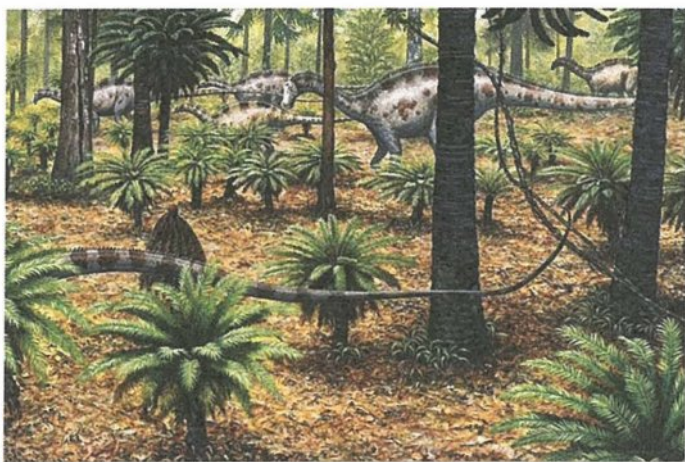
Figure 26.1 Dinosaurs in a cycad forrest.

About 250 species of cycads still exist today, thriving in tropical and subtropical areas, although in many areas the existence of some species is threatened. They live in the tropical and subtropical area of the east coast and in the south-west area of Western Australia. There are none in Victoria or South Australia, although there are fossil beds of ancient cycads in Victoria.

One reason cycads are interesting to chemists is because **cycads contain toxins in their tissues**.

A **toxin** is a substance which is poisonous to humans or other organisms. Many plants have, over many centuries, developed toxins in some part of their structure such as leaves and fruits. Toxins as part of plant structures are an important mechanism to protect them from organisms that would otherwise destroy them. There are a few types of insects that can eat cycads with no obvious ill effects, and the toxin absorbed into their bodies protects them against predators. Perhaps the development of toxins in their fronds and seed, prevented them from being eaten out of existence by dinosaurs?

Modern cycads are highly **toxic to vertebrates**. They contain chemicals, such as cycasin and macrozamin which are powerful neurotoxins (they interfere with the functioning of the nervous system) and carcinogens (they cause cancer). Eating cycads produces symptoms such as vomiting, diarrhoea and abdominal cramps, followed by loss of coordination and paralysis. This can lead to death from dehydration or liver failure. Low dose exposure can have cumulative effects. It can cause DNA mutations that lead to cancer, especially in the liver and kidneys and may also cause diabetes.
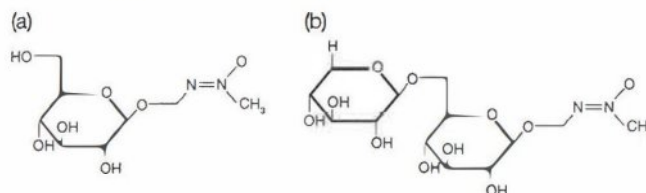
Figure 26.2 Cycad toxins. (a) Cycasin. (b) Macrozamin.

Macrozamia communis is the most commonly occurring and most widespread cycad in NSW. It is also the most southerly occurring cycad species in the world.

Name derivation: Macrozamia from the Greek makros (large) and Zamia (a genus of cycads).

Communis – latin for common as it is abundant in dense stands and sometimes dominates the shrub layer.

Its common name '**Burrawang**' is derived from the Dharuk language spoken by tribes living in the Sydney and Illawarra regions.

The cycad Macrozamia – before and after the fruit ripens.

Detailed information about the distribution of some cycads is not available because some species are at risk of extinction. Cycads have been harvested in the past to extract starch from their stems.

Macrozamia occur naturally along the coast and the slopes and ridges of the Great Dividing Range, extending from Taree to Bega. They are abundant in wet to dry sclerophyll forests. They prefer warm to hot summers and cold winters. They are also quite popular in suburban gardens, where they grow in pots or in the ground.

Figure 26.4 Distribution of *Macrozamia communis*.

Macrozamia is one of the cycads that has provided a good source of food for Aboriginals and Torres Strait Islanders. Like other cycads, Macrozamia have male and female cones on separate plants, the male cone releases pollen which is carried by wind to the female cones. The female cone swells and forms a fruit with seeds covered by the fleshy part which is usually bright orange to red in colour.

Cycads produce cones which have **large numbers of seeds** – each cone may contain hundreds of seeds. The hard kernel in the centre of these seeds is particularly toxic, but the outer fleshy part has for hundreds of years been a good **source of starch** in the diet of indigenous peoples. Aboriginal people are thought to have burnt areas around stands of cycads to remove plant competitors and thus increase the availability of cycad fruits as a food source.

Indigenous people in many areas of the world, including **Aboriginal and Torres Strait Islander peoples** have, over many hundreds of years, worked out independently a number of methods to detoxify cycad fruits so they can be eaten safely.

All parts of the plant are toxic. The toxins in the fruits of the female plants tend to be **relatively soluble in water**, more soluble than the starches desired for food. So one method to detoxify them, consists of pounding them, soaking in a stream for 4 to 5 days, then heating and drying. This process produces a paste or flour which can be baked to make bread free of toxins. Sago starch, a commonly used thickener, stabiliser and gelling agent used in the food industry, is also made from the pith of cycads.

Figure 26.5 Worldwide distribution of cycads.

QUESTIONS

1. Describe the importance of solubility to Aboriginal and Torres Strait Islander peoples in removing toxins from foods.
2. In some places the use of plants such as cycads is now discouraged. Suggest reasons for this.
3. Research one of the following topics. As with all research topics, before you start you should consult your teacher about the length of time your research should take and how your information is to be presented.
   (a) Find out which species of cycads grow in the area where you live and how they were processed and used by native people. Are they still used in this way? You might find it helpful to consult your local AECG group (Aboriginal Education Consultative Group) and local land council.
   (b) Cycads such as Macrozamia contains toxins. Research any other foods used by Aboriginal and Torres Strait Islander peoples that contain toxins, the types of toxins they contain and how the toxins are removed.
   (c) The toxicity of cycads to our pets and livestock.

Figure 26.6 A male cycad plant.

27 Precipitation

Sometimes when two clear solutions are mixed together they become cloudy and, when left standing for a while, a solid settles to the bottom of the container. This solid is called a precipitate.

A **precipitate** is an insoluble ionic compound, formed as a solid when two soluble ionic compounds are mixed.
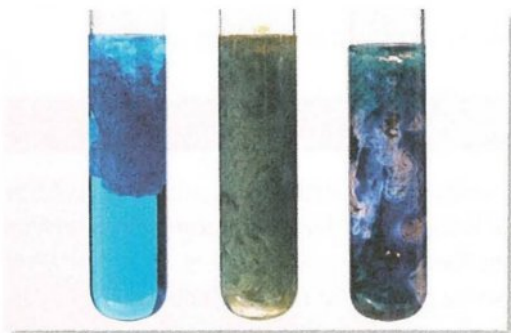

Figure 27.1 Insoluble hydroxide precipitates.

For example, potassium iodide and lead nitrate are both soluble ionic compounds. They dissolve in water to form clear, colourless solutions. However, if you add these two solutions together, a chemical reaction occurs – they produce a vivid yellow precipitate and another clear, colourless solution.

The symbolic equation for this reaction is:

$$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)$$
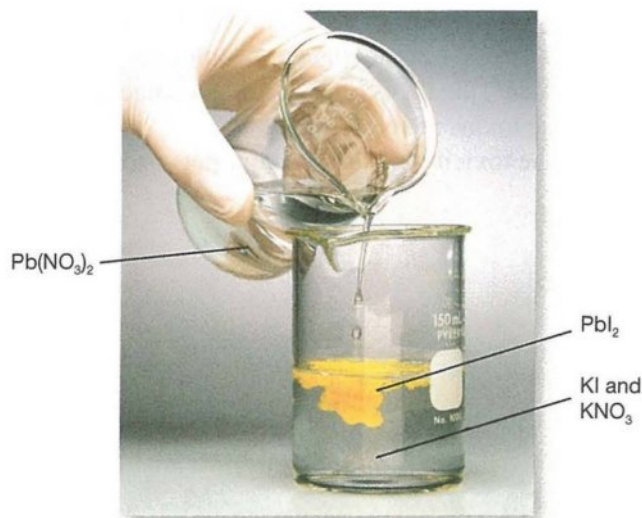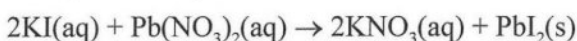
Figure 27.2 Precipitation of lead iodide.

When these two solutions are mixed, the ions present are K^+, I^-, Pb^{2+} and NO_3^-. The lead and iodide ions are attracted together very strongly. They form ionic bonds in a crystal lattice, so we see lead iodide precipitate out of solution. Because the lead and iodide ions are more strongly attracted to each other than to water, lead iodide (PbI_2) is insoluble in water.

The potassium and nitrate ions would form potassium nitrate, but this is soluble in water. The potassium and nitrate ions are attracted to water molecules more strongly than to each other – so the ions stay apart. We call K^+ and NO_3^- ions **spectator ions** as they do not take part in the precipitation reaction.

We can write an equation showing only the ions that are reacting. This is called an **ionic equation**. Since the spectator ions are not changed by the reaction we can leave them out. The ionic equation for this reaction then becomes:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$
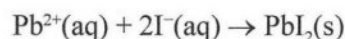
We can predict when a precipitation will form by using solubility rules.

Table 27.1 Some solubility rules.

Soluble	Insoluble
• All nitrates. • All acetates. • All sulfates (except those of Ca, Ba, Pb, Hg and Ag). • All chlorides, bromides and iodides (except Pb, Hg, Ag). • All ammonium compounds. • All sodium and potassium compounds.	• All carbonates (except those of Na, K, NH_4^+). • All oxides and hydroxides (except Na, K, Ca, Mg, Ba and NH_4^+). • All sulfides (except those of Na, K, Mg, Ca, Ba and NH_4^+). • All phosphates (except Na, K, and NH_4^+).

QUESTIONS

1. Define the following terms.
    (a) Precipitate.
    (b) Spectator ion.
2. Using the solubility rules in Table 9.1, identify any precipitate formed when the following pairs of solutions are mixed.
    (a) Lead nitrate and potassium iodide.
    (b) Sodium chloride and magnesium sulfate.
    (c) Ammonium carbonate and calcium chloride.
    (d) Silver nitrate and potassium chloride.
    (e) Sodium sulfate and barium nitrate.
3. For each part of Question 2, write ionic equations identifying any precipitate and spectator ions.
4. Research applications of precipitation reactions in everyday life or in industry.
5. Check your knowledge with this quick quiz.
    (a) Identify the term for an insoluble substance produced by a reaction in solution.
    (b) Ions that take no part in a precipitation reaction are called .... ions.
    (c) Cloudiness indicates the formation of a ....

28 Investigating Solubility Rules

Solubility rules are based on the results of **experiments** that involve mixing solutions to see if a precipitate is produced.

A few drops of solutions containing different ions can be mixed in a test tube and the formation of any precipitate indicates that an insoluble compound is formed by mixing the two ions.

Alternatively, a chart can be used like the one shown in Figure 28.1 to record experimental results. This allows many tests to be carried out quickly using minimal quantities of chemicals in solution. This chart shows the results of an experiment where a sheet of plastic is ruled up the same as the result chart and a group of students is given a series of dropper bottles, each containing one of the ions shown as headings for the columns and rows. Two dropper bottles are selected and a drop from each is placed in the relevant named squares.

For example, in the square at the top left corner, the students would place a drop of sodium ions and also a drop of chloride ions.

If no precipitate is produced, the relevant square is left blank on the record sheet below. If a precipitate is produced then X in the appropriate square indicates that a precipitate was formed and its colour would be recorded.

If a chemical is produced which is only slightly soluble, then a small amount of precipitate may occur and this may look like a cloudy solution.

Where there is **no X**, the ions **do not form a precipitate**. For example, in the top left hand corner, the mixing of sodium and chloride ions does not produce a precipitate because sodium chloride is soluble.

Based on such results we can make **generalisations**, for example:

- If you look at the last column, on the right hand end of the table, you can see that all the metal ions listed have insoluble carbonates except sodium carbonate which is soluble. For example:
$$Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$$
This tells us that most carbonates are insoluble.

- The top line of the table shows us that sodium ions did not form a precipitate with any of the anions. This indicates that sodium salts tend to be soluble.

QUESTIONS

1. (a) Describe how you carried out a first-hand investigation using microtechniques to determine the solubility of some salts in solution through precipitation reactions.
   (b) Identify safety precautions you needed to take when carrying out this experiment.

2. Based on the results shown in Figure 28.1, deduce a generalisation about the following.
   (a) The solubility of hydroxides.
   (b) The solubility of silver compounds.
   (c) The solubility of Cu^{2+} compounds.

3. (a) Write equations for all precipitate reactions that are indicated in the result chart of Figure 28.1.
   (b) Explain why it is important that this experiment be carried out using dilute solutions.

4. Some students carried out the experiment described in the text, using dilute solutions, but found that most squares contained a precipitate. Suggest what could have caused these results.

When magnesium ions and hydroxide ions are mixed, insoluble magnesium hydroxide forms as a precipittate.
$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$$

All sodium salts are soluble.

No X indicates a precipitate does not form when these ions are mixed, e.g.

	Cl^-	NO_3^-	I^-	OH^-	CO_3^{2-}
Na^+					
Mg^{2+}				(X)	X
Ca^{2+}					X
Ba^{2+}					X
Zn^{2+}				X	X
Fe^{2+}				X	X
Cu^{2+}				X	X
Ag^+	(X)		X	X	X

Magnesium and carbonate ions form a precipitate of insoluble magnesium carbonate.
$$Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

When silver ions and chloride ions are mixed, insoluble silver chloride is produced as a precipitate.
$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

All nitrates are soluble.

All metal ions form insoluble carbonates except sodium carbonate which is soluble. So most carbonates are insoluble, e.g.
$$Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$$

Figure 28.1 Experimental solubility chart shows some typical results and how you could interpret them.

29 Solubility Tables and Measurement

You will recall that **solubility** is a measure of the degree to which a solute is soluble in a solvent. The solubility of a substance is the amount of that substance that will dissolve in a given amount of solvent. Usually water is the solvent used.

Different ways of expressing solubility

A substance is said to be soluble if more than 0.1 g of that substance dissolves in 100 mL of solvent. A substance is insoluble if mixing equal volumes of 0.1 mole per litre solutions produces a precipitate.

Substances with a solubility greater than 10^{-1} moles/litre of solution are considered soluble, whereas those with a solubility less than 10^{-4} moles/litre are considered insoluble. In between these limits substances are considered slightly or partially soluble.

Measuring solubility

A known amount of the solvent, e.g. 100 mL of water is placed in a container such as a beaker.

The chemical to be tested is added, a little at a time and stirred vigorously. This is repeated until the point is reached where the substance does not all dissolve – a **saturated solution** is reached. For example, 35.7 g of sodium chloride will dissolve in 100 mL of water at 20°C, so we say the solubility of NaCl is 35.7 g/100 mL water at 20°C.

The solubility of substances can be summarised in a solubility table which shows the amount of each substance that will dissolve at different temperatures and pressures, for example Table 29.1. This shows the amount (in grams) of some ionic compounds that will dissolve in 100 mL water, at three different temperatures. All measurements are made at a pressure of 1 atmosphere.

Table 29.1 Table of some solubilities (mol L^{-1}).

Ionic compound	0°C	20°C	80°C
Aluminium chloride	43.9	45.8	48.6
Ammonium acetate	102	143	533
Barium chloride	31.2	35.8	52.5
Calcium sulfate	0.223	0.255	0.234
Silver nitrate	122	216	585
Sodium carbonate	7	21.5	43.9

You can see at once that solubility varies enormously, even among compounds that are all ionic. You can also see that, for these solids, it increases as the temperature increases.

Note that solubility can also be dependent on the presence of other substances. For example, organic substances can be made less soluble if an ionic substance is added; the solubility of aluminium in water is increased if the water is more acidic.

QUESTIONS

1. Describe the experiment you performed to determine the solubility of a substance at different temperatures.
2. Based on information in Table 29.1, answer the following questions about the compounds listed.
   (a) Which of the compounds listed are the two most soluble?
   (b) Which compound is the least soluble?
   (c) Is there another compound listed that is not very soluble?
3. The list below shows the solubilities in water of a number of gases at 293 K.

Gas	Solubility (g/100 g water)	Gas	Solubility (g/100 g water)
Ammonia	52.9	Hydrogen	0.00016
Carbon dioxide	0.169	Hydrogen sulfide	0.385
Carbon monoxide	0.0028	Methane	0.0023
Chlorine	0.729	Nitrogen	0.0019
Ethane	0.0062	Oxygen	0.0043
Ethene	0.0149	Sulfur dioxide	11.28

   (a) At what temperature, in degrees Celsius, was the solubility of these gases tested?
   (b) List the gases in order of solubility, starting from the least soluble.
   (c) Based on solubility, which of the gases listed would make the largest contribution to acid rain formation? Explain.
4. Four different salts are dissolved in water at 50°C and the following data recorded.

Salt	Solubility at 50°C
P	10 g in 50 g water
Q	15 g in 60 g water
R	18 g in 40 g water
S	20 g in 70 g water

List the four salts in order of increasing solubility.

30 Solubility and Temperature

The **solubility of a substance varies with temperature**.

Scientists plot the relationship between the temperature and solubility of a substance on a **solubility curve**. This shows the maximum mass of a solute that can be dissolved in 100 g of a solvent at any given temperature. You can use a solubility curve to determine the solubility of a substance at any temperature shown on the graph.

Dissolving solids

The solubility of a solid solute depends on the temperature of the solvent. Solids generally become more soluble as the temperature increases. Adding heat, causes increased vibration of particles. This breaks the bonds holding the molecules in the solid together and also the bonds holding the molecules of water together. New bonds form between the solute and the solvent – we say that the solute dissolves.

There are a few exceptions, for example calcium sulfate and sodium sulfate which become less soluble as temperature increases. Also the solubility of sodium chloride and potassium chloride show little variation with temperature.
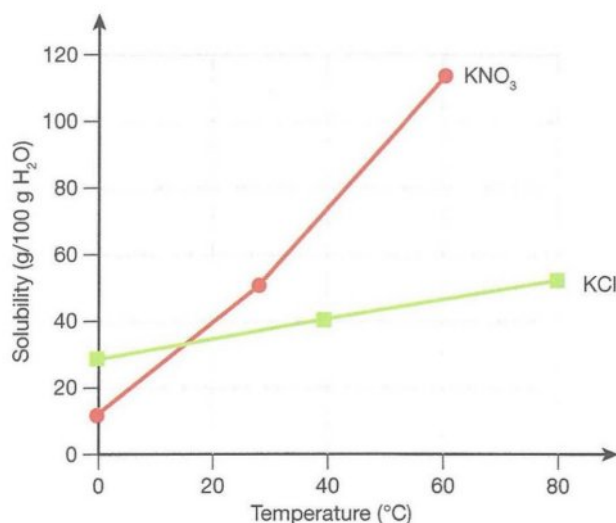

Figure 30.1 Solubility of solids.

Dissolving gases

The solubility of a gas in a solvent depends on the temperature of the solvent, but gases are more soluble at a lower temperature. Adding heat increases the kinetic energy of the gas particles so they break intermolecular bonds, and escape from the solution – less gas remains dissolved in the solvent.
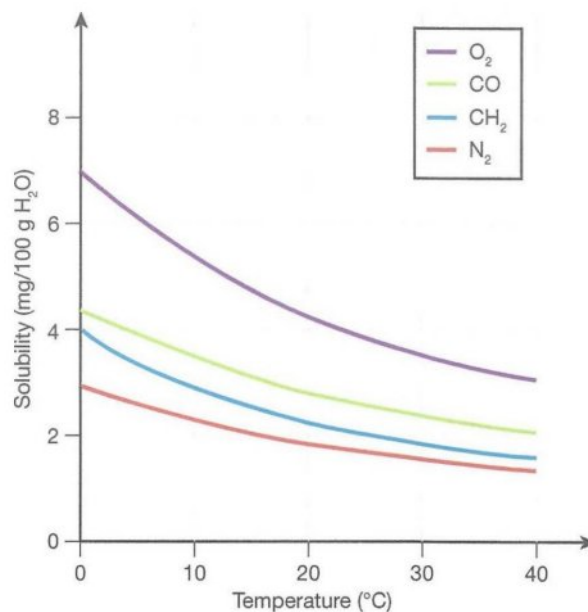
Figure 30.2 Solubility of gases.

You have probably noticed that a glass of soft drink, left sitting on the table on a warm day will go flat. This is because soft drink contains **carbon dioxide gas** dissolved in it to make the drink fizzy. As the soft drink warms up, the gas comes out of solution, leaving the drink without bubbles (flat).

When power plants discharge warm water into lakes and rivers, they can kill the aquatic plants and animals living there. The rise in temperature of the water means that less atmospheric **oxygen gas** dissolves in the water, and both plants and animals need this oxygen for respiration. Studies show that 4 to 5 parts per million (ppm) of dissolved oxygen is the minimum amount that will support a fish population and it is usually around 9 ppm or higher in good fishing waters.

Other factors besides temperature also affect the concentration of dissolved gases. For example, water pollution and the saltiness of water can affect the concentration of dissolved oxygen. At the same temperature and pressure, salt water holds about 20% less dissolved oxygen than fresh water.

Dissolving liquids

When a liquid such as ethanol dissolves in water, we say it is miscible in water. A liquid which does not dissolve forms a separate layer either above or below the water (depending on density) and it is referred to as immiscible.

For liquids which are miscible with water, temperature has little effect on their solubility. The solubility of an organic liquid is affected more by the number of carbon atoms present and also its polarity.

1. Complete the following statements.
   (a) In general, solids are (more/less) soluble in water at higher temperatures, whereas gases become (more/less) soluble in water as temperature rises.
   (b) An increase in temperature of water has the least effect on the solubility of a (solid, gas/liquid).

2. Figure 30.1 shows the solubility with temperature change for two ionic compounds.
   (a) Name those compounds.
   (b) Outline any trend shown by these two graphs.
   (c) Which compound is more soluble at 10°C and at 100°C?
   (d) Do both solids show the same increase in solubility as the temperature increases from 0°C to 100°C?

3. Most ionic solids dissolve faster in hot water than cold water. Explain in terms of the kinetic particle theory.

4. Use Figures 30.1 and 30.2 to determine the solubilities of the following.
   (a) KNO_3 at 30°C.
   (b) KCl at 30°C.
   (c) CH_4 at 30°C.
   (d) O_2 at 30°C.

5. The solubility curve for potassium bromide is shown below.

Solubility curve for KBr
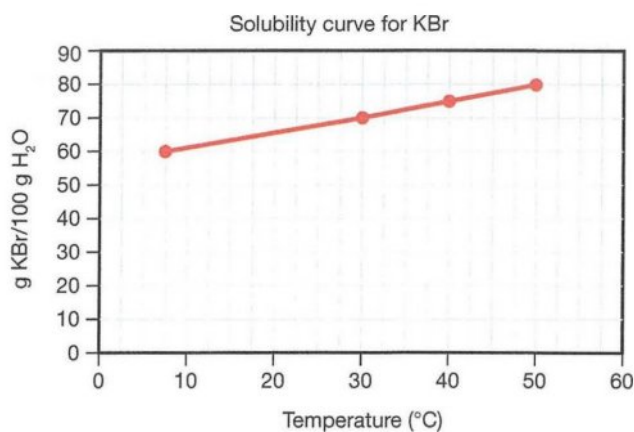
Compare the solubility of potassium bromide at 10 and 50 degrees Celsius and determine how much potassium bromide will crystallise out when the saturated solution is cooled from 50°C to 10°C.

6. For Figure 30.2, describe any trend evident in the solubility curves.

7. The following table gives data of the concentration of a gas dissolved in water at different temperatures. Plot a line graph of water temperature versus concentration of this gas.

Temperature (°C)	Concentration of dissolved gas (mg L^{-1})
0	14.5
20	8.5
25	8.0
40	6.0

8. The main salt in sea water is sodium chloride and its concentration in the oceans of the world varies only from 33 to 37 grams per litre. From 2011 to 2015 NASA mapped the salinity of the surface waters of the ocean from space, using a sensor in a satellite orbiting the Earth.
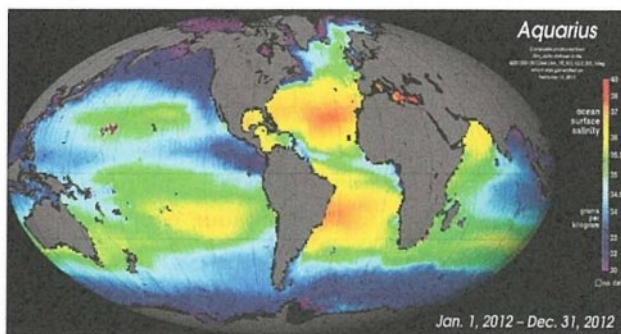
They found that, although the overall salinity is fairly constant, there are areas where it does vary in a way that could not be accounted for by differences in temperature of the water. As shown in the map above, there is a distinct decrease in salinity near the equator and also at both poles.
   (a) Research reasons for this variation.
   (b) Where is water at its saltiest?
   (c) Why is it important for scientists to study the salinity of the ocean?

9. Some people claim to be able to taste a difference in tea and coffee when brewed at different temperatures. Suggest what could cause these differences in taste.

10. Deduce how you could make use of the different solubilities of solids in water to separate the components of a mixture, for example a mixture of sand and salt (sodium chloride).

11. Research one of the following.
   (a) Sources of dissolved oxygen in ocean water.
   (b) The effects of environmental change on dissolved oxygen concentrations of the oceans and the organisms that live there.
   (c) Factors other than temperature that can affect the dissolved oxygen concentration of waterways.

31 Solubility Curves

A solubility curve provides a graphical representation of the solubility of a substance. For example, Figure 40.1 shows a solubility curve for copper sulfate. This shows the maximum mass of copper sulfate that can be dissolved in 100 g of water at any temperature from 0°C to 100°C. You may have produced a curve such as this in the laboratory.
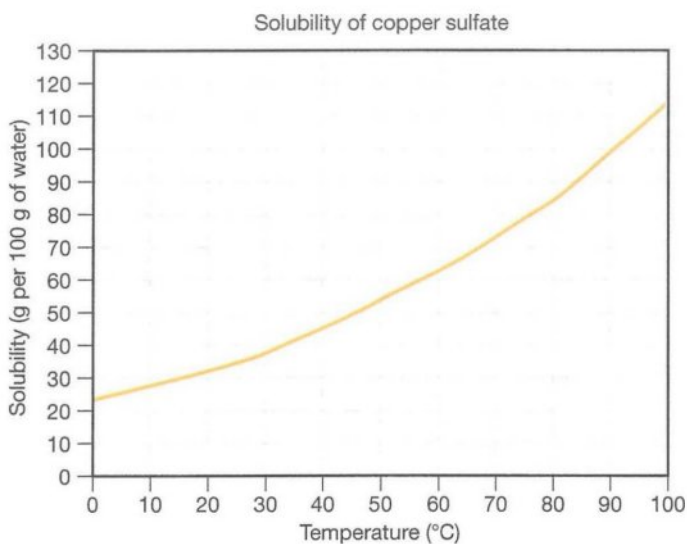

Figure 31.1 Solubility curve for copper sulfate.

To understand solubility curves and their uses, you need to first understand saturated solutions.

Saturation

You have already seen that to measure solubility you add more and more of a solute to water, constantly stirring, until you reach a point where no more of the solute will dissolve. At that point the solution is said to be a **saturated solution**. If a saturated solution is cooled, some of the solute will come out of solution. The maximum amount of solute dissolved at each temperature can be plotted to produce a solubility curve.

Using Figure 31.1, you would have a saturated solution of copper sulfate if you dissolved 30 g of copper sulfate in 100 g of water at 15°C. In fact, any solution whose concentration falls along the line of the graph in Figure 31.1 would be a concentrated copper sulfate solution.

Sometimes a hot, saturated solution can be cooled slowly and carefully to avoid crystallisation. The solution formed is called a **supersaturated solution** because it contains a higher concentration of the solute than the solubility curve shows is needed to form a saturated solution. However, as soon as the supersaturated solution is disturbed, the excess dissolved solute will crystallise out.

Uses of solubility curves

Solubility curves are very useful. They can be used as a **quantitative and predictive tool in biological, domestic and industrial contexts**. They allow chemists to know accurately the temperature at which crystallisation will occur and the amount of the chemical which will crystallise at any given temperature. Their uses include the following.

*   **Find out how much of a solid will dissolve at any given temperature**. For example, Figure 31.1 tells us that at 40°C, we can dissolve 46 grams of copper sulfate in 100 g of water. This is important in industries for example, solubility curves for fertilisers help determine just how much of a particular fertiliser can be dissolved in a given volume of water. Any more fertiliser added would be wasted as it would not dissolve and so could not be taken up by plant roots.

*   Show **how solubility of a substance changes** over a range of temperatures. The slope of the graph in Figure 31.1 tells us that the solubility of copper sulfate increases with increasing temperature.

*   **Compare the solubilities of different substances**. Comparing solubility curves for different solutes allows you to see which substances are more or less soluble at any temperature and how this changes with variations in temperature.

*   **Work out the mass of crystals which will be deposited when a saturated solution is cooled**. If the solubility of 100 mL of a solvent is 40 g at 60°C and 100 g at 80°C, then cooling a saturated solution of that substance from 80°C to 60°C will result in $(100 - 40 = 60)$ grams of that substance being deposited in the form of crystals as it comes out of solution.

*   Solubility curves can be used to **determine the purity of proteins and also drugs such as insulin**. Solubility in water is an important property as it indicates the likely biological activity of a drug and it must be soluble in water to be able to be carried through the blood and act at its target area.

*   Solubility curves can be **used to separate, concentrate and purify chemicals** in many situations such as the pharmaceutical, food and cosmetic industries. Different solutes will crystallise at different temperatures due to their different solubilities. For example, amino acids and antibiotics must be extracted from the mixture for use in foods, medicines and polymers. Solubility curves can be used in this process of separation.

Products such as sugar and salt (sodium chloride) are also usually **extracted from solutions by crystallisation**. Margarine, cooking fat and ice cream can be obtained using a crystalliser which continually stirs the product while removing heat, until a temperature is achieved at which it crystallises. The crystals are so tiny (10 to 20 microns) that the texture is smooth and creamy.

QUESTIONS

1. Distinguish between the terms, unsaturated, saturated and supersaturated.

2. The graph below compares the solubility of three ionic salts at different temperatures. Answer the questions below using information from this graph.

Solubility of three ionic salts.
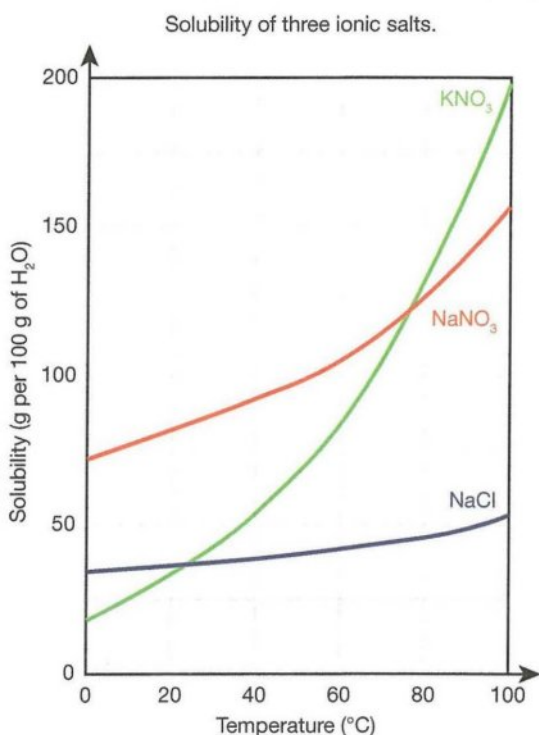
(a) Is it correct to say that potassium nitrate is the most soluble of these three compounds?

(b) Based on this information alone, could you make any generalisations about the solubility of sodium salts, potassium salts or nitrates?

(c) Based on the information in the graph, how could you separate a mixture of potassium nitrate and sodium nitrate?

(d) 150 g of sodium nitrate is added to 100 mL of water at 80°C making a supersaturated solution. What mass of crystals would form if this solution is cooled to 50°C?

(e) At what temperature do $NaNO_3$ and KNO_3 have the same solubility?

(f) How much sodium nitrate will be needed to dissolve in 100 g of water to form a saturated solution at 50°C?

(g) Which substance shows the least effect of temperature on solubility?

(h) 60 g of potassium nitrate is added to 100 g of water at 55°C and allowed to cool. At what temperature will the first crystals appear?

3. Answer the questions below about the solubility of some salts based on their solubility curves in the graph.
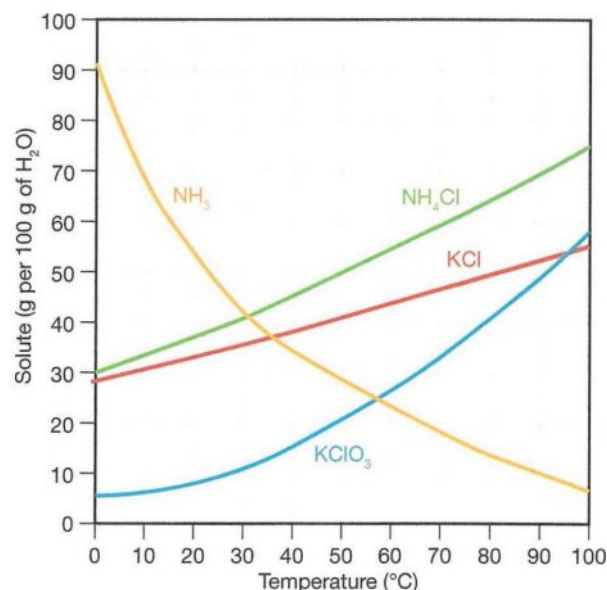
(a) Does temperature have the greater effect on solubility for potassium or ammonium chloride?

(b) Which of these four solutes is the least soluble at a temperature of 50°C?

(c) Identify any substance(s) graphed which is a gas.

(d) At what temperature do potassium chloride and ammonium chloride have the same solubility?

(e) If you add 60 g of potassium chloride to 100 g of water at 80°C, how much solid will remain undissolved?

(f) How much ammonium chloride will dissolve in 50 mL water at 50°C?

(g) Compare the solubilities of ammonia (NH_3) and potassium chlorate ($KClO_3$).

4. Water is used for cooling purposes in industries such as in the production of electricity. During this process the water becomes hot. An electricity generation plant used water from a lake to cool equipment. The water then flowed through channels exposed to the atmosphere to cool it and was released back into the lake while still slightly warm. Biologists observed a large drop in the population of aquatic organisms in the lake. Suggest reasons for this.

5. Research and discuss uses of solubility curves in biological, domestic or industrial contexts.

32 Saturated Solutions, K_{sp} and Solubility

When a salt such as sodium chloride dissolves in water it completely dissociates into separate hydrated cations and anions:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

When silver chloride is first added to water, there are no silver or chloride ions present. As it dissociates, these ions are produced, and as their concentrations increase, they are more likely to collide and re-form solid silver chloride. Eventually equilibrium is reached.
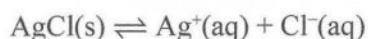
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

No more solid can dissolve, this solution is said to be **saturated**.

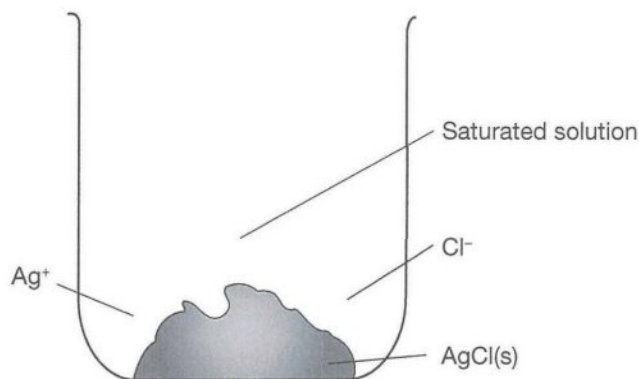**Figure 32.1** A saturated solution of AgCl.

An equilibrium expression can be written for this reaction:

$$K_{eq} = \frac{[Ag^+(aq)][Cl^-(aq)]}{[AgCl(s)]}$$

The concentration of AgCl(s) is a constant and can be thought of as having a value of 1.

Excess solid present at equilibrium has no effect on the position of equilibrium. Adding more solid would increase the surface area exposed to the water and you might expect that this would make more of the solid dissolve. Increasing the surface area not only increases the rate of dissolving. However, it also increases the rate at which solid is re-formed from dissolved ions, because this process also takes place on the surface of the solid. So, adding more solid increases the rate of reaction in both directions equally, and that means that the equilibrium position does not change. Hence, we can leave any solids out of the equilibrium constant calculation, and we can write:

$$K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$

A high K_{sp} value tells us that a salt is very soluble, whereas a low value indicates low solubility. You can see some examples in the next table.

Table 32.1 Some solubility constants, at 25°C.

Ionic solid	K_{sp}	Ionic solid	K_{sp}
$PbCl_2$	1.6×10^{-5}	$CaCO_3$	4.7×10^{-9}
$AgCl$	1.6×10^{-10}	$CuCO_3$	2.5×10^{-10}
$AgBr$	5.0×10^{-13}	$MgCO_3$	4.0×10^{-5}
AgI	1.5×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
Ag_2SO_4	1.2×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}
$CaSO_4$	2.5×10^{-5}	$Al(OH)_3$	5.0×10^{-33}
$PbSO_4$	1.3×10^{-8}	FeS	4.0×10^{-19}
$BaSO_4$	1.1×10^{-10}	Cu_2S	1.2×10^{-49}

We can calculate the K_{sp} expression using the concentration of ions present in the solution at equilibrium.
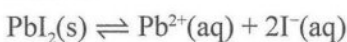
Example 1:
In a saturated solution of lead(II) iodide at equilibrium, held at constant temperature, the concentration of ions present was measured as:
Concentration of lead(II) ions $[Pb^{2+}] = 0.0117$ mol L^{-1}
Concentration of iodide ions $[I^-] = 0.0234$ mol L^{-1}

Calculate the K_{sp} value for lead(II) iodide at this temperature.

Answer:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$
$$\begin{aligned} K_{sp} &= [Pb^{2+}(aq)][I^-(aq)]^2 \\ &= 0.0117 \times 0.0234^2 \\ &= 6.4 \times 10^{-6} \end{aligned}$$

The solubility product constant of lead(II) iodide was 6.4×10^{-6}.

Solubility versus solubility constant

Make sure you understand the difference between the solubility of a substance and its solubility product. The difference between solubility and solubility product is important when describing the solubility of ionic salts that are slightly soluble or almost insoluble.

The solubility product (K_{sp}) is an **equilibrium constant**, and, just like other solubility constants you have looked at, it is affected by temperature. *But* at any one temperature, there is only one value for the solubility product of each chemical. There is only one value for K_{sp} for any solid at a particular temperature.

On the other hand, **solubility is an equilibrium position** and it has a huge number of possible values at any one temperature, depending on the conditions such as concentration. For example, a silver chloride solution becomes saturated (forming a precipitate) at different points depending on the concentration of silver and chloride ions present.
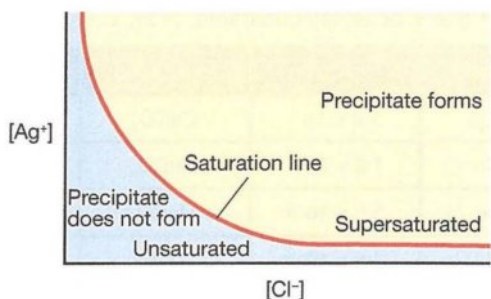
Figure 32.2 Formation of a silver chloride precipitate as ion concentration changes (temperature constant).

Notice that solubility is defined in terms of concentration of solute whereas K_{sp} is defined in terms of activity of ions and solute rather than concentration.
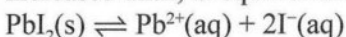
We can **calculate K_{sp}** of a compound **from its solubility**. The next example is just a step harder than Example 1, because instead of being told the concentration of ions at equilibrium, you have to first work that out from the solubility.

Example 2:
The solubility of lead(II) iodide is 0.028 mol L^{-1} at constant temperature. Calculate the K_{sp} value for lead(II) iodide at this same temperature.

Answer:
Initially the system contained only solid lead iodide and water, with no lead or iodide ions. As the lead iodide dissociated, the concentration of lead and iodide ions increased until, at equilibrium:
$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
Solubility of PbI_2 = 0.028 mol L^{-1}

The PbI_2 releases twice as many iodide ions compared to the number of lead ions, as seen in the equation. So:

$[Pb^{2+}]$ at equilibrium = 0.028 mol L^{-1}

$[I^-]$ at equilibrium = $2 \times 0.028 = 0.056$ mol L^{-1}

We now have the concentration of ions present at equilibrium so we can calculate K_{sp}.

$K_{sp} = [Pb^{2+}(aq)]\,[I^-(aq)]^2$
$\quad = 0.028 \times 0.056^2 = 8.78 \times 10^{-5}$
K_{sp} for lead(II) iodide = 8.78×10^{-5}

Note: Did you notice that the two calculations for the K_{sp} of PbI_2 (Examples 1 and 2) have produced different answers? What could cause this to happen? The concentrations must have been measured at different temperatures.

Calculating molar solubility

We can also do the reverse calculation. We can use the K_{sp} values of salts to calculate their molar solubility.

Example 3:
If the K_{sp} of silver iodide (AgI) is 1.5×10^{-16}, calculate its molar solubility.

Answer:
$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$
$K_{eq} = \dfrac{[Ag^+(aq)]\,[I^-(aq)]}{[AgCl(s)]}$
If $[Ag^+]$ at equilibrium = s mol L^{-1}
Then $[I^-] = s$ mol L^{-1}
$K_{sp} = [Ag^+(aq)]\,[Cl^-(aq)]$
$1.5 \times 10^{-16} = s^2$
So solubility = $\sqrt{1.5 \times 10^{-16}}$
$\quad = 1.225 \times 10^{-8}$ mol L^{-1}
The solubility of AgCl = 1.225×10^{-8} mol L^{-1}

QUESTIONS

1. (a) Define solubility.
   (b) What is K_{sp}?
   (c) Outline the relationship between solubility and K_{sp}.
2. Based on the K_{sp} values in Table 32.1, list the following compounds in order of solubility, starting with the most soluble:
   AgBr, AgCl, AgI, BaSO$_4$, CaSO$_4$
3. If the K_{sp} of silver bromide (AgBr) = 5.0×10^{-13}, calculate its solubility at the same temperature in mol L^{-1}.
4. If the K_{sp} of magnesium hydroxide (Mg(OH)$_2$) = 8.9×10^{-12}, calculate its molar solubility at the same temperature in mol L^{-1}.
5. If the solubility of copper(I) bromide is experimentally measured at 2.5×10^{-4} mol L^{-1}, calculate its K_{sp} value at the same temperature.
6. The solubility of lead chromate (PbCrO$_4$) in water is measured as 1.34×10^{-7} mol L^{-1}. Calculate the solubility product for lead chromate.
7. Aqueous solutions containing sulfate ions and barium ions are mixed in a beaker and a white precipitate of barium sulfate forms. The K_{sp} of BaSO$_4$ is 1×10^{-10} at 25°C.
   (a) Write an ionic equation for the precipitation of BaSO$_4$.
   (b) Write the equilibrium constant expression for the reaction.
   (c) Write the expression for the solubility product of BaSO$_4$.
   (d) Calculate the solubility of BaSO$_4$ in water at 25°C.
8. (a) Outline an experiment you could carry out to measure the solubility product (K_{sp}) of a sparingly soluble salt.
   (b) 5.7 grams of silver sulfate will dissolve in one litre of water. Calculate:
      (i) The solubility of silver sulfate.
      (ii) The concentration of ions present at equilibrium.
      (iii) The K_{sp} value at the same temperature.

33 Predicting the Formation Of a Precipitate

You have used K_{sp} values to:

- Calculate the concentration of ions in a saturated solution.
- Calculate the solubility of an ionic compound.
- Now you will use it to see whether or not a precipitate forms when ionic solutions are mixed.

You will recall that a precipitate is an insoluble ionic solid formed when cations and anions combine in aqueous solution. A precipitate does not always form when ions react in solution. The ability to predict when a precipitate will form can be quite useful. Precipitates can help determine the identity of ions in solution, they can be used to remove unwanted chemicals from the water supply, and to treat waste water, they are used in industrial productions, and precipitation can be used to extract metals and strengthen alloys.

K_{sp} and predicting precipitation

You can use K_{sp} to decide whether or not a precipitate will form when two aqueous solutions are mixed. Some of the salt will be precipitated until the ionic product is equal to the solubility product.

A precipitate forms when ionic product > K_{sp}.

Table 33.1 Ionic product, K_{sp} and precipitation.

Factor	Solution is	Precipitation
Ionic product < K_{sp}	Unsaturated	No precipitation
Ionic product = K_{sp}	Saturated	Solution at equilibrium precipitation
Ionic product > K_{sp}	Supersaturated	Precipitation

(A supersaturated solution contains more of the dissolved substance than could be dissolved under normal circumstances, for instance, if you add more ions to an already saturated solution.)
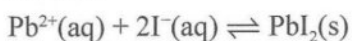
Example:
A solution containing lead ions is mixed with a solution containing iodide ions.
$[Pb^{2+}] = 1.0 \times 10^{-3} \, mol \, L^{-1}$
$[I^-] = 2.0 \times 10^{-3} \, mol \, L^{-1}$
Will a precipitate occur if $K_{sp} = 4.0 \times 10^{-9}$?

Answer:

$Pb^{2+}(aq) + 2I^-(aq) \rightleftharpoons PbI_2(s)$
Ionic product $= [Pb^{2+}(aq)] \, [I^-(aq)]^2$
$= (1 \times 10^{-3}) \, (2 \times 10^{-3})^2$
$= 4 \times 10^{-9}$
$K_{sp} = 4.0 \times 10^{-9}$

The precipitate will occur and the mixture will be at equilibrium.

The common ion effect

Sometimes two mixed solutions contain a common ion and this reduces the solubility of any precipitate forming – this is called **the common ion effect**. This effect occurs regardless of the solubility of the salt – it occurs for both very soluble and sparingly soluble salts.

A **common ion** refers to an ion that is entering the solution from two different sources, for example adding sodium chloride to a silver chloride precipitate at equilibrium – they both share a common ion (Cl^- ion).

The effect of adding the common ion is that it reduces the solubility of an ionic precipitate.

The common ion effect can happen if you have a solution, e.g. lead iodide and you add to it another solution containing either lead ions or iodide ions.

The common ion effect can also happen if you dissolve a salt in a solution instead of in water, for instance, if you dissolved copper sulfate in copper carbonate solution or in sodium sulfate solution.

In all of these examples an ion is being introduced to the mixture from two sources.

Why does having a common ion affect the solubility of a salt?

Adding sodium chloride to a silver chloride precipitate would reduce the solubility of the silver chloride. This can be predicted by Le Châtelier's principle.

Imagine a silver chloride precipitate and solution is at equilibrium: $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

Then more chloride ions are added, for example by adding sodium chloride solution.

From what you already know about disturbing an equilibrium, you can probably predict what will happen.

The equilibrium will move right to use up the added Cl^- ions and try to return the equilibrium back towards its original position (Le Châtelier).

Moving the equilibrium right means that more salt precipitates, in other words, the silver chloride has become less soluble.

Solubility has been decreased by adding a common ion (chloride ions).

This also means that silver chloride will be more soluble in pure water than in a salt water. If silver ions or chloride ions are already present in the solute, this will reduce the solubility of silver chloride.

1. Identify three ways in which you can use the solubility product constant (K_{sp}).

2. Equal volumes of 0.02 mol L^{-1} thallium nitrate ($TlNO_3$) and 0.004 mol L^{-1} sodium chloride are mixed. K_{sp} for $TlCl = 2 \times 10^{-4}$. Will a precipitate be formed?

3. Calculate the silver ion concentration in a saturated solution of silver carbonate if K_{sp} for silver carbonate $= 6.16 \times 10^{-12}$.

4. 100 mL of a 0.004 mol L^{-1} $MgCl_2$ solution is mixed with 100 mL of 0.005 mol L^{-1} solution of K_2CO_3. If the solubility product of magnesium carbonate is 1×10^{-5}, predict whether a precipitate will form.

5. The solubility constants of two salts are provided in the table.

Salt	K_{sp}
Silver chloride (AgCl)	2.0×10^{-10}
Silver carbonate (Ag_2CO_3)	8.0×10^{-12}

   (a) Can you determine which salt is more soluble just by looking at K_{sp} values?

   (b) Calculate the solubility (in mol L^{-1}) of AgCl in a 0.10 mol L^{-1} solution of NaCl.

   (c) Calculate the solubility (mol L^{-1}) of silver carbonate.

   (d) Compare the solubility of silver chloride and silver carbonate.

6. (a) What is a common ion?

   (b) Describe the effect of mixing solutions containing a common ion.

7. Calcium fluoride is a sparingly soluble salt.

   (a) Write an equation to show the precipitation of calcium fluoride in aqueous solution from its ions.

   (b) State the solubility product expression (K_{sp}) for calcium fluoride.

   (c) The K_{sp} for calcium fluoride $= 3.2 \times 10^{-11}$. 500 mL of a 2×10^{-3} mol L^{-1} aqueous solution of calcium ions is mixed with 500 mL of a 4×10^{-2} mol L^{-1} solution of fluoride ions. Describe what happens to the equilibrium reaction and deduce whether a precipitate will be formed. Show all working and explain your reasoning.

8. Calcium carbonate forms a saturated solution with $K_{sp} = 5.0 \times 10^{-10}$.

   (a) What is the concentration of ions present in the solution?

   (b) Calcium carbonate is dissolved in a 0.1 mol L^{-1} solution of sodium carbonate. Calculate its solubility in this sodium carbonate solution.

9. Barium sulfate is dissolved in water and then in a solution of barium nitrate. What effect will dissolving the barium sulfate in barium nitrate have on the solubility of the barium sulfate. Explain.

10. Check your knowledge with this quick quiz.

    (a) K_{sp} values can be used to:
       (i) Calculate the concentration of .... in a saturated solution.
       (ii) Calculate the .... of an ionic compound.
       (iii) To see whether or not a .... forms when ionic solutions are mixed.

    (b) Solubility can be (increased/decreased) by the addition of a common ion.

    (c) Identify a way of bringing about the common ion effect.

    (d) If you had a saturated solution of calcium sulfate, what could you add to make the calcium sufate precipitate out?

11. Below is a list of answers given by students during tests on equilibrium. Decide which you think are true and which are false.

    (a) If the forward reaction in an equilibrium system is endothermic then the reverse reaction must be exothermic.

    (b) We know the reaction is at equilibrium because it has the same number of moles of reactants and products.

    (c) When you add a chemical to an equilibrium system, Le Châtelier's principle makes it go back to the way it was beforehand.

    (d) If you add a catalyst to a system at equilibrium, you will get more product.

    (e) The value of the equilibrium constant is not altered by adding a reactant to a system at equilibrium.

    (f) When you first set up an equilibrium reaction, Le Châtelier's principle determines the yield of product.

34 Revision Of Solution Equilibria

Use the following multiple choice questions to help you revise solution equilibria. If you are unsure about any questions, please consult your teacher.

1. The dissolution of ionic compounds in water occurs because water molecules are:
   (A) Neutral.
   (B) Polar.
   (C) Covalently bonded.
   (D) Uncharged.
2. All solutions are:
   (A) Coloured.
   (B) Colourless.
   (C) Clear.
   (D) Concentrated.
3. All solutions are:
   (A) Homogeneous mixtures.
   (B) Heterogeneous mixtures.
   (C) Precipitates.
   (D) Pure compounds.
4. When an ionic compound is placed in water or an aqueous solution, the breaking up of its ionic lattice is called:
   (A) Sedimentation.
   (B) Ionisation.
   (C) Precipitation.
   (D) Dissolution.
5. The photograph shows a chemical reaction.

Pb(NO₃)₂ — PbI₂ — KI and KNO₃
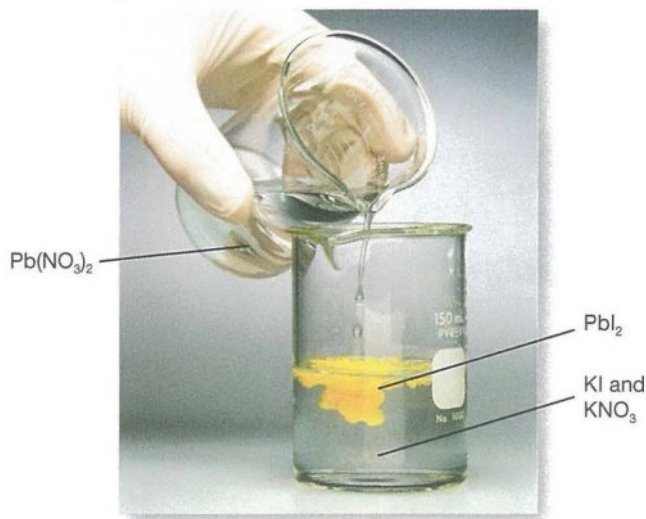
This photograph illustrates:
   (A) Sedimentation.
   (B) Ionisation.
   (C) Precipitation.
   (D) Removal of cycad toxins.

For the next three questions, use these solubility rules.

Table 34.1 Some solubility rules.

Soluble	Insoluble
• All nitrates. • All acetates. • All sulfates (except those of Ca, Ba, Pb, Hg and Ag). • All chlorides, bromides and iodides (except Pb, Hg, Ag). • All ammonium compounds. • All sodium and potassium compounds.	• All carbonates (except those of Na, K, NH₄⁺). • All oxides and hydroxides (except Na, K, Ca, Mg, Ba and NH₄⁺). • All sulfides (except those of Na, K, Mg, Ca, Ba and NH₄⁺). • All phosphates (except Na, K, and NH₄⁺).

6. From which of the following mixed solutions are you likely to get little or no precipitate formed?
   (A) Ammonium nitrate and sodium carbonate.
   (B) Silver nitrate and potassium bromide.
   (C) Sodium hydroxide and magnesium chloride.
   (D) Copper sulfate and barium chloride.
7. A test tube contains a mixture of the following ions: Cu^{2+}, Mg^{2+}, Pb^{2+} and Ag^+. Dilute hydrochloric acid is added and two of the ions precipitate out as chloride salts. Those two ions would most likely be:
   (A) Cu^{2+} and Pb^{2+}
   (B) Cu^{2+} and Ag^+
   (C) Mg^{2+} and Ag^+
   (D) Pb^{2+} and Ag^+
8. When lead nitrate and sodium sulfate are mixed the result would be:
   (A) A precipitate of lead sulfate.
   (B) A precipitate of sodium nitrate.
   (C) A precipitate of lead nitrate.
   (D) No precipitate would form.
9. To produce a precipitate of silver sulfate you could mix solutions of:
   (A) Silver nitrate and ammonium sulfide.
   (B) Silver nitrate and sodium sulfate.
   (C) Silver sulfate and silver chloride.
   (D) Potassium sulfate and silver.
10. Solubility rules are determined by:
   (A) Looking up textbooks.
   (B) Teachers decide about them.
   (C) Experimentation.
   (D) University professors make the rules.
11. Which statement about solubility is correct?
   (A) All substances become more soluble as temperature increases.
   (B) Only gases become more soluble as temperature increases.
   (C) Solubility varies with temperature.
   (D) Solids become less soluble as temperature increases.

12. A saturated solution occurs when:
    (A) No more of a solid can be dissolved in it at that temperature,
    (B) You have to cool the solution to dissolve more solid.
    (C) A solution is cooled slowly to avoid crystallisation.
    (D) A solubility curve is drawn to show what is happening.

13. The solubility product constant (K_{sp}) for magnesium phosphate $Mg_3(PO_4)_2$ is found by:
    (A) $[Mg^{2+}][PO_4^{3-}]$
    (B) $2[Mg^{2+}]\,3[PO_4^{3-}]$
    (C) $[Mg^{2+}]^3\,[PO_4^{3-}]^2$
    (D) $[Mg_3]\,[(PO_4)_2]$

14. Solubility product only applies to:
    (A) Soluble salts.
    (B) Insoluble salts.
    (C) Sparingly soluble salts.
    (D) Liquid salts.

Use the following information to answer the next TWO questions.

A solution containing magnesium ions at a concentration of 5×10^{-7} mol L^{-1} is mixed with a solution containing hydroxide ions at a concentration of 0.01 mol L^{-1}. The K_{sp} value for $Mg(OH)_2 = 1 \times 10^{-11}$.

15. The ionic product will have a value of:
    (A) 1×10^{-7}
    (B) 5×10^{-7}
    (C) 1×10^{-11}
    (D) 5×10^{-11}

16. Which of the following do you predict to happen?
    (A) A precipitate will form because ionic product $> K_{sp}$.
    (B) A precipitate will form because ionic product $< K_{sp}$.
    (C) A precipitate will not form because ionic product $> K_{sp}$.
    (D) A precipitate will not form because ionic product $< K_{sp}$.

INQUIRY QUESTION

How does solubility relate to chemical equilibrium?

35 Revision Of Equilibrium and Acid Reactions

Congratulations, you have completed the first module of year 12 chemistry. This chapter contains short answer questions to help you revise the work you have covered.

By now you will have realised that chemical systems may be open or closed and they can include observable physical and chemical changes. You have studied the setting up of equilibrium reactions in closed systems and the effects that changes have upon the position of equilibrium, using Le Châtelier's principle to help predict effects of changes on an equilibrium position. You can now calculate equilibrium constants and predict equilibrium positions and whether or not a precipitate will occur.

Answering these questions will help you determine your strongest and weakest areas. You should first focus your revision on any weak areas and always consult your teacher if you do not understand any concepts.

QUESTIONS

Static and Dynamic Equilibrium

1. Combustion reactions are (reversible/irreversible).
2. Identify three salts of transition elements that change colour as their degree of oxidation or state of dehydration changes.
3. Copper(I) chloride is green and copper(II) chloride is blue. Write formulas for these salts.
4. Iron(II) chloride tetrahydrate is green and iron(III) chloride hexahydrate is mustard yellow. Write formulas for these salts.
5. The formula of blue copper sulfate crystals is $CuSO_5.5H_2O$. What happens to this compound when it is heated?
6. Hydrated crystals of cobalt chloride ($CoCl_2.6H_2O$) is a pink/purple colour. When heated it goes blue. Explain.
7. How else could you get cobalt chloride to go blue, other than heating it?
8. Define a closed chemical system.
9. Identify three examples of types of chemical reactions that go to completion and cannot be reversed.
10. Identify an example of a static equilibrium.
11. Define a chemical system at dynamic equilibrium.
12. List the characteristics of an equilibrium system.

13. What does this graph tell you about a chemical equilibrium?
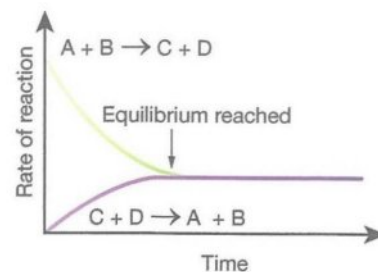
14. On the following graph, indicate when equilibrium is reached.
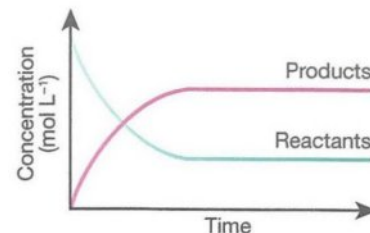
15. The total energy in a system is called ....
16. The measure of the dispersal of energy in a system is called ....
17. Chemical reactions are favoured by (increase/decrease) in enthalpy.
18. Chemical reactions are favoured by (increase/decrease) in entropy.
19. Combustion reactions are (endothermic/exothermic), their enthalpy change is (positive/negative) and their entropy (increases/decreases).
20. Write an equation for photosynthesis.
21. Photosynthesis is (reversible/irreversible), its enthalpy of reaction is (positive/negative) and it is endothermic/exothermic.
22. Use two energy profiles to distinguish between an exothermic reaction and an endothermic reaction. On each diagram label the energy of reactants, energy of products, activation energy and change in enthalpy.
23. What is meant by activation energy?
24. Which area under the following graph (red or yellow) shows the particles which have reached activation energy?
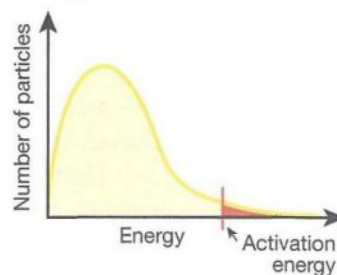
25. Outline the collision theory.
26. Identify four factors that can affect reaction rates.
27. Do the factors you listed in answer to Question 27, also have an effect on the equilibrium position?

Factors That Affect Equilibrium

1. You investigated the ferrocyanate equilibrium system represented by the equation:
$$Fe^{3+}(aq) + SCN^-_{(aq)} \rightleftharpoons [FeSCN]^{2+} \quad \Delta H \text{ is negative}$$
   Yellow colourless blood-red
   Identify the effect of the following changes on the colour of this system and account for these changes.
   (a) Warming.
   (b) Adding some potassium thiocyanate.
   (c) Adding silver nitrate solution.
   (d) Add potassium chloride solution.
   (e) Add a solution of $FeCl_3$.

2. You investigated the cobalt chloride equilibrium.
$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$$
   Pink   colourless   blue
   (a) In very dry atmospheric conditions, what colour change would you expect to see in a substance impregnated with cobalt chloride?
   (b) If the forward reaction as written is endothermic, would you need to warm or cool the equilibrium to make it go pinker?
   (c) What effect would adding ethanol have on the equilibrium?
   (d) If you added sodium chloride solution, what would be the effect?

3. You investigated the NO_2/N_2O_4 equilibrium.
$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -57.2 \text{ kJ mol}^{-1} N_2O_4$$
   Brown   colourless
   Identify a change you could make to cause the equilibrium mixture to darken in colour.

4. You also investigated the chromate/dichromate equilibrium system.
$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O$$
   Yellow   orange
   (a) What effect would adding a few drops of dilute aqueous hydrochloric acid have on this equilibrium? Make a prediction based on Le Châtelier's principle.
   (b) Explain the change in terms of collision theory.

5. Identify two ways to increase pressure on a system containing one or more gases.

6. In the Haber process, used to produce ammonia industrially, the reaction that occurs is:
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$$
   (a) Use Le Châtelier's principle to predict any change in equilibrium when it is disturbed by increasing the pressure on this system.
   (b) Explain the change in terms of collision theory.

7. Does adding a catalyst to a reaction at equilibrium:
   (a) Affect reaction rate?
   (b) Change the position of equilibrium?

8. In an equilibrium reaction, the forward reaction is endothermic, cooling the system will favour the (forward/reverse) reaction.

9. Le Châtelier's principle is used to (explain/predict) the change in an equilibrium system when it is disturbed.

10. What type of chemical must be present for a change in pressure to alter an equilibrium?

Calculating the Equilibrium Constant

1. State the equilibrium constant expression for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2. Identify two uses for equilibrium constants.

3. What is K_a?

4. Which of the following factors can change the value of an equilibrium constant?
   Changing the concentration, adding or removing a catalyst, heating or cooling the system.

5. Which of the following factors can change the position of an equilibrium?
   Changing the concentration, adding or removing a catalyst, heating or cooling the system.

6. If a reaction is endothermic, cooling the system favours the (reactants/products).

7. The addition of a catalyst can increase the speed of the (forward reaction/reverse reaction/both reactions).

8. Write the equation for the dissociation of carbonic acid in water.

9. Write the equilibrium dissociation constant expression for carbonic acid in aqueous solution.

10. You studied the following equilibrium reaction.
$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$
   What instrument could you use to determine the concentration of ions at equilibrium?

11. What colour is the iron thiocyanate complex in Question 10?

12. Would the equilibrium constant for this reaction be the same or different if you started the reaction with the thiocyanate complex rather than with iron and thiocyanate ions?

13. Outline the conditions used to maximise yield in the industrial production of ammonia by the Haber-Bosch process. The equilibrium reaction can be represented as:
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + energy$$

14. Identify an equilibrium system in the atmosphere.
15. Write the equation you would use to calculate the K_b value for the following reaction
    $$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
16. How would you calculate the ionic product of water?
17. Which is the stronger acid, hydrocyanic acid ($K_a = 6.3 \times 10^{-10}$) or hydrofluoric acid ($K_a = 7.6 \times 10^{-4}$)?
18. What effect would an increase in temperature have on the value of K_a for the exothermic dissociation of acetic acid?
19. Complete the ICE table to show concentrations at equilibrium.

Concentration	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
Initial	0.0015	0.0030	0
Change			+0.0002
Equilibrium			

20. If the equilibrium constant for a reaction $= 1.1 \times 10^{-7}$, what would be the equilibrium constant for the reverse reaction?
21. For the reaction, $H_2(g) + I_2(g) \rightarrow 2HI(g)$ the equilibrium constant $= 0.52 \times 10^4$ What is the [HI] at equilibrium when the concentrations of reacting ions is:

$[H_2(g)]$ mol L^{-1}	$[I_2(g)]$ mol L^{-1}
4.789×10^{-4}	4.789×10^{-4}

Solution Equilibria

1. What does this picture illustrate?
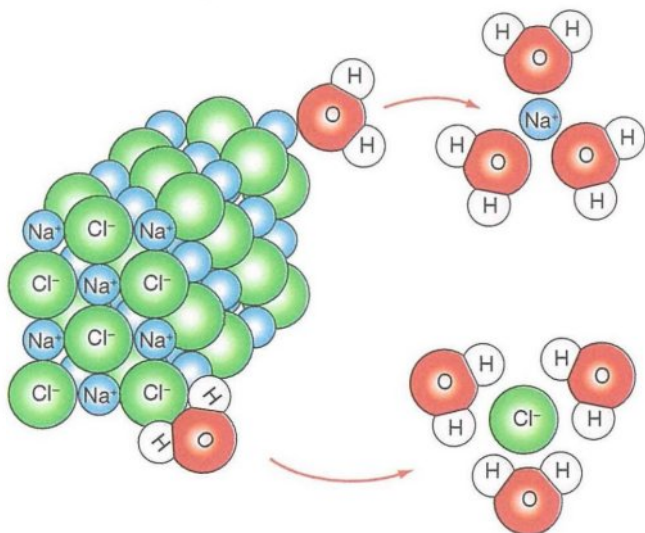
2. You are given the following solubility chart, use this to deduce four solubility rules.

S – soluble, I – insoluble

	Bromide Br$^-$	Chlorates ClO$_3^-$	Phosphate PO$_4^{3-}$	Dichromate Cr$_2$O$_7^{2-}$
Aluminium Al^{3+}	S	S	I	I
Ammonium NH$_4^+$	S	S	S	S
Calcium Ca^{2+}	S	S	I	I
Copper(II) Cu^{2+}	S	S	I	I
Iron(II) Fe^{2+}	S	S	I	I
Iron(III) Fe^{3+}	S	S	I	I
Magnesium Mg^{2+}	S	S	I	I
Potassium K$^+$	S	S	S	S
Silver Ag$^+$	I	S	I	I
Sodium Na$^+$	S	S	S	S
Zinc Zn^{2+}	S	S	I	I

3. (a) State the equilibrium constant relationship for solubility of lead sulfate.
   (b) Calculate the ionic constant if $[Pb^{2+}(aq)] = [SO_4^{2-}(aq)] = 0.0016$ mol L^{-1}.
   (c) If K_{sp} for lead sulfate $= 1.6 \times 10^{-8}$, will a precipitate form when concentrations are as stated in part (b)?
4. All solutions are (transparent/colourless).
5. Identify one important reason that water is important to humans.
6. How is the solubility of substances in water important in the use of cycads for food by Aboriginal and Torres Strait Islander peoples?
7. A solution which has dissolved as much solute as possible, at that temperature, is said to be
   ....
8. The solubility of solids in water usually (increases/decreases) as the temperature rises.
9. The solubility of gases in water usually (increases/decreases) as the temperature rises.
10. How is the solubility of liquids in water affected by temperature?
11. Use the table to determine which salt is more soluble.
12. Magnesium hydroxide dissolves in water, and has $K_{sp} = 1.2 \times 10^{-11}$ mol L^{-1}.

Ionic solid	K_{sp}
Cu(OH)$_2$	1.6×10^{-19}
Ca(OH)$_2$	1.3×10^{-6}

   $$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$
   Calculate its solubility in mol L^{-1}.

Notes