Equilibria

Why focus on G&T and higher achievers?

Within the education system every child has the right to develop their learning so as to maximise their potential.

These exercises are designed to give students enthuse and enrich activities that although related to the curriculum are in fact taking the learning experience to the next level whilst also showing chemistry in a familiar context. This has been found to be a successful model for not only improving learning but also for raising levels of motivation. Higher achieving students can find the restraints of the standard curriculum to be demotivating leading to underachievement.

The different activities are designed to improve a number of skills including practical work/dexterity, thinking/analysis skills, literacy, research activities, use of models and teamwork. Students should also gain confidence through the activities and improve the ability to express themselves.

Some of the activities would appear to be complex for KS3 (year 9), however at this stage in their learning high achieving students are open to new concepts and are ready to explore issues without pre-conceptions. They are keen to link ideas and develop concepts and understanding. It can prove to be an uplifting experience.

Introduction

There are many situations when one or more factors have differing affects on a system. Knowledge of equilibria and the factors that can affect it enable chemists to be able to follow a reaction. This knowledge can then be used to affect the position of the equilibrium in order to more effectively develop products.

This programme is designed to develop students understanding through basic concepts such as reversible and irreversible reaction, looking at both physical and chemical changes, to dynamic equilibria and factors that effect equilibria. Working through the activities will also develop thinking and research skills.

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<td>Screaming Jelly Babies</td>
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<td>Blue bottle experiment</td>
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<td>Oscillating reaction</td>
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The first activity looks at a reversible reaction – Heating ammonium chloride. This should be contrasted with irreversible (under normal conditions) reactions such as burning magnesium ribbon in air (oxygen). The second activity illustrates, rather dramatically, an irreversible reaction. Screaming jelly babies relies upon the thermal decomposition of potassium chlorate enabling the combustion of the sugar in the jelly baby – a reaction difficult to reverse under normal conditions. These activities provide a basis for discussing types of reactions. There is also ample opportunity to broaden the learning to include hydration, combustion, energy and fuels.

Having explored the fundamentals of types of reactions the Blue Bottle experiment looks at a specific example of a reversible reaction. It is easy to illustrate the principle with this redox reaction where glucose is used to reduce methylene blue to a colourless form. By shaking the bottle the concentration of dissolved oxygen is increased and the solution turns blue as the methylene blue is oxidised. On standing oxygen comes out of solution and the methylene blue is again reduced. This is a very visible example of the process. Links are provided in the text for a number of equilibrium reactions.

Another visible version of this is the Oscillating Reaction which exhibits patterns of oscillation from red to blue over a period of several minutes. It provides an illustration of how a series of interconnected redox equilibria and their rates can lead to a repeating cycle of reactions, made visible by the inclusion of a suitable redox indicator.

The next logical step is to look at what factors affect the position of the equilibrium and the following two activities explore the effect of concentration and temperature. This can be linked to industrial applications such as the Haber Process and the Contact Process. These are important industrial processes and it is worth discussing the economics of production and why it is important to maximise production – but at a reasonable cost. These areas are of particular value to both key stage 4 and 5. Links to animations of the process are included in the text.

Many of the factors involved in the study of equilibria can be consolidated in the Equilibrium Reactions activity. This is designed for key stage 5 students but can be used with higher achieving year 11 students. It is designed with Assessment for Learning in mind and has a formative assessment bias. It aims to consolidate the learning through discussion of observations made of demonstrations and working through questions covering the whole topic. The diagnostic test provides a more summative test of understanding.
Aims and objectives

The aims and objectives of these activities are:

- Developing questioning skills through problem solving.
- Exploring the use of models to expand understanding
- Developing practical skills and dexterity.
- Promoting independent learning.

Chemistry topics:

- Reversible and irreversible reactions.
- Equilibria.
- Dynamic equilibria.
- Factors affecting the position of equilibria.
- Le Chatellier’s Principle.
- Industrial applications of equilibria.

These exercises can be used with key stages 3, 4, and 5 as indicated on the Possible Routes.

These activities have proved very successful with high achieving key stage 3 students who have followed the prescribed pathway and have been stimulated into further independent learning.

At key stage 4 this activity enhances understanding of key industrial processes such as the Haber and Contact Processes.

As well as developing key concepts and understanding, these exercises provide a reinforcement and revision tool for a number of topics from the A level syllabus.

At all levels there is promotion of questioning skills, independent learning and research skills.
The introduction leads into the first activities that explore the idea of reversible and irreversible reactions.

These ideas can then be developed by investigating the properties of reactions in equilibrium. This then links to the importance of equilibria in industrial processes.

It is possible to further develop the industrial applications by exploring the factors that affect the position of the equilibrium.

Drawing together the learning to date students can consolidate their understanding using this AfL exercise.

Possible routes

Introduction

Reversible/Irreversible Reactions

Equilibrium Reactions

Factors Affecting Equilibria

Diagnostic Test

AFL

Key

KS3 G&T
KS4
KS5
KS4 G&T

This summative test probes the level of knowledge and understanding.
Reversible and Non-Reversible Reactions

Boiling an egg and burning wood or paper in air are similar processes in that afterwards it is impossible to get back to what you started with. These are both one-way, or irreversible, reactions, but many processes and reactions can be reversed by changing the conditions.

Most physical changes are easily reversed; for instance jelly sets on cooling but becomes a liquid again if warmed. Water, as ice, can be heated, becoming first liquid water and then steam, which can then be condensed back to water and frozen to re-form ice:

\[ \text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \]
\[ \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) \]

These equations can be put together to show that, overall, the changes can operate in either direction:

\[ \text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \]

When a compound is split up by the action of heat, the reaction may be reversible or irreversible. When the reaction is non-reversible it is called thermal decomposition:

Solid potassium chlorate decomposes to produce solid potassium chloride and oxygen gas: the two products cannot be made to recombine:

\[ 2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g) \]

This can be illustrated in the following activity – The Howling/Screaming Jelly Babies. This is an exciting teacher demonstration that illustrates the production of oxygen by burning a jelly baby in the gas produced. This also links to such topics as combustion, exothermic reactions and fuels.

In order to show the students the progression towards the idea of equilibria it is worth demonstrating an irreversible reaction such as burning a little magnesium ribbon (taking care that no one looks directly at the flame and the teacher takes appropriate safety precautions). If this is not possible the link below has video of magnesium burning in oxygen.

Magnesium in oxygen
http://www.chemistry-videos.org.uk/chem%20clips/Burning/magnesium.html

It is worth revising the observations such as shiny metal to white powder, plus of course heat. The next stage is to look at a reversible reaction and a good class practical is the heating of ammonium chloride as shown below.
Activity 1: Heating ammonium chloride

Topic
Reversible reactions.

Timing
10 mins.

Description
This activity shows how to decompose ammonium chloride into ammonia and hydrogen chloride through heating, and how they recombine to form the original reactant as they cool. This is an example of a reversible reaction. It illustrates:

- the effect of raising the temperature of a reaction at equilibrium on the yield of the exothermic and endothermic reactions
- the effect of lowering the temperature of a reaction at equilibrium on the yield of the exothermic and endothermic reactions

Apparatus and equipment (per group)
- Test-tube
- Mineral wool plug
- 250 cm³ beaker for cold water bath
- Bunsen burner
- Clamp and stand.

Chemicals (per group)
- Ammonium chloride (powdered)(Harmful).

Teaching tips
Ensure that the reaction test-tube is clamped at the end nearest the mineral wool plug.

Background theory
Some reactions are easily reversible and others are not.

Health & Safety
Wear eye protection.

Answers
1. Ammonium chloride
2. (a) breaking down into smaller molecules
   (b) a reaction that can go forwards or backwards
   (c) substance produced by a reaction
   (d) a product is produced by the formation of new bonds.

\[
\text{ammonium chloride (white solid)} \rightleftharpoons \text{ammonia (colourless gases)} + \text{hydrogen chloride (colourless gases)}
\]
Heating ammonium chloride

Introduction
In some chemical reactions, the products can react to form the original reactants. These are called reversible reactions.

For example, ammonium chloride (harmful) is a white solid that breaks down into ammonia (toxic) and hydrogen chloride (corrosive and toxic) gases when heated.

These gases react to form ammonium chloride

What to record
Record any observations.

What to do

1. Set up the apparatus as shown.
2. Heat the ammonium chloride.
3. Allow to cool.

Health & Safety
Wear eye protection.

Questions
1. What is the white solid that is formed on cooling?
2. What do the following words mean (a) decomposition, (b) reversible, (c) product, (d) reaction?
3. Write a word equation for the reaction you have observed.
Activity 2: The howling/screaming jelly baby

Reacting a ‘jelly baby’ with molten potassium chlorate. This experiment is reproduced from the Chemistry For Non-Specialists Course Book.

Supplementary Risk Assessment (to meet the COSHH and / or Management Regulations)

(To supplement Model Risk Assessments in other CLEAPSS publications, such as Hazcards, the Laboratory Handbook, Recipe Cards and various guides and guidance leaflets. This will eventually be incorporated into one of those publications.)

Details of operation:

15 g of reagent-grade potassium chlorate(V) is weighed into a Pyrex boiling tube. The tube is clamped at a slight angle to the vertical. The apparatus is surrounded by safety screens and the potassium chlorate(V) is heated until it melts. The demonstrator, wearing a face shield and heat-resistant gloves, uses tongs to drop a jelly baby into the melt.

(The above details are similar to those in various publications, including those of the Royal Society of Chemistry, the 21st Century Science project and the Salters’ Chemistry Club Handbook.)

Schools are advised not to deviate from the details described in this risk assessment. If any variation is required, members should contact CLEAPSS for a Special Risk Assessment.

| Substance(s) possibly hazardous to health, etc: | (a) Potassium chlorate(V).  
(b) Jelly babies are a form of confectionery, with stated contents of sugar, glucose syrup, water, gelatine, citric acid, flavourings, colours. |
| Classification under CHIP Regulations: | (a) OXIDISING and HARMFUL (R9: Explosive when mixed with combustible material; R20/22: Harmful by inhalation and if swallowed).  
(b) - |
| Particular risks / precautions: | See CLEAPSS Hazcard 77. Bretherick’s Handbook of Reactive Chemical Hazards (6th edition, 1999, Butterworth) states: “Potassium chlorate: Although most explosive incidents have involved mixtures of the chlorate with combustible materials, the exothermic decomposition of the chlorate to chloride and oxygen can accelerate to explosion if a sufficient quantity and powerful enough heating are involved...”.  
“Potassium chlorate with sugars: A stoichiometric mixture with sucrose ignites at 159 °C and has been evaluated as a rocket propellant. Dry powdered mixtures with glucose containing above 50% chlorate explode under a hammer blow. Pyrotechnic mixtures with lactose begin to react exothermically at about 200 °C, when the lactose melts and carbon is formed...”.  
A recirculatory fume cupboard caught fire with this experiment. It appears that the sparks were sucked onto the prefilter which is made of paper. The result is shown overleaf.  
There has been a serious incident reported in the USA where the boiling tube exploded. Possible explanations include the addition of citric or tartaric acid to make the US jelly baby (Gummy bear) sour tasting, which would be more reactive than a jelly baby. It is also possible that the demonstrator deviated from the normal experiment by adding other food stuffs to molten potassium chlorate(V). |
**Risk assessment**

Potassium chlorate(V) is notoriously unstable. The thermal decomposition of potassium chlorate(V) has been a common activity in school science in the past. Catalysed by manganese dioxide, it demonstrates catalysis in a clear and striking manner, although problems have arisen when the manganese dioxide has been impure or charcoal (very similar in appearance) has been used in its place. Nevertheless, the use of potassium chlorate(V) in schools is well established and guidance on safe use in some contexts is given on the relevant CLEAPSS *Hazcard*.

This activity involves the use of a jelly baby which is not covered by the *Hazcard* or similar safety texts. Most of the texts used by education employers as model risk assessments warn of the risk of dangerous or unstable mixtures with sugars and recommend that such mixtures should not be made. A jelly baby contains sugars but it is a single lump rather than crystals or powder, thus the surface area exposed (and hence the rate of reaction) is less. In addition, the sugars will be diluted by the water present, further reducing the rate of reaction and making an explosion much less likely.

The conclusion is that, notwithstanding the general advice that chlorate / sugar mixtures should not be made in schools, jelly babies present a safe but spectacular demonstration of the power of potassium chlorate as an oxidising agent and the energy stored in foodstuffs, provided that certain safety precautions are adhered to.

- The activity must be carried out only by teachers who should practice it in advance.
- They should NOT be tempted to increase the scale of the operation.
- Make sure that there are no fire alarms that use smoke sensors in the laboratory (or in the corridor if the door is opened to disperse the fumes). Laboratory fire alarms should use heat sensors as recommended by the DCSF in *Science Accommodation in Secondary Schools*, BB80.
- Teachers must take steps to prevent theft of the chemicals, in case pupils are tempted to repeat the activity outside school.
- Use UK jelly babies such as those made by Bassetts. Do not use ‘sour’ versions from any source,
- In case of explosion, the apparatus should be surrounded by safety screens (or in part by a wall). A closed / sealed apparatus must NOT be used.
- This reaction should be carried out on the open bench with the windows open. Fume cupboards are NOT designed to cope with this amount of smoke in such a short time and smoke will leak out.
Ejected molten liquids have been known to melt plastic or crack glass windows. The sparks have ignited the prefilter in recirculatory fume cupboards.

- The reaction is very vigorous and molten potassium chlorate(V) and decomposition products are likely to shoot out of the boiling tube. The safety screens should be arranged to prevent the ejected particles from scattering around the room and especially from landing on combustible objects. There should be heat-resistant mats to protect the bench.
- Bench mats and safety screens may be spattered with potassium chlorate(V). After the reaction, this should be carefully washed away with plenty of water, to prevent the possibility of inadvertent combustion.
- Spectators must be several metres away from the demonstration and should wear eye protection.
- The demonstrator will, inevitably, be closer to the demonstration than the spectators and should make use of the additional protection provided by a face shield.
- The demonstrator’s hand is at some risk during the few seconds when the jelly baby is being dropped into the melt, even if tongs are used. Heat-resistant gloves should be worn.
- As impurities can cause an explosion, care should be taken to ensure that the potassium chlorate(V) is pure (use reagent grade) and that the boiling tube is clean (and free, for example, from traces of carbon).
- Clamps used should not have rubber grips, as these may melt because of the heat of the reaction and so permit the boiling tube to move.
- Do not substitute sodium chlorate(V) for potassium chlorate(V).

COSHH stands for Control of Substances Hazardous to Health. The regulations require that an assessment of risk must be made before substances hazardous to health are handled. The substances covered are the reactants, the products and any intermediate or side products that are very toxic, toxic, harmful, corrosive or irritant. Just because a substance carries no hazard label does not mean that it is completely safe.
Systems at equilibrium

Physical Equilibrium
When sugar is added to a water it begins to dissolve. The structure of the crystal begins to break down and individual particles are able to move from the solid into the liquid forming a solution. At the same time a few particles of sugar will ‘fall out of solution’ and be deposited back onto the surface of the solid. Eventually there comes a point when the surface area of the solid is so small that fewer and fewer particles are entering the solution, and the concentration of sugar in the solution. is so high, that the rate at which particles of sugar fall out of solution begins to increase.

Eventually, if there is enough sugar, a balance point is reached and the solution is said to be saturated. At this point it seems that no more sugar is dissolving, but actually the rate at which it dissolves is now the same as the rate at which the solid reforms. The system is said to be at equilibrium. Like all equilibrium systems, this equilibrium can be affected by temperature.

An equilibrium can only be established in an enclosed system – one from which reactants and products cannot escape. Solids cannot escape from solutions, but gaseous reactions can only reach equilibrium in sealed containers.

Chemical Equilibrium
Balance points are reached in many reversible chemical reactions, when neither the forward nor the backward reaction is complete.

If the reaction can go both ways, how do I know which is forward?

By convention the reactants are shown on the left side: of the stoichiometric equation and the products on the right. The left-to-right reaction is the forward reaction.

The reaction between ethanol and ethanoic acid
Most people are familiar with ethanol as being the ‘active’ constituent of beers, wines and spirits, whereas ethanoic acid is usually associated with chips - it is in vinegar. When the two substances are mixed, they react slowly to form a compound, an ester called ethyl ethanoate: it has a distinctive sweet and fruity smell, and is used to make varnishes and glues. This esterification reaction, which is typical of alcohols and organic acids (see Module 7), is relatively easy to monitor and so has become a frequently used example in the study of chemical equilibrium.

The forward reaction:

\[
\text{CH}_3\text{CH}_2\text{OH}(l) + \text{CH}_3\text{COOH}(l) \to \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l)
\]

ethanol ethanoic acid ethyl ethanoate water

As the reaction proceeds so the chemicals are used up - the concentrations of the reactants decrease - and the reaction begins to slow down.
The back reaction:
\[ \text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O(}\text{l}) \rightarrow \text{CH}_3\text{CH}_2\text{OH(}\text{l}) + \text{CH}_3\text{COOH(}\text{l}) \]

As the forward reaction slows down so the back reaction speeds up. As the concentrations of the products increase, they begin to react together to form ethanol and ethanoic acid. Eventually, the rates of both reactions are equal - the system has reached a balance point and it is at equilibrium. Note though, the reaction *has not stopped* - it is just going equally as fast in both directions – the equilibrium is called a dynamic equilibrium.

All equilibrium processes, both physical and chemical, are dynamic. It is important to note that when a system has reached equilibrium:

(a) Each substance is being produced by one reaction as fast as it is being used by the reverse reaction. So, at equilibrium the concentrations of the reactants and products do not change.

\[ \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O} \]

A system of equilibrium

(b) The forward and backward reactions still occur but at equal rates.

To show that a reaction can go in either direction the two equations can be put together and the single arrows \( \rightarrow \) are replaced by the equilibrium symbol, a double arrow \( \rightleftharpoons \), as in the esterification reaction:

\[ \text{CH}_3\text{CH}_2\text{OH(}\text{l}) + \text{CH}_3\text{COOH(}\text{l}) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l}) + \text{H}_2\text{O(}\text{l}) \]

In practice, this reaction takes several weeks to reach equilibrium; the reaction can be speeded up by heating or by using a small amount of acid as a catalyst.

Videos of various equilibria can be found on:

http://www.chemistry-videos.org.uk/chem%20clips/Equilibria/equilibria%20general%20index.html

**Factors Affecting Systems at Equilibrium**

Equilibrium reactions are of theoretical interest to the chemist in the laboratory, who can provide valuable information about them to the chemical industry, where many are of vital importance. However, if some of the products continually recombine to reform starting substances, then product yields will be lower than anticipated and may make a commercial process uneconomical.

Chemists have had to find ways of encouraging the forward reaction to proceed.

**REMOVAL OF CHEMICALS CAN AFFECT THE REACTION**

In the esterification reaction,
\[
\text{CH}_3\text{CH}_2\text{OH}(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l)
\]

it can be seen that if water was removed from the system then the equilibrium balance would be upset, as shown below:

\[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \\
\rightleftharpoons \\
\text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}
\end{array}
\]

So if water is removed, say, by adding a powerful dehydrating agent, the ethyl ethanoate has nothing to react with and the reverse reaction is prevented. The equilibrium tries to re-establish itself by producing more ethyl ethanoate and water. If we continue removing water, the forward reaction can proceed until all of the reactants are converted to the ester.

The effects of changing conditions on a system at equilibrium can be predicted using Le Chatelier’s Principle.

Le Chatelier’s Principle states that:

If a system at equilibrium is disturbed by changing the conditions, the system will react in such away as to oppose the change.

In other words, if something is done to the equilibrium system, the position of equilibrium will change in order to reduce or remove the effects of the disturbance, and to get back into balance.

**EFFECTS OF PRESSURE CHANGES ON THE EQUILIBRIUM STATE IN GASEOUS REACTIONS**

This phenomenon is well illustrated using the conversion of nitrogen and hydrogen to ammonia by the Haber Process:

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)
\]

1 mole 3 moles 2 moles

- The equation shows that a total of 4 moles of reacting gas produces
- We know that the volume occupied by a gas at constant pressure is proportional to the number of moles of gas.

If the pressure on the reacting system is increased, Le Chatelier’s Principle tells us that the system will try to reduce the pressure again by reducing the number of particles- so increasing the space available for them.
The four moles of reacting gases occupy a larger volume than two moles of ammonia - so the increased pressure results in more ammonia being formed.

Increasing the pressure on this reaction also has the advantage of increasing the concentration of the gas molecules so the reaction will go faster.

**THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM STATE**

The effect of temperature on a system at equilibrium will depend on whether or not the reaction takes in or gives out heat during its course, *e.g.* in the reaction to produce ammonia:

\[
N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}
\]

The reaction to produce ammonia is *exothermic* - it produces heat. Using Le Chatelier’s Principle we can see that if this heat were removed, by using a lower temperature, it would ‘encourage’ the production of more ammonia (so releasing more heat to maintain the balance).

Unfortunately, although a low temperature increases the *yield* of ammonia, the reaction becomes uneconomically *slow*, as now there are fewer sufficiently energetic collisions between the particles. Obviously the industrial chemist faces the problem of reconciling both the kinetic and equilibrium considerations for this reaction to make economical to operate. In practice a compromise is reached by selecting an optimum operating temperature and pressure.

In general, when the temperature of a reacting system at equilibrium is raised:

- If the forward reaction is exothermic, increasing the temperature will tend to inhibit the reaction and decrease the concentration of products.
- If the forward reaction is endothermic, the system will tend to absorb the extra heat energy resulting in more products.

**THE EFFECT OF CATALYSTS ON THE EQUILIBRIUM STATE**

A catalyst can speed up both the forward and backward reactions and so enable the equilibrium state to be reached more quickly. Catalysts do not, however, affect the relative proportions (concentrations) of the reactants or products, so they do not affect the position of equilibrium.

The following demonstrations can be used to show how changes in concentration of one species can shift the equilibrium in one direction or another.
Activity 3: The Blue Bottle Experiment

Topic
General interest, problem-solving, chemical reactions.

Timing
1 min upwards.

Level
Primary or lower secondary.

Description
A colourless solution in a flask is shaken. It turns blue and then gradually back to colourless. The cycle can be repeated many times.

Apparatus
- One 1 dm$^3$ conical flask with stopper.
- Access to a nitrogen cylinder (optional).
- Access to a fume cupboard (optional).

Chemicals
The quantities given are for one demonstration (See CLEAPSS Recipe Book sheet 63).
- 8 g of potassium hydroxide or 6 g of sodium hydroxide (corrosive) See CLEAPSS Hazcard 91.
- 10 g of glucose (dextrose).
- 0.05 g of methylene blue (harmful solid) See CLEAPSS Hazcard 32.
- 50 cm$^3$ of ethanol (Highly flammable) See CLEAPSS Hazcard 40A.

Method

Before the demonstration
Make a solution of 0.05 g of methylene blue in 50 cm$^3$ of ethanol (0.1 %). Weigh 8 g of potassium hydroxide or 6 g of sodium hydroxide into a 1 dm$^3$ conical flask. Add 300 cm$^3$ of water and 10 g of glucose and swirl until the solids are dissolved. Add 5 cm$^3$ of the methylene blue solution. None of the quantities is critical. The resulting blue solution will turn colourless after about one minute). Stopper the flask (the product is an irritant.

The demonstration
Shake the flask vigorously so that air dissolves in the solution. The colour will change to blue. This will fade back to colourless over about 30 seconds. The more shaking, the longer the blue colour will take to fade. The process can be repeated for over 20 cycles. After some hours, the solution will turn yellow and the colour changes will fail to occur.

Visual tips
A white laboratory coat provides the ideal background.

Teaching tips
On a cold day, it may be necessary to warm the solution to 25–30 °C or the colour changes will be very slow.

The demonstration can be used to start a discussion on what is causing the colour changes. Students’ suggestions can be tried out as far as is practicable.

**Theory**

Glucose is a reducing agent and in alkaline solution will reduce methylene blue to a colourless form. Shaking the solution admits oxygen which will re-oxidise the methylene blue back to the blue form.

**Extensions**

To confirm that oxygen is responsible for the colour change, nitrogen can be bubbled through the solution for a couple of minutes to displace air from the solution and the flask. If the stopper is now replaced and the bottle shaken, no colour change will occur. Reintroducing the air by pouring the solution into another flask and shaking will restore the system. Natural gas can be used (in a fume cupboard) if nitrogen is not available. Some teachers may wish to present this experiment as a magic trick. The colour change can be brought about by simply pouring the solution from a sufficient height into a large beaker. This experiment can be a popular open-day activity. If visitors are to be allowed to shake the bottle themselves it might be wise to use a plastic screw-top pop bottle to eliminate the risk of the stopper coming off or the bottle being dropped and broken. The solution does not appear to interact with the plastic over a period of a day but it would be wise to try out the bottle you intend to use. Redox indicators other than methylene blue can be used. In each case add the stated amount of indicator to the basic recipe of 10 g of glucose and 8 g of potassium hydroxide in 300 cm$^3$ of water.

1. **Phenosafranine (irritant).** This is red when oxidised and colourless when reduced. Use about 6 drops of a 0.2 % solution in water for a bottle that goes pink on shaking and colourless on standing. The initial pink colour takes some time to turn colourless at first. A mixture of phenosafranine (6 drops) and methylene blue (about 20 drops of the 0.1 % solution in ethanol) gives a bottle which will turn pink on gentle shaking through purple with more shaking and eventually blue. It will reverse the sequence on standing.

2. **Indigo carmine (low hazard).** Use 4 cm$^3$ of a 1 % solution in water. The mixture will turn from yellow to red-brown with gentle shaking and to pale green with more vigorous shaking. The changes reverse on standing.

3. **Resazurin (irritant).** Use about 4 drops of a 1 % solution in water. This goes from pale blue to a purple-pink colour on shaking and reverses on standing. On first adding the dye, the solution is dark blue. This fades after about one minute.

Mixtures of the above dyes can also be used.

**Further details**


The blue bottle experiment revisited gives some details of the reaction mechanism and alternative dyes.

**Health & Safety**

Wear eye protection.
Activity 4: A colourful oscillating reaction - demonstration
(see CLEAPSS Recipe book sheet 63)

Teacher notes and procedure
Acidified sodium bromate and bromide solution are mixed, then propanedioic (malonic) acid, ferroin indicator and a surface active agent added. The mixture exhibits patterns of oscillation from red to blue over a period of several minutes. It provides an illustration of how a series of interconnected redox equilibria and their rates can lead to a repeating cycle of reactions, made visible by the inclusion of a suitable redox indicator.

Lesson organisation
The experiment provides an interesting and colourful demonstration, but the reactions involved and the mechanism are complex – see Teaching Notes.

Time required should be about 10 min.

Procedure
a) Place 6 cm$^3$ of solution A in a small beaker, using a measuring cylinder.
b) Add 0.5 cm$^3$ of solution B, using a syringe.
c) Add 1.0 cm$^3$ of solution C, using a syringe. A brown colour appears. When this disappears, add 1.0 cm$^3$ of ferroin solution, using a syringe.
d) Add 1 drop of 'Photoflo' (or equivalent) solution, using a dropping pipette.
e) Swirl to mix well and pour enough of the mixture in to the petri dish to half-fill it. Wait for the oscillations to begin.

Teaching notes
A member of the audience with a stopwatch could be asked to time the oscillation.

Theory
This reaction is an example of a class of reactions called Belousov-Zhabotinsky (BZ) reactions.

The overall reaction is usually given as:

$$3\text{CH}_2\text{(CO}_2\text{H)}_2\text{(aq)} + 4\text{BrO}_3^-\text{(aq)} \rightarrow 4\text{Br}^-\text{(aq)} + 9\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$$

This is a version of the classic Belousov-Zhabotinksy oscillating reaction. Its detailed mechanism is very complicated. However, it is suffice to say that the oscillation is brought about by two autocatalytic steps. Bromine is an intermediate in the reaction scheme – the red colour that is observed. An analogy with predator-prey relationships might be one way to give students some idea of what is going on. For example a population of rabbits (analogous to the bromine) will increase rapidly (exponentially) if there is plenty of food (reactants). However, the plentiful supply of rabbits will stimulate a rapid increase in the fox.
population (another intermediate that reacts with the bromine) which will then deplete the rabbits. Lacking rabbits, the foxes will die, bringing us back to square one, ready for a rapid increase in rabbits and so on.

**Extensions**

The reaction can be investigated using a colorimeter with a chart recorder or interfaced to a computer. See for example R. Edwards, *Interfacing Chemistry Experiments*, London: RSC, 1993.

References: Further details can be obtained in:  
or in *Chemical Demonstrations – Volume 2*, B.Shakhashiri, University of Wisconsin Press, 1986.

**Web Links**

[http://www.faidherbe.org/site/cours/dupuis/oscil.htm](http://www.faidherbe.org/site/cours/dupuis/oscil.htm)

An extensive article on oscillating reactions, with some good pictures, and detailed mechanisms.

**A colourful oscillating reaction**

**Technician notes**

**Apparatus and chemicals**

For one demonstration:

- Eye protection (Goggles when preparing Solution A - see note 2)
- Beakers (100 cm³), 4
- Petri dish
- Measuring cylinder (10 cm³)
- Plastic syringes (1 or 2 cm³), 3
- Dropping pipette

- Sodium bromate(V) (Oxidising, Toxic), 5 g (enough for 10 experiments)
- Concentrated sulfuric acid (Corrosive), 2 cm³
- Sodium bromide, NaBr (Low hazard), 1 g
- Propanedioic (malonic) acid (Harmful), 1 g
- Ferroin indicator solution, 1 cm³
- ‘Photoflo’ solution, 1 drop (see note 1)
- Distilled or deionised water, about 100 cm³

**Technical notes**

- Sodium bromate(V) (Oxidising, Toxic). Refer to CLEAPSS Hazcard 80.  
- Concentrated sulfuric acid (Corrosive). Refer to CLEAPSS Hazcard 98A.  
- Sodium bromide (Low hazard) Refer to CLEAPSS Hazcard 47B.  
- Propanedioic (malonic) acid (Harmful). Refer CLEAPSS Hazcard 36B.  
- Ferroin indicator. Refer to CLEAPSS Recipe Book sheet 49

1 ‘Photoflo’ solution - can be found at any photography shop. It is a surface-active agent used in photographic developing and printing.
In advance of the demonstration, prepare the following solutions in small beakers:

Solution A: 5 g of sodium bromate and 2 cm$^3$ of concentrated sulfuric acid in 67 cm$^3$ of distilled or deionised water.
Solution B: 1 g of sodium bromide in 10 cm$^3$ of distilled or deionised water.
Solution C: 1 g of propanedioic acid in 10 cm$^3$ of distilled or deionised water.

Another example of this can be demonstrated using cobalt chloride solution. If saturated sodium chloride is used instead of hydrochloric acid it can be adapted to a class practical (although a larger volume of sodium chloride will be needed).

**Activity 5: The equilibrium of the cobalt chloride–water system**

**Topic**
Equilibria, transition elements – ligands.

**Timing**
20 min.

**Description**
In this experiment students observe colour changes in the cobalt chloride–water system by the addition of various reagents which affect the position of equilibrium. The different colours of the reactants and products allow you to observe the effect on the position of equilibrium of the addition of water and chloride ions and the removal of water.

**Apparatus (per group)**
Safety goggles must be worn

- One plastic well-plate (24 wells) – eg Sigma ref: M9655.

**Chemicals (per group)**

- Solutions contained in plastic pipettes, see overleaf
- Cobalt chloride (aqueous solution) 0.1 mol dm$^{-3}$ (Toxic) See CLEAPSS Hazcard 25
- Cobalt chloride (ethanol solution) 0.1 mol dm$^{-3}$ (Highly Flammable) See CLEAPSS Hazcard 40A
- Concentrated hydrochloric acid (Corrosive) See CLEAPSS Hazcard 47A
- Concentrated sulphuric acid (Corrosive) See CLEAPSS Hazcard 98A
- Potassium chloride 0.1 mol dm$^{-3}$
- Deionised water
- Potassium chloride powder. See CLEAPSS Recipe book sheet 34
Procedure

Follow the instructions carefully recording the colours of the solutions at each stage. Appropriate care should be taken when using concentrated acids.

2. Add eight drops of water to wells A2–A5 and carefully swirl the well-plate for 1 min.
3. Add eight drops of potassium chloride solution to wells A6 and B1. Swirl the well-plate gently for 1 min.
4. Add 10 drops of concentrated hydrochloric acid to well A3 and enough solid potassium chloride to wells A4 and A5 to cover the bottoms of the wells. Swirl carefully for 1 min.
5. Add 20 drops, five drops at a time with gentle swirling, of concentrated sulphuric acid to wells A5–B1.
6. Add 20 drops of concentrated hydrochloric acid to wells B3 and B4, swirling gently.
7. Finally, add 30 drops of water to well B4.

Questions

1. Can you give explanations for all your observations – writing equations where appropriate?

Observations

The addition of water turns the blue ethanolic solutions of cobalt chloride from blue to pink. Adding potassium chloride solution to ethanolic cobalt chloride solution also causes a blue to pink colour change. Strongly dehydrating conditions (shifting the position of the equilibrium to the right) are required to generate the blue tetrachlorocobalt(II) complex from the pink hexa-aquacobalt(II) ion.

The following extract from the SSERC Bulletin 220 Spring 2006 illustrates the effect of temperature on the equilibrium to the extent that a particular equilibrium can be ‘conditioned’ to change colour at a set temperature.
Activity 6: The equilibrium of the cobalt chloride–water system; temperature

Introduction

In SSERC bulletin 219[1] we gave details of a simple demonstration showing the effect of temperature change on the position of an equilibrium. Using the solution of cobalt chloride and additional chloride ions the colour change between blue and pink takes place over a particular smallish temperature range with an intermediate colour of mauve.

When the solution is blue the predominant species is the tetrachlorocobaltate anion with very little hexa-aquocobaltate present. When it is pink the latter cation is the most populous species. The mauve solution contains both of the coloured ions in approximately equal mol proporitons. An easy way of convincing pupils of this is to them to hold a blue test-tube across a pink and see the mauve colour in the area of overlap (Figure 4).

By altering the proportions of cobalt salt and extra chloride added, the solution can be tuned to change colour at different temperatures. A set of tubes so tuned can function as a crude thermometer.

What you will need

Chemicals
cobalt(II) chloride
industrial methylated spirits (IMS, clear) distilled or de-ionised water
hydrochloric acid (concentrated)
sodium chloride

Equipment
balance
spatula
weighing boat
test tubes, 5 off
pipettes, 5 cm³ or small measuring cylinder
measuring cylinder, 100 cm³
burettes, 1 cm³, 5 off
beakers, 250 cm³, 3 off
supply of hot water (also iced water optional)
thermometer, 0-100°C

Preparation of solutions

Dissolve 2 g of cobalt chloride in 100 cm³ of IMS and 16 cm³ of distilled water.

Tuning each tubeful - Dispense three aliquots of 5 cm³ of the cobalt solution into 3 test tubes labelled A, B and C. Place one tube in a water bath (250 cm³ beaker three quarters filled with water at 20°C). Run in concentrated hydrochloric acid from the burette, dropwise with shaking or stirring and allowing time for temperature equalization, until the solution just turns blue. That tubeful is now tuned to change colour slightly below 20°C. Repeat with tubes B and C in the beaker waterbaths at other temperatures, say 30°C and 40°C.

The equilibrium equation can be expressed as follows:

\[
[\text{CoCl}_2(\text{aq}) + 4\text{Cl}^- + 2\text{H}_2\text{O} (\text{aq})]^{2-} \rightleftharpoons \text{CoCl}_4^{2-} (\text{aq}) + 4\text{H}^+ (\text{aq})
\]

Now place the three tuned tubes in turn in 5 beaker waterbaths and see if the colour change is remembered. Alternatively place them together in the same waterbath, raise the temperature slowly and observe the colour in the tubes turn blue in succession at their tuned temperature. Could this be the next executive desk toy?

Curricular references

Higher Chemistry, Unit 3, Chemical Reactions, (c) - the concept of dynamic equilibrium and shifting the equilibrium position.
Advanced Higher Chemistry, Unit 2: Principles of Chemical Equilibrium.

Reference
1. SSERC Bulletin No. 219, Autumn 2006, p6

Variations
1. The chloride could be supplied by using saturated sodium chloride solution instead of the acid. This avoids the corrosiveness of the acid. However, owing to the limited solubility of the salt, a larger volume of up to 10 cm³ is needed to supply a sufficiently high concentration of chloride ions.
2. Using a small scale as described above gives the advantage of a more rapid temperature equilibration. A teacher demonstration might need a larger scale.
3. Ideas for a further extension would be to use it as the basis of an investigation on a more quantitative basis. Using a colorimeter, the concentration of each species could be measured and thus the constancy of the equilibrium constant at a given temperature. If the equilibrium constant were measured at a few temperatures the enthalpy of the reaction could be calculated.
Animations/Simulations of reactions at Equilibrium

Below are websites offering animations/simulations illustrating a number of reactions at equilibrium and the effects of varying a number of factors (e.g. temperature and concentration):

http://www.rsc.org/education/chemistryteachers/Index_Results.asp?Page=1&ID=11490&Search
http://www.rsc.org/education/chemistryteachers/Index_Results.asp?Page=1&ID=11491&Search
http://www.rsc.org/education/chemistryteachers/Index_Results.asp?Page=1&ID=11492&Search

Industrial Processes that involve Equilibrium

We will now look at some other important industrial applications of the chemical principles studied so far. Each of these processes involves at least one step that reaches equilibrium, and so the position of the equilibrium has to be altered in order to make the process economically viable. Although both raising the temperature and increasing the concentration of reactants can speed up reactions, the latter method is costly and the former may destroy some substances in the process. The use of a suitable catalyst is generally more efficient and economical in the long run. A considerable amount of time and money is invested in the development of catalysts. The detailed composition of an industrial catalyst is often a well-guarded secret.

The production of ammonia by the Haber Process utilises all four factors that affect equilibrium reactions:

- a) We have seen that raising the temperature in this reaction inhibits production of ammonia, but the reaction is slow at low temperature. An optimum yield is attained by using a compromise temperature of about 500 °C.
- b) High pressure improves yield, but the cost of building and running a plant that can withstand very high pressure is very expensive. In practice, both the rate of production and yields are improved at a moderate operational pressure of 15-30 MPa (150-300 atm).
- c) Iron, with some potassium oxide or aluminium oxide added as a promoter, is used as the catalyst.
- d) Ammonia is removed as it forms - when cooled it condenses easily at high pressure - which encourages a higher yield of product.

Only 15-20% of the gases react each time that they pass through the reactor; unreacted hydrogen and nitrogen are recycled, with more being fed in to maintain the pressure. Once started, the process is continuous until the whole plant is closed for maintenance.

A website offering an animation of the Haber process where variables can be adjusted is:

http://www.freezeray.com/flashFiles/theHaberProcess.htm
THE CONTACT PROCESS

Sulfuric acid is used in many important manufacturing processes. Some examples are:

- pharmaceuticals/insecticides;
- making detergents;
- cleaning steel before galvanising or 'tinning', etc.
- electrolyte in car batteries;
- paint manufacture;
- making fertilisers;
- extracting metals from their ores;
- manufacture of rayon and other fibres;
- making paper.

In 1990, the total world-wide output of sulfuric acid, per day, was about 200 000 tonnes. Production begins with the burning of molten sulfur in dry air to produce sulfur dioxide:

\[ S(l) + O_2(g) \rightarrow SO_2(g) \]

An initial input of heat is needed to get the reaction started, but then it is so exothermic that the reaction is self-sustaining, and some of the excess energy released can be used to produce steam at high pressure that can in turn power pumps and provide heat elsewhere in the plant.

The second and key part of this process is also the most problematic:

\[ 2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -197 \, \text{kJ mol}^{-1} \]

The conversion of sulfur dioxide to sulfur trioxide is slow and involves a chemical equilibrium. If we apply Le Chatelier’s Principle, we can see that the forward process would be favoured by:

a) a low temperature;
b) high pressure.

However, in commercial processes scientific theory must be tempered with economics. Cooling the reacting system would make the reaction unprofitably slow, and building chemical plants that operate at high pressures is very costly. The problems of economic production are overcome by:

a) Using a catalyst. Vanadium(V) oxide (V$_2$O$_5$) is the principal catalyst; although less efficient than the platinum catalysts used in earlier years, it is cheaper and less easily poisoned by impurities in the sulfur dioxide. The catalyst is said to be surface active; it ‘holds’ the molecules of sulfur dioxide and oxygen at its surface long enough for the reaction to take place (adsorption). The product which is released or ‘desorbed’, is sulfur trioxide. Vanadium(V) oxide is mixed with other substances and formed into cylinders which offer a large surface and allow good flow of gases.
b) A compromise temperature of 450°C is used; at this temperature the forward reaction is fast and the back reaction slow: 97% of the sulfur dioxide can be converted to products. A lower temperature also has the dual benefits of keeping production costs down and minimising corrosion in the reaction vessels.

c) A pressure of a few atmospheres is needed to keep the gases moving through the reactors. Sulfur trioxide is not dissolved directly into water as the reaction is violent and would produce corrosive gases.

\[ \text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq) \]

Instead, the final stage involves the gas being slowly absorbed into concentrated sulfuric acid, to produce ‘oleum’ or ‘fuming sulfuric acid’ - an oily liquid - (H$_2$S$_2$O$_7$) which can be mixed with dilute sulphuric acid to produce the final product of the required concentration:

\[ \text{SO}_3(g) + \text{H}_2\text{SO}_4(l) \rightarrow \text{H}_2\text{S}_2\text{O}_7(l) \]

\[ \text{H}_2\text{S}_2\text{O}_7(l) + \text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{SO}_4(l) \]

A useful website that illustrates the industrial manufacture of sulphuric acid including video, background and worksheets is:

http://www.rsc.org/Education/Teachers/Resources/Alchemy/index2.htm
Activity 7: Consolidation

The following activity is a good exercise for the assessment of understanding of all the aspects of equilibria. It probes some misconceptions and leads into assessment for learning and self assessment.

Equilibrium reactions

In this activity, students decide whether statements about equilibrium reactions are true or false and review their decisions in a group discussion.

- The resource is designed to check and make explicit the following misconceptions that:
- all of a reactant added to an equilibrium mixture is used up before equilibrium is restored
- when additional reactant is added to a system in equilibrium the value of the equilibrium constant increases
- equilibrium is reached when the concentration of reactants equals the concentration of products
- a high value of the equilibrium constant is associated with a fast reaction
- the rate of the forward reaction increases from mixing reactants until equilibrium is established
- catalysts affect forward and reverse reactions in an equilibrium system in different ways
- heating an equilibrium mixture decreases the rate of an exothermic reaction.

Learning objectives

Students will understand:

- the effect of concentration, catalyst and temperature on equilibrium reactions.

Sequence of activities

Demonstrate the consequence of adding a reactant to a system in equilibrium.

Mix together in a large conical flask a little iron(III) chloride solution and potassium thiocyanate solution and dilute with distilled water.

Describe the equilibrium system

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

yellow, colourless, blood red

- Add some potassium thiocyanate to the flask.
- Ask students about their observations.

If possible, show an animation of the formation of an equilibrium mixture before sharing the learning objective with students.

Hand out a Worksheet to each student. Circulate and support the students as they:

- work individually
- complete the table on the Worksheet to decide whether the provided statements are true
or false
  • explain why the statements ticked as false are wrong.

Arrange the students into groups of three. Ask them to:
  • compare the judgements they have made with each other
  • agree a group response to each statement
  • select a spokesperson.

Draw the groups into a plenary.
Invite each spokesperson to comment on one of the statements. Encourage other groups to add to the comments.

Ask each student to:
  • write down changes to their thinking as a result of talking and listening to others
  • hand in their Worksheets.

Give written feedback. Acknowledge achievement and give suggestions that help students to move forward.

Assessment for learning commentary
The initial demonstration (adding a reactant to a system in equilibrium) focuses student attention to the learning objective.

Working in a small group, the students articulate and assess their ideas. The plenary provokes a further evaluation of their initial responses to the statements.

The teacher provides written feedback on the students’ ideas to acknowledge achievement and to provide comment that leads students to recognise their next steps and how to take those steps.

Equilibrium reactions

Worksheet
Read each of the statements below.

Tick one of the boxes to show that you think the statement is true, false or that you are unsure whether it is true or not.

When a reactant is added to a system in equilibrium, the forward reaction will occur to use up all the added material and so restore the equilibrium.

When a reactant is added to a system in equilibrium, more product is produced but the value of the equilibrium constant, \( K \), remains unaltered.

A system reaches equilibrium when the concentration of the reactants is equal to the concentration of the
products.

A high value of the equilibrium constant, $K$, means that the forward reaction is very fast.

When the reactants of an equilibrium system are mixed together the rate of the forward reaction increases until equilibrium is established.

A catalyst increases the rate of reaction of both the forward and reverse reactions.

In an equilibrium system in which the forward reaction is endothermic, the reverse reaction is exothermic.

If a system in equilibrium where the forward reaction is endothermic is heated, the rate of the forward reaction increases but the rate of the reverse reaction decreases.

<table>
<thead>
<tr>
<th>Statement</th>
<th>The statement is true</th>
<th>The statement is false</th>
<th>I am unsure</th>
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</tbody>
</table>

For each statement that you think is false, explain why you think it is wrong.

Write down any changes in your thinking as a result your discussions.

**For the demonstration**
Animation showing the formation of an equilibrium mixture (if available).

**Equipment**
For the demonstration

500 cm$^3$ conical flask

Potassium (or ammonium) thiocyanate solution 0.5 mol dm$^{-3}$ (solid – Harmful; solution – Low Hazard) See CLEAPSS Hazcard 9B

Iron(III) chloride solution 0.5 mol dm$^{-3}$ (solid – Harmful; solution - Irritant) See CLEAPSS Hazcard 55C

Distilled water.
Notes on statements about equilibrium reactions

1. False
   Some, but not all, of the added reactant will be used up as the system reaches equilibrium.

2. True
   The value of the equilibrium constant is not altered by adding a reactant to a system in equilibrium.

3. False
   The concentrations of reactants and products do not have to be equal for an equilibrium to be reached.

4. False
   There is no link between the equilibrium constant and the rate of the reactions in the equilibrium system.

5. False
   The rate of the forward reaction will be at a maximum when reactants are first mixed and will fall as they are used up reaching a constant value equal to the rate of the reverse reaction when equilibrium is reached.

6. True
   A catalyst increases both forward and reverse reactions to the same extent and therefore does not alter the equilibrium position or the value of the equilibrium constant.

7. True
   If the forward reaction in an equilibrium system is endothermic then the reverse reaction must be exothermic.

8. False
   If a system in equilibrium, where the forward reaction is endothermic, is heated, then the rate of reaction of both forward and reverse reactions will increase. However, the rate of the forward reaction will increase more than that of the reverse reaction so that the position of equilibrium moves towards the products.
Activity 8: Diagnostic test

1. What is Le Chatelier’s principle? (1)

2. When an equal quantity of iron(II) sulfate solution is added to silver nitrate solution of the same concentration, an equilibrium mixture is formed and a precipitate of silver is seen. The ionic equation is:

   \[ \text{Fe}^{2+}(aq) + \text{Ag}^+(aq) \rightleftharpoons \text{Ag}(s) + \text{Fe}^{3+}(aq) \]

   a) What would happen if the concentration of the iron(II) sulfate solution was increased? (2)
   b) What would you expect to see if iron(III) sulfate solution was added to the equilibrium mixture? (2)

3. Using an example for each, explain the difference between reactions involving:

   a) thermal dissociation; (2)
   b) thermal decomposition. (2)

4. In the Haber process, ammonia is made in an exothermic reaction between hydrogen and nitrogen gases:

   \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1} \]

   Explain, with reasons, what the effect would be on the proportion of ammonia in the equilibrium mixture if:

   a) the temperature was increased; (3)
   b) the pressure on the system was increased. (3)

5. a) Write an equation for the reaction between ethanol and ethanoic acid. (2)
    b) Write an expression for the equilibrium constant for this reaction. (3)

Total Mark = 20
1 If an equilibrium is disturbed by changing the conditions, the position of the equilibrium moves to try to counteract that change.

2 a) The equilibrium would shift to the right, i.e. more silver would be deposited and the solution would look ‘brownish green’.

b) The equilibrium would shift to the left, i.e. some silver would dissolve.

3 a) Thermal dissociation is a reversible reaction which is dependent on temperature, i.e. heating or cooling can reverse the process such as in the dissociation of ammonium chloride into ammonia and hydrogen chloride:

\[ \text{NH}_4\text{Cl}(s) = \text{NH}_3(g) + \text{HCl}(g) \]

Other common examples are given below: award yourself a mark for any one.

\[ 2\text{HgO}(s) = 2\text{Hg}(l) + \text{O}_2(g) \]
\[ \text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g) \]
\[ \text{N}_2\text{O}_4(g) = 2\text{NO}_2(g) \]
Dinitrogen Nitrogen tetroxide dioxide

b) Thermal decomposition occurs when substances are completely ‘broken down’ by heat, a process which cannot be easily reversed.

Four common examples are given: award a mark for each correct formula and number of moles.

\[ 2\text{KClO}_3(s) \rightarrow 2\text{KCl}(s) + 3\text{O}_2(g) \]
Potassium Potassium chlorate chloride

\[ \text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g) \]
Ammonium Dinitrogen nitrate oxide

\[ 2\text{Pb(NO}_3)_2(s) \rightarrow 2\text{PbO}(s) + \text{O}_2(g) + 4\text{NO}_2(g) \]
Lead(II) Lead(II) nitrate oxide

\[ 2\text{AgNO}_3(s) \rightarrow 2\text{Ag}(s) + \text{O}_2(g) + 2\text{NO}_2(g) \]
Silver Nitrogen nitrate dioxide
4. a) An exothermic reaction generates heat. The equilibrium position shifts to the left to resist the increase in temperature, and so less ammonia is produced.

b) There are only 2 moles of products on the right-hand side of the equation, which will then occupy a smaller volume. The equilibrium position shifts to the right to resist the increase in pressure: more ammonia is produced.

5. a) The equation for the reaction between ethanol and ethanoic acid is:

\[ \text{C}_2\text{H}_5\text{OH}(l) + \text{CH}_3\text{COOH}(l) = \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l) \]  

(Left side of equation correct = 1 mark; right side of equation correct = 1 mark)

b) The equilibrium constant is given by

\[ K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] \times [\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}] \times [\text{CH}_3\text{COOH}]} \]  

(1 mark each for correct symbol for equilibrium constant; numerator and denominator)
<table>
<thead>
<tr>
<th><strong>Glossary</strong></th>
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<tbody>
<tr>
<td>catalyst</td>
<td>A substance that increases the rate of a reaction.</td>
</tr>
<tr>
<td>dynamic equilibrium</td>
<td>An equilibrium where the rate of the forward reaction equals the rate of the reverse reaction.</td>
</tr>
<tr>
<td>endothermic</td>
<td>Endothermic reactions absorb heat from the environment.</td>
</tr>
<tr>
<td>equilibrium</td>
<td>At equilibrium the concentration of reactants and products is constant.</td>
</tr>
<tr>
<td>exothermic</td>
<td>Exothermic reactions release energy to the environment.</td>
</tr>
<tr>
<td>irreversible reaction (non-reversible)</td>
<td>Reactions that cannot be reversed by simple means.</td>
</tr>
<tr>
<td>Le Chatelier’s principle</td>
<td>The position of equilibrium shifts to oppose any change imposed upon it.</td>
</tr>
<tr>
<td>reversible reaction</td>
<td>Changes that can go forwards or backwards.</td>
</tr>
<tr>
<td>thermal decomposition</td>
<td>The irreversible splitting of a substance by heat.</td>
</tr>
<tr>
<td>thermal dissociation</td>
<td>A reaction that can be reversed by altering the temperature.</td>
</tr>
</tbody>
</table>