

In this chapter, you will investigate the ideas of reversibility and irreversibility of chemical systems. This study of reversible reactions will introduce the concept of chemical equilibrium.

Various factors can change the position of a chemical equilibrium. Le Châtelier's principle enables you to understand the effects of changes in concentrations in solutions, pressures of gases and temperature on an equilibrium.

The fact that many reactions do not proceed to completion has serious consequences on the efficiency of chemical manufacturing industries. An understanding of the principles of equilibrium allows you to adjust the reaction conditions used for an industrial process to ensure optimum efficiency.

You will also learn how to write a mathematical relationship, known as an equilibrium law, for an equilibrium system. This law can be used to calculate the relative amounts of reactants and products present when a reaction is at equilibrium.

### Science understanding

- chemical systems include physical changes and chemical reactions and may be open (which allow matter and energy to be exchanged with the surroundings) or closed (which allow energy, but not matter, to be exchanged with the surroundings)
- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- over time, in a closed system, reversible physical and chemical changes may reach a state of dynamic equilibrium, with the relative concentrations of products and reactants defining the position of equilibrium
- the characteristics of a system in dynamic equilibrium can be described and explained in terms of reaction rates and macroscopic properties
- the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions
- the effect of changes of temperature on chemical systems initially at equilibrium can be predicted by considering the enthalpy changes for the forward and reverse reactions; this can be represented on energy profile diagrams and explained by the changes in the rates of the forward and reverse reactions
- the effects of changes in concentration of solutions and partial pressures of gases on chemical systems initially at equilibrium can be predicted and explained by applying collision theory to the forward and reverse reactions
- the effects of changes in temperature, concentration of species in solution, partial pressures of gases, total volume and the addition of a catalyst on equilibrium systems can be predicted using Le Châtelier's principle
- equilibrium law expressions can be written for homogeneous and heterogeneous systems; the equilibrium constant ( $K_c$ ), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium
- the relative amounts of reactants and products (equilibrium position) can be predicted qualitatively using equilibrium constants ( $K_c$ )

## 2.1 Chemical systems

In this section, you will learn that some reactions can occur in both the forward and reverse directions. These reactions are called ‘reversible reactions’.

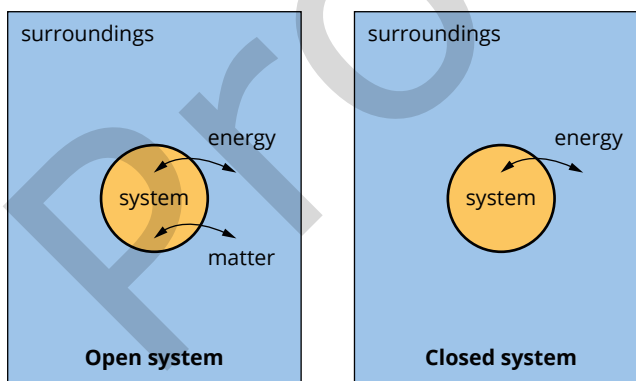
Reversible chemical systems are encountered in many everyday situations, including chemical manufacturing processes, the reactions of ions within cells in your body and the reactions that carbon dioxide undergoes in the environment.

### OPEN AND CLOSED SYSTEMS

In Year 11, you learnt that a chemical reaction can be regarded as a **system**, with everything else around it (the rest of the universe) being the **surroundings**. In an **endothermic** reaction, the chemical system absorbs energy from the surroundings, whereas in an **exothermic** reaction, energy is released to the surroundings.

Figure 2.1.1 illustrates how you can distinguish between two different types of systems: open systems and closed systems.

The most common situation is an open system. In an **open system**, matter and energy can be exchanged with the surroundings. In contrast, a **closed system** can exchange energy but not matter with the surroundings.

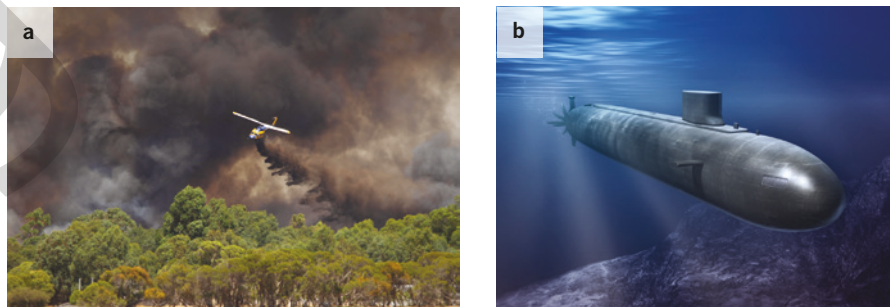


**i** Open systems exchange energy and matter with the surroundings.

Closed systems only exchange energy with the surroundings.

**FIGURE 2.1.1** Open systems exchange energy and matter with the surroundings. Closed systems only exchange energy with the surroundings.

Some everyday examples of open and closed systems are illustrated in Figure 2.1.2.

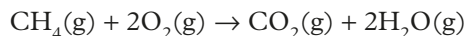


**FIGURE 2.1.2** Examples of open and closed systems. (a) A bushfire burning through a forest on 3 February 2014 in Banjip, Western Australia. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation underwater. The carefully monitored environment of the submarine can be regarded as a closed system.

## IRREVERSIBLE AND REVERSIBLE SYSTEMS

When some chemical reactions occur, the products cannot be converted back to the reactants. Such reactions, which occur in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake (Figure 2.1.3) involves several irreversible reactions. Combustion reactions such as the burning of methane are also irreversible:



Once a fuel has burnt, the products, carbon dioxide and water, do not react with each other under normal conditions.

However, other reactions are **reversible reactions**, where the products, once formed, can react again re-forming the reactants.

## REVERSIBILITY OF PHYSICAL AND CHEMICAL CHANGES

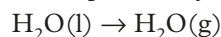
Three examples of systems that can be reversible are:

- the evaporation and condensation of water
- a saturated sugar solution
- the reaction of haemoglobin and oxygen gas.

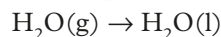
### Evaporation and condensation of water

You are familiar with the idea that a physical change, such as a change of state, can be reversed. The evaporation of water from lakes and rivers leading to cloud formation and eventually rain is an example of a physical change. Water can cycle between the different phases of solid, liquid and gas because each process is reversible.

The evaporation of water can be expressed by the equation:



The condensation of water can be expressed by the equation:



In chemistry, a double arrow ( $\rightleftharpoons$ ) is used when writing a chemical equation to show a reversible process. In this way, you can show the phase changes associated with water using the following equation:



As you can see in the diagram of water in two glasses in Figure 2.1.4, these changes of state can occur in either open or closed systems.

In a closed system, the water vapour cannot escape. In general, reversible reactions in a closed system eventually reach a situation where the rates of the forward and reverse reactions are equal. At this point, there will appear to be no further change to the observer. The system is described as having reached a state of **equilibrium**.

However, in an open system, although water can evaporate and condense, the rate of each process is not equal. Gaseous water molecules are escaping into the atmosphere, so the rate of the reverse reaction (condensation) does not become equal to the rate of the forward reaction. Equilibrium is not achieved in an open system.

### Saturated sugar solutions

Consider a **saturated solution** (a solution that contains the maximum possible concentration of a solute) of sugar in contact with undissolved sugar crystals at a constant temperature (Figure 2.1.5).

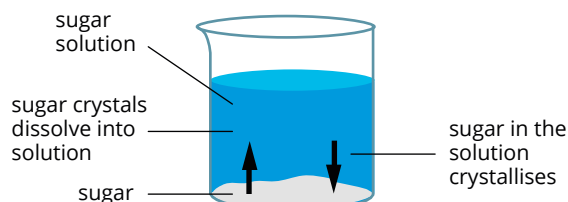


FIGURE 2.1.5 A representation of the reactions occurring in a saturated sugar solution



FIGURE 2.1.3 Baking a cake involves a series of irreversible chemical reactions.

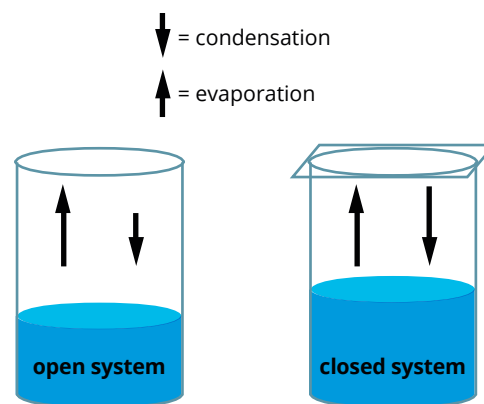
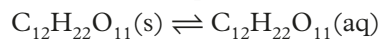


FIGURE 2.1.4 A physical change—the condensation and evaporation of water—in open and closed systems. In the open system, all the water eventually evaporates.

The sugar molecules ( $C_{12}H_{22}O_{11}$ ) are dissolving at the same rate as they are crystallising and the mass of sugar crystals present is constant. The process is reversible and at equilibrium. It can be represented by the equation:



Even though there is no lid on the beaker, this system can be regarded as a closed system. No gas is involved, so there is no loss of the reactant or product molecules to the surroundings.

## Haemoglobin and oxygen gas

Haemoglobin is a large protein molecule that is the pigment in red blood cells (Figure 2.1.6). It is responsible for the transport of oxygen from your lungs to the cells in the body. When you inhale, oxygen from the air combines with haemoglobin in the small blood vessels in the lining of the lungs to form oxyhaemoglobin.



The reaction between haemoglobin and oxygen gas is a reversible chemical reaction. The oxyhaemoglobin is transported through the blood system to other cells in the body where oxygen is released:

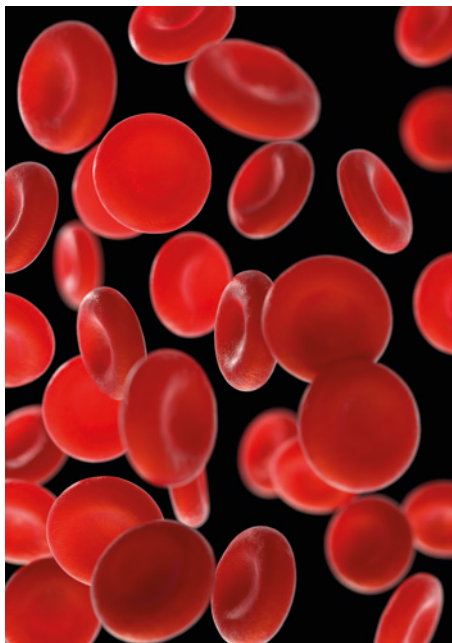


The oxygen is used by cells for respiration, to provide energy for the body.

The reaction can therefore be written as:



Although this can be regarded as an open system overall, an equilibrium is established in the blood as it flows through the body. During this period, it may be thought of as a closed system because there is no loss of reactants or products to the surroundings.

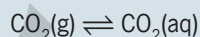


**FIGURE 2.1.6** Blood cells contain a red pigment, haemoglobin, that transports oxygen from the lungs to other cells in the body.

### CHEMFILE

#### Soft drink and equilibrium

In a sealed bottle of soft drink,  $CO_2$  gas is in equilibrium with dissolved  $CO_2$  according to the equation:



The rate at which the gas dissolves in the solution is equal to the rate at which it leaves the solution to form a gas. To someone looking at the bottle, there appears to be nothing happening.

When the cap is removed from the bottle, the pressure is reduced and carbon dioxide escapes to the atmosphere. The system changes from a closed system to an open system and a net reverse reaction occurs as carbon dioxide comes out of solution. Bubbles of gas are observed when the bottle is opened.

This normally happens slowly, but when Mentos® mints are added to a bottle of soft drink, the drink erupts violently as you can see in Figure 2.1.7. The high surface area of the mints provides many sites for bubbles to form, increasing

the rate of the reaction, and quickly producing an eruption of soft drink from the bottle.



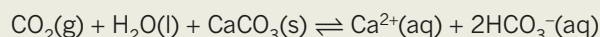
**FIGURE 2.1.7** Erupting soft drink when mints have been added

## CHEMISTRY IN ACTION

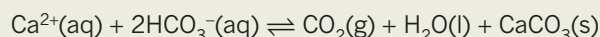
### Limestone caves

An example of reversibility in nature is the formation of stalactites and stalagmites in limestone caves.

The main mineral in limestone is calcite ( $\text{CaCO}_3$ ). Water saturated with carbon dioxide from the atmosphere drips through the roof of the cave, resulting in the following reaction:



As the water seeps through the rocks, it becomes saturated with  $\text{Ca}^{2+}$  ions and  $\text{HCO}_3^{-}$  ions. The water then evaporates and the reverse reaction produces stalactites from the ceiling of the cave:



Some of the solution drips onto the floor of the cave, where more deposits of  $\text{CaCO}_3$  are produced, forming stalagmites. Stalactites and stalagmites grow in pairs and can produce the beautiful columns like the ones seen in the Ngilgi cave system seen in Figure 2.1.8.



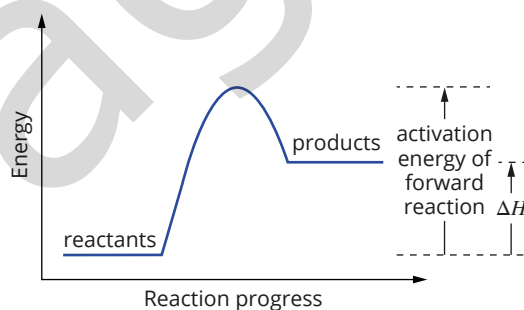
**FIGURE 2.1.8** Stalactites in the Ngilgi Cave in Western Australia. They are made of the mineral calcite.

### EXPLAINING REVERSIBILITY

The reason why reversible reactions can occur can be understood by referring to an energy profile diagram like the ones you saw in Chapter 1.

When particles collide, the energy associated with collisions can break bonds in the reacting particles, allowing them to rearrange to form new products. The energy required to break the bonds of the reactants is known as the **activation energy** of the reaction.

You can see from the energy profile diagram in Figure 2.1.9 that once the products form, it is possible for the reverse process to occur. If the newly formed product particles collide with enough energy to break their bonds (equal to the activation energy of the reverse reaction), then it is possible to re-form the original reactants.



**FIGURE 2.1.9** An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward (formation of products) and reverse (re-formation of reactants) reactions.

Note that if the forward reaction is endothermic, the reverse reaction will be exothermic, and vice versa.

## 2.1 Review

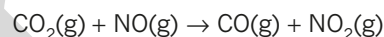
### SUMMARY

- In a closed system, only energy, not matter, is exchanged with the surroundings.
- In an open system, both matter and energy are exchanged between the system and the surroundings.
- A reversible reaction is a reaction in which the products can be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot be converted back to the reactants.
- Reactions where the activation energy for the forward and reverse reactions are similar, are likely to be reversible.
- Reversible reactions can reach a point where the rates of the forward and reverse reactions are equal. At this point, equilibrium has been achieved.
- Equilibrium can be achieved in closed systems, but not in open systems.

### KEY QUESTIONS

- 1 Which one of the following statements about a closed system is correct?
  - A A closed system must be completely sealed to stop reactants or products from escaping.
  - B In a closed system, the reactants and products cannot be exchanged with the surroundings.
  - C Energy cannot enter or leave a closed system.
  - D In a closed system, only products remain when the reaction is complete.
- 2 Indicate whether the following processes occur in open or closed systems.
  - a A saturated solution of salt in a glass:  
 $\text{NaCl(s)} \rightleftharpoons \text{NaCl(aq)}$
  - b Solid  $(\text{NH}_4)_2\text{SO}_4$  reacting with NaOH solution in a beaker:  
 $(\text{NH}_4)_2\text{SO}_4(\text{s}) + 2\text{NaOH(aq)} \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{NH}_3(\text{g}) + \text{H}_2\text{O(l)}$
  - c A beaker containing a solution of  $\text{CH}_3\text{COOH}$  which ionises:  
 $\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
  - d Burning toast
- 3 Select the correct answers from the list to complete the following paragraph about equilibrium. Some terms may be used more than once.  
rates, processes, remains constant, increases, decreases, energy, matter, reversible, irreversible  
Equilibrium occurs when there is a \_\_\_\_\_ reaction in a closed system. \_\_\_\_\_ can be added to the system but \_\_\_\_\_ cannot be added or removed. At equilibrium, the \_\_\_\_\_ of the forward and reverse reactions are equal. The total mass of reactants and products present in the reaction \_\_\_\_\_.

- 4 Figure 2.1.10 shows the energy profile diagram for the reaction:



What is the activation energy for the reverse reaction in  $\text{kJ mol}^{-1}$ ?

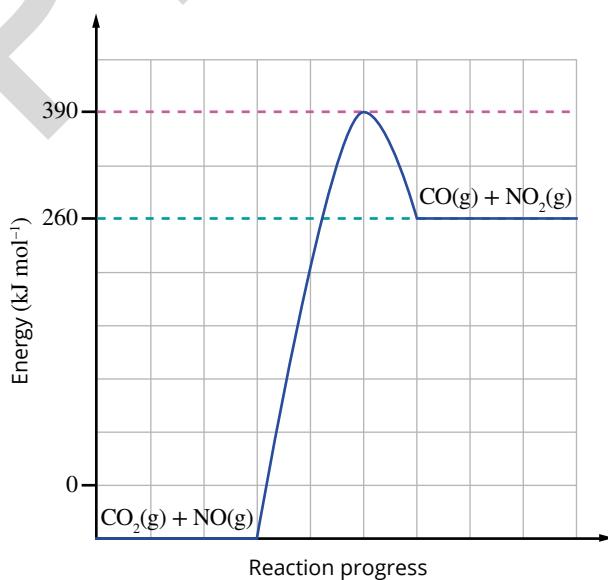


FIGURE 2.1.10 An energy profile diagram

## 2.2 Dynamic equilibrium

In the previous section, you learnt that reversible reactions can occur in both the forward and reverse directions.

Some reversible reactions can reach a point where they appear to stop. To someone observing an equilibrium system, it would appear as if nothing is changing. At this point, the concentrations of the reactants and products remain constant, even though there are still reactants remaining.

The fact that many reactions do not proceed to completion has serious consequences for the production of chemicals by industry. The presence of large amounts of unreacted starting materials in reaction mixtures is wasteful and costly. The profitability of an industry depends on the yield of the reaction—the extent of conversion of reactants into products.

Although these reactions appear to stop, they actually continue to proceed. As reactants are forming products, the products are re-forming reactants at the same rate. This situation can be likened to the queue shown in Figure 2.2.1. Although the length of the queue may seem constant, people at the front are continually leaving the queue and others are joining it at the back at the same rate.



**FIGURE 2.2.1** A queue of constant length can be likened to a reaction that appears to have stopped, with people leaving the queue at one end at the same rate as others join it at the other end.

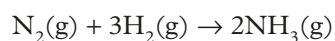
In this section, you will look more closely at how the particles in a chemical reaction behave as a reaction reaches an equilibrium.

### EXPLAINING EQUILIBRIUM

As you have seen, in reversible reactions the formation of products as a result of collisions between reactant particles is not the end of the process. Once some products are formed, collisions between product particles can result in the reactants being re-formed.

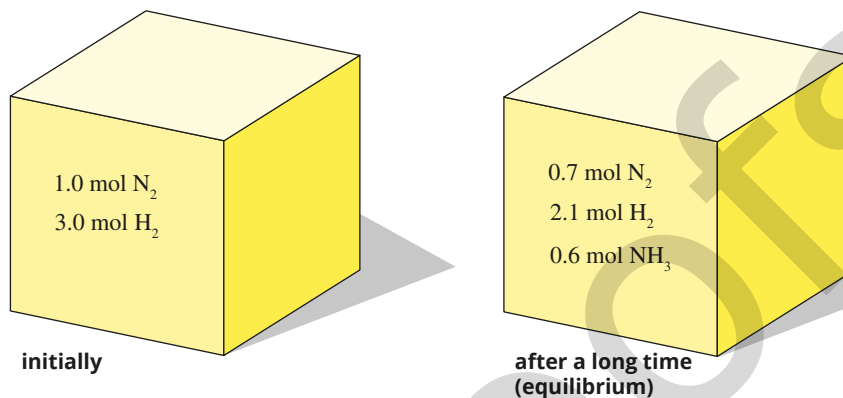
Consider the production of ammonia from hydrogen gas and nitrogen gas, known as the Haber process.

The equation for the reaction can be written as:



Suppose you mix 1 mol of nitrogen gas and 3 mol of hydrogen gas in a sealed container. From the equation, you might expect that 2 mol of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to ‘stop’ when much less than 2 mol of ammonia is present, as shown in Figure 2.2.2.

volume = 1 L  
temperature = 400°C



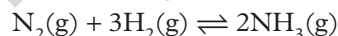
**FIGURE 2.2.2** When 1 mol of nitrogen and 3 mol of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

**i** Reversible reactions can reach a state of equilibrium where the overall concentrations of reactants and products do not change.

The reaction vessel this process occurs in can be thought of as a closed system from which the reactants and products cannot escape. Reversible reactions in a closed system eventually reach a situation where the rate of the forward reaction and the rate of the reverse reaction are equal.

At this point, there appears to be no further change to the observer. When the reaction appears to have ‘stopped’, the system is described as having reached equilibrium. At equilibrium, there still may be significant amounts of reactants in the system.

Because the reaction between nitrogen and hydrogen to form ammonia is a reversible reaction, it is best written using an equilibrium arrow:



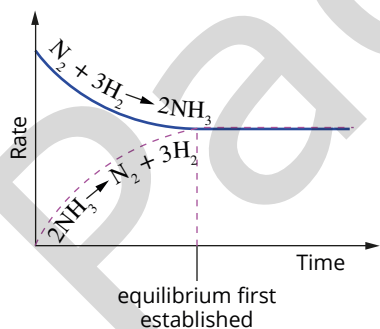
Equilibrium arrows indicate that the reaction can occur in both the forward and reverse directions. These arrows should not be used where the reaction can only proceed one way.

The idea that processes can be reversed can be used to understand why this reaction reaches equilibrium. When nitrogen gas and hydrogen gas are added to a sealed container at a constant temperature, a sequence of events occurs that can be illustrated by a plot of reaction rate versus time, like the one shown in Figure 2.2.3.

If you consider the graph in Figure 2.2.3, you can understand the following.

- Nitrogen and hydrogen gas molecules collide with each other and form ammonia. As the forward reaction,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$ , proceeds, the concentrations of nitrogen and hydrogen decrease, so the frequency of collisions between molecules decreases and the rate of the production of ammonia decreases.
- At the same time as ammonia is being formed, some ammonia molecules collide and decompose to re-form nitrogen and hydrogen:  $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ .
- Eventually the forward and reverse reactions proceed at the same rate. When this situation is reached, ammonia is formed at exactly the same rate as it is breaking down. The concentrations of ammonia, nitrogen and hydrogen then remain constant. To an observer, the reaction now appears to have stopped with no observable change.

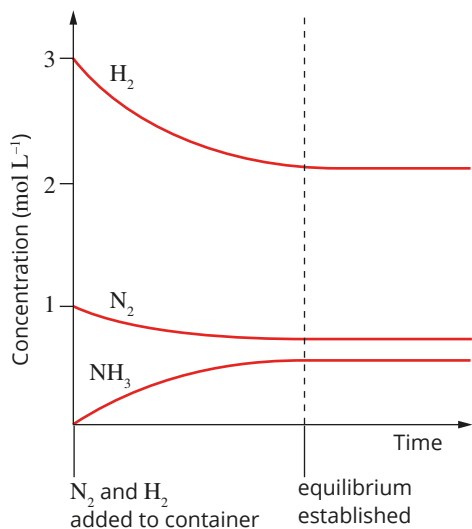
In a closed system at constant pressure and temperature, no further change will take place. The reaction has reached a point of balance—an equilibrium.



**FIGURE 2.2.3** The variation of the rates of the forward and reverse reactions with time when nitrogen and hydrogen are mixed



The concentration versus time graph in Figure 2.2.4 shows the changes in concentrations of the chemicals with time. Equilibrium is established when there is no longer any change in any of the concentrations.

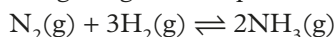


**FIGURE 2.2.4** Changes in the concentrations of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  as a mixture of nitrogen and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of  $\text{N}_2$  that reacts, three times as much  $\text{H}_2$  reacts and twice as much  $\text{NH}_3$  is produced.

**i** When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time or reaction rate versus time.

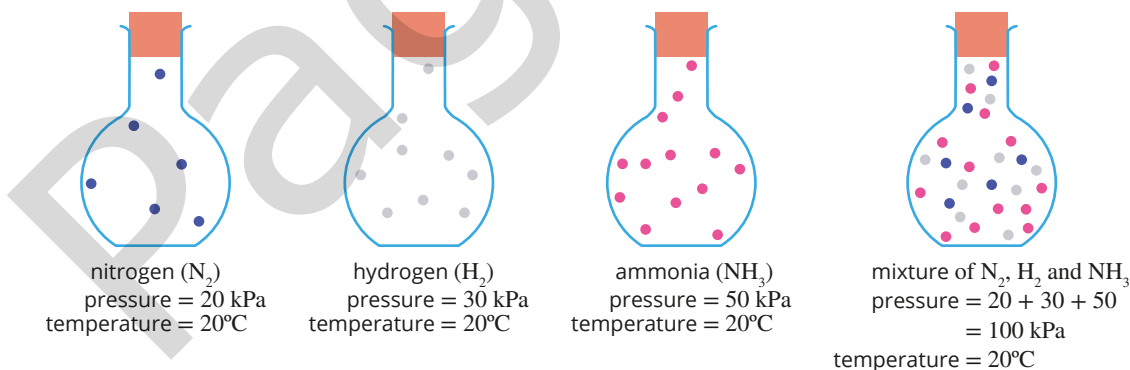
## Partial pressures

The pressure exerted by an individual gas in a container is known as its **partial pressure**. In a vessel containing the gaseous equilibrium:



the partial pressure of the nitrogen gas is the pressure that amount of nitrogen would exert if it were the only gas in the container. Similarly, the partial pressure of the hydrogen and the partial pressure of the ammonia are the pressures these gases would exert if they were the only gases in the container. The molecules of each gas move independently and collide with the walls of the container almost as though the other gases were not there.

The total pressure of a gas mixture is the sum of the effects of the collisions of all the individual gases. Therefore, the total pressure of the gaseous mixture of nitrogen, hydrogen and ammonia shown in Figure 2.2.5 is the sum of their partial pressures.

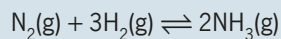


**FIGURE 2.2.5** The total pressure of a mixture of gases is the sum of the partial pressures (individual pressures) of each of the gases in a mixture.

## CHEMFILE

### Fritz Haber

Fritz Haber (Figure 2.2.6) was a German chemist who invented the process for producing ammonia that now bears his name. The reaction produces ammonia from atmospheric nitrogen and hydrogen according to the equation:



The Haber process made it feasible to produce fertilisers with a high nitrogen content. This allowed for better crop yields in agriculture. Easy access to reasonably priced fertilisers has saved lives and reduced starvation in many areas across the world. This fact was acknowledged when Haber was awarded the Nobel Prize in Chemistry in 1918, following the end of the World War I.

However, Haber's involvement in the production and use of chemical weapons by the German army in World War I made the award of a Nobel Prize controversial to many scientists who considered him to be guilty of war crimes.

You will learn more about the importance of Haber and his process in Chapter 11.



**FIGURE 2.2.6** Fritz Haber (1868–1934) invented a process for producing ammonia from atmospheric nitrogen and hydrogen. He was awarded the Nobel Prize in Chemistry in 1918.

Increasing the amount of gas in a container of fixed volume or reducing the volume of the container will increase both the partial pressure and the concentration of the gas.

The changes that occur when nitrogen and hydrogen gas form an equilibrium mixture with ammonia gas can be described by measuring the partial pressures of the individual gases. At equilibrium, the partial pressures of the three gases will be constant.

## DYNAMIC STATE OF EQUILIBRIUM

Chemical equilibrium can be described as a dynamic state because the forward and reverse reactions have not ceased. Instead, they occur simultaneously at the same rate.

During **dynamic equilibrium**:

- the **macroscopic properties** are constant. This means that the amount and concentrations of reactants and products, the pressure and the temperature are constant
- the reaction is 'incomplete' and *all* of the substances (that is, the reactants and products) are present in the equilibrium mixture
- at the molecular level, bonds are constantly being broken and new bonds are being formed as the reactants and products continue to be converted from one to another.

**i** Dynamic equilibrium is reached by reversible physical or chemical reactions taking place in a closed system.

The decomposition of dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) to nitrogen dioxide ( $\text{NO}_2$ ) is an example of a reversible reaction that reaches a dynamic equilibrium. The progression of this reaction from pure  $\text{N}_2\text{O}_4$  to the equilibrium mixture containing both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  can be monitored through the changing colour of the gases in the reaction vessel.  $\text{N}_2\text{O}_4$  is colourless and  $\text{NO}_2$  is dark brown.

The reaction occurs according to the following equation:

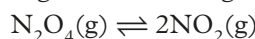
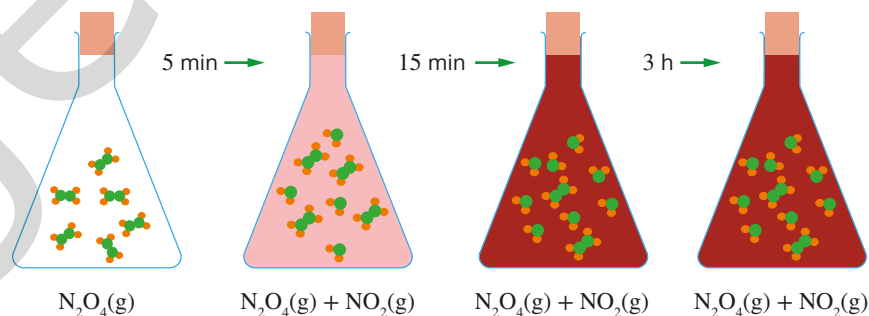


Figure 2.2.7 illustrates the observations made of a reaction vessel that is injected with some pure  $\text{N}_2\text{O}_4$ . As the forward reaction proceeds, the formation of a dark brown gas is observed. The depth of colour increases until equilibrium is reached at which point there is no further change in the colour.



**FIGURE 2.2.7** The decomposition of dinitrogen tetroxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

**EXTENSION**

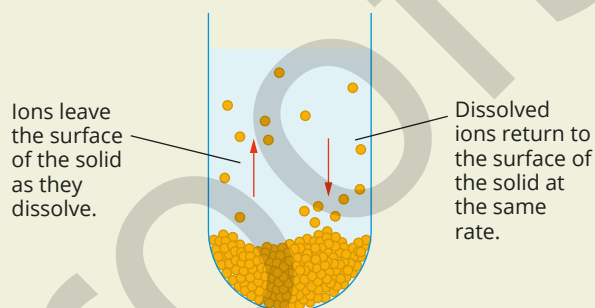
## Investigating dynamic equilibrium

Chemists can use radioactive isotopes to investigate systems in dynamic equilibrium. Radioactive isotopes behave chemically in the same way as non-radioactive atoms of the same element, but their presence and location can be easily determined by a radiation detector.

When solid sodium iodide (NaI) is added to water, it dissolves readily at first. As the concentration of dissolved sodium iodide increases, a saturated solution forms and no further solid dissolves. The concentrations of the  $\text{Na}^+$  ions and  $\text{I}^-$  ions in solution remain constant and some solid NaI is always present on the bottom of the test tube.

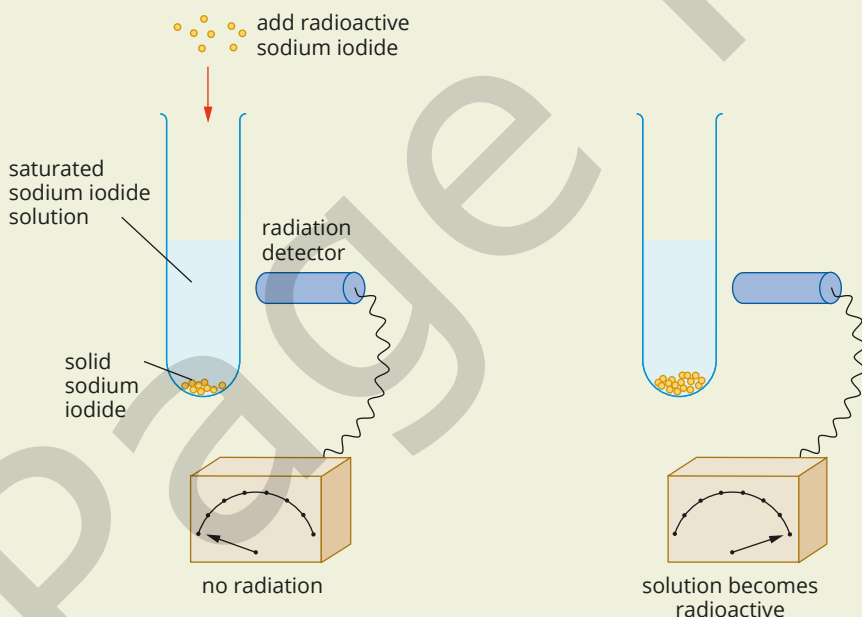
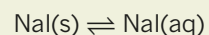
When solid sodium iodide containing radioactive iodide ions is added to a saturated solution, the subsequent movement of these 'labelled' ions can be traced. Figure 2.2.8 shows that although solid sodium iodide is still observed in the bottom of the flask, the solution quickly becomes radioactive.

The radioactivity of the solution shows that some of the radioactive sodium iodide has dissolved. The concentration of sodium iodide remains constant, so particles that were not radioactive must have crystallised from the solution at the same rate as the radioactive solid was dissolving (Figure 2.2.9).



**FIGURE 2.2.9** The cyclic dissolving and redepositing of ions in a saturated solution is an example of dynamic equilibrium.

Even though you see nothing happening, there must be continual activity at the surface of the solid. The process is a dynamic equilibrium:

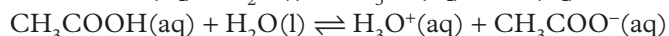
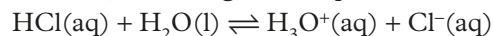


**FIGURE 2.2.8** This experiment shows that a dynamic equilibrium between the solid and dissolved ions is present in a saturated solution.

## EXTENT OF REACTION

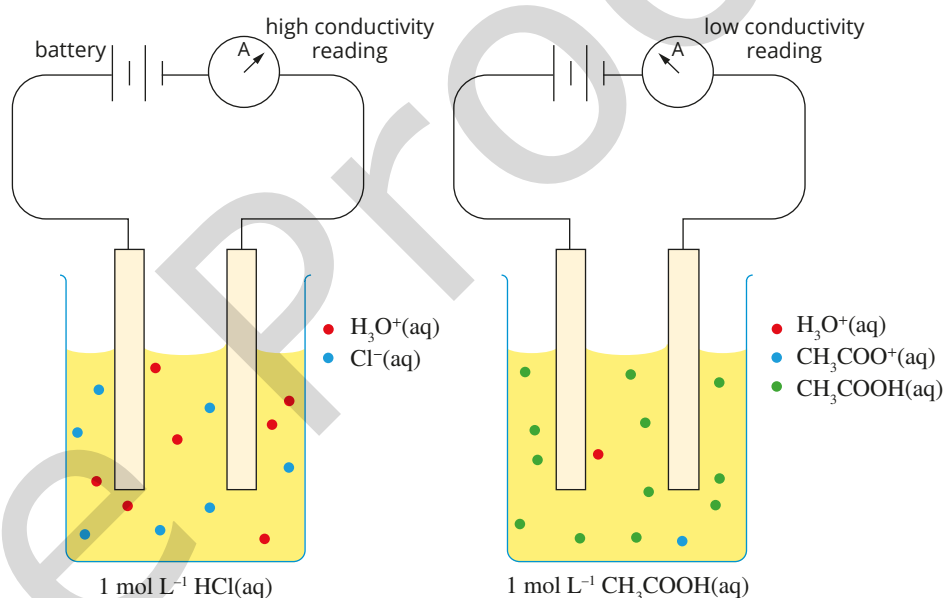
You have seen that reactions are reversible, but not all reactions proceed to the same extent before they reach equilibrium. This can be shown with a simple experiment.

Both hydrogen chloride (HCl) and ethanoic acid (acetic) acid ( $\text{CH}_3\text{COOH}$ ) react with water to form ions, according to the equations:



Solutions of both chemicals conduct electricity because they contain mobile ions. The relative conductivity of the solutions is proportional to the number of free ions in the solution. By measuring the electrical conductivity of solutions of the same concentration, you can compare how much each compound ionises in water.

Figure 2.2.10 shows the results obtained from such an experiment. You can see that when hydrogen chloride dissolves in water, the solution formed (called hydrochloric acid) is a much better conductor than the ethanoic acid solution. Both solutions were formed by adding the same number of moles of acid molecules to identical volumes of water.



**FIGURE 2.2.10** This experiment compares the electrical conductivity of  $1 \text{ mol L}^{-1}$  solutions of hydrogen chloride and ethanoic acid.

Ethanoic acid is a weak acid and will therefore only partially ionise in an aqueous solution. Hydrochloric acid is a strong acid that almost completely ionises in aqueous solution. The concept of equilibrium allows a better explanation of the idea of strong and weak acids by looking at the extent of the ionisation reaction.

The difference in conductivity observed in the experiment arises because these reactions occur to remarkably different extents. At equilibrium in a  $1 \text{ mol L}^{-1}$  solution, at  $25^\circ\text{C}$ , almost all the HCl molecules are ionised, whereas only approximately 1% of the  $\text{CH}_3\text{COOH}$  molecules are ionised.

So, different reactions proceed to different extents. The ratios of reactants to products are different for different equilibrium systems.

It is important to note that the **extent of reaction** describes how much product is formed when the system reaches equilibrium. However, the **rate of reaction** is a measure of the change in concentration of the reactants and products with time and is not directly related to the extent of reaction. The rates of reversible reactions range from very slow to very fast and determine how long the reaction takes to reach equilibrium.

**i** The extent of a reaction does not give any information about how fast a reaction will proceed. It only indicates how much product is formed once the system is at equilibrium.

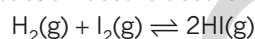
## 2.2 Review

### SUMMARY

- At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This is called a state of dynamic equilibrium.
- Different reactions proceed to different extents.
- The relative ratios of reactants to products when equilibrium is reached are different for different reactions.
- The extent of reaction indicates how much product is formed at equilibrium, whereas the rate of reaction is a measure of the change in concentration of the reactants and products with time.

### KEY QUESTIONS

- 1 Which one of the following statements about the extent of reaction is true?
  - A The extent of reaction indicates the rate of the reaction, and indicates the time taken to reach equilibrium.
  - B The extent of reaction is the point when there are equal amounts of reactants and products.
  - C The extent of reaction indicates how far the reaction has proceeded in the forward direction when equilibrium is achieved.
  - D The extent of reaction indicates the rate of reaction and is the point when the rate of the forward reaction is equal to the rate of the reverse reaction.
- 2 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:



On the rate-time graph for this system in Figure 2.2.10, label the lines for the forward and reverse reactions with the appropriate chemical equation. Also label the point when equilibrium is first established.

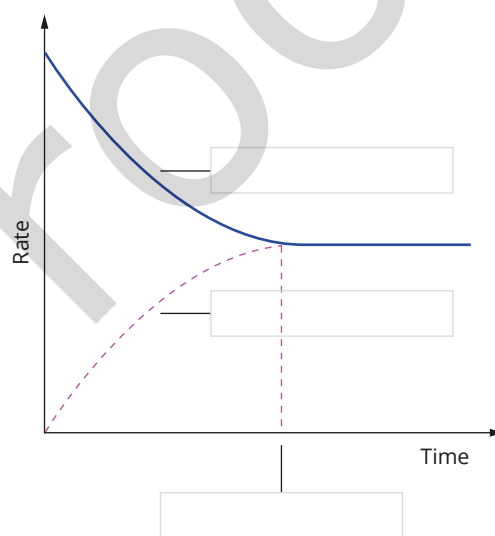


FIGURE 2.2.10 Rate-time graph

- 3 Fill in the blanks to complete the sentences about dynamic equilibrium.

In a \_\_\_\_\_ system, as the concentrations of the reactants decreases, the rate of the forward reaction also \_\_\_\_\_. The collisions between these reactant molecules occur \_\_\_\_\_ frequently. Once some product starts to form, the \_\_\_\_\_ reaction occurs and the frequency of collisions between product molecules \_\_\_\_\_. At equilibrium, the rates of the forward and backward reactions are \_\_\_\_\_ and the concentrations of all species do not change.

## 2.2 Review *continued*

- 4 The graph below shows the concentration versus time plot for the decomposition of dinitrogen tetroxide:  
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  at  $100^\circ\text{C}$  in a 1 L reaction vessel.  
 $\text{N}_2\text{O}_4$  is a colourless gas and  $\text{NO}_2$  is brown. Use the graph in Figure 2.2.11 to answer the following questions.

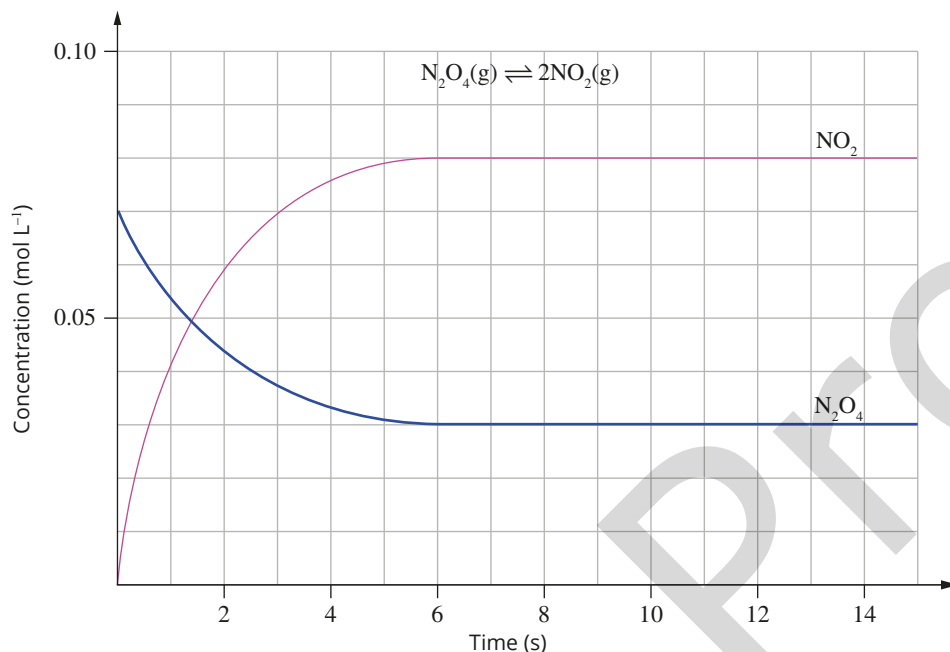


FIGURE 2.2.11 Concentration–time graph.

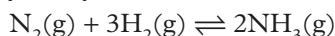
- What is the initial concentration of  $\text{N}_2\text{O}_4$  in the flask?
- What is the initial concentration of  $\text{NO}_2$  in the flask?
- What is the concentration of  $\text{N}_2\text{O}_4$  at equilibrium?
- What is the concentration of  $\text{NO}_2$  at equilibrium?
- Over the course of the reaction, how many moles of  $\text{N}_2\text{O}_4$  decompose?
- What do the horizontal regions of the graph indicate?
- How long does it take for equilibrium to be reached?
- A student studying this reaction records her observations over time. What will she observe as the reaction proceeds?

## 2.3 The equilibrium law

In this section, you will investigate the relationship between the quantities of reactants and the quantities of products present when a system reaches equilibrium. This relationship allows you to qualitatively predict the relative amounts of reactants and products in individual equilibrium systems.

### REACTION QUOTIENT

Consider the equilibrium system you were introduced to in section 2.2:



An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 2.3.1 shows the concentrations of each of these gases in four different equilibrium mixtures at a constant temperature of 400°C. The values of the fraction  $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  for each mixture are also given.

The fraction  $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  is called the **reaction quotient** ( $Q_c$ ) or **concentration fraction** of the mixture.

**TABLE 2.3.1** Concentrations of reactants and products present in equilibrium mixtures

Equilibrium mixture	$[\text{N}_2]$ (mol L <sup>-1</sup> )	$[\text{H}_2]$ (mol L <sup>-1</sup> )	$[\text{NH}_3]$ (mol L <sup>-1</sup> )	$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
1	0.25	0.75	0.074	0.052
2	0.25	0.65	0.089	0.052
3	0.0025	0.0055	$4.6 \times 10^{-6}$	0.051
4	0.0011	0.0011	$2.7 \times 10^{-7}$	0.051

As you can see in Table 2.3.1, the reaction quotient  $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  has an almost constant value of 0.052 for each equilibrium mixture regardless of the concentration of each component. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the respective reactant and product concentrations used in the reaction quotient.

While the reaction quotient can be calculated for any mixture of reactants and products at any time during a reaction, it is only when the mixture is at equilibrium that it gives a constant value. At equilibrium, the value of the reaction quotient is equal to the **equilibrium constant**,  $K_c$ .

In general, for chemical reactions at equilibrium:

- different chemical reactions have different values of  $K_c$
- the size of  $K_c$  indicates the proportions (relative amounts) of reactants and products in the equilibrium mixture
- for a particular reaction,  $K_c$  is constant for all equilibrium mixtures at a fixed temperature.

### CHEMFILE

#### Equilibria in biological systems

Although the principles you will learn in this section and the other sections in this chapter will be restricted to chemical equilibria, the same principles can be applied to other systems in our surroundings. For example, on the African plains of Tanzania, there is a delicate balance of herbivores such as zebras and wildebeest, and carnivores such as lions (Figure 2.3.1). If the populations change because of drought or disease, the relative numbers change and a new balance is established. This new balance can be predicted in much the same way as occurs for chemical equilibrium.



**FIGURE 2.3.1** The populations of zebras and lions in Africa can be understood by using the principles of equilibrium.

**i**  $K_c$  is the equilibrium constant for a reaction. The value of  $K_c$  is different for different reactions.

## EXPRESSION FOR THE EQUILIBRIUM LAW

By studying a large number of reversible systems such as the one between nitrogen, hydrogen and ammonia in the previous example, chemists have been able to develop the concept of the equilibrium law.

The **equilibrium law** states that the:

- equilibrium constant,  $K_c$ , is the concentrations of products divided by the concentrations of reactants at equilibrium
- index of each component concentration is the same as the coefficient for the substances in the balanced chemical equation.

For the general equation  $aW + bX \rightleftharpoons cY + dZ$  at equilibrium at a particular temperature, the equilibrium expression can be written as:

$$K_c = \frac{[Y]^c [Z]^d}{[W]^a [X]^b}$$

where  $K_c$  is the equilibrium constant.

A useful way of remembering the equilibrium law is that:

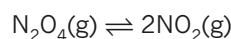
$K_c$  can be represented as  $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ . Remember that if there is more than one product or reactant, you must multiply the terms.

**i** When you write an equilibrium expression, the concentrations of the products are always on the top of the expression.

### Worked example 2.3.1

#### DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

The decomposition of  $N_2O_4$  is a reversible reaction that occurs according to the equation:



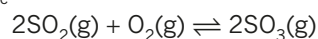
Write the expression for the equilibrium constant  $K_c$ .

Thinking	Working
Identify the reactants and products. The reactants appear in the denominator of the expression and the products in the numerator.	$N_2O_4$ is a reactant so it appears in the denominator of the expression. $NO_2$ is a product so it appears in the numerator of the expression.
Write the expression for $K_c$ . $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Remember that the index of each component concentration is the same as its coefficient in the balanced chemical equation.	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

### Worked example 2.3.1: Try yourself

#### DETERMINING THE EXPRESSION FOR THE EQUILIBRIUM CONSTANT FOR AN EQUILIBRIUM SYSTEM

Write the expression for  $K_c$  for the reversible reaction:

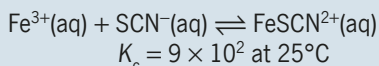




## CHEMFILE

### Equilibrium in the theatre

A yellow solution containing  $\text{Fe}^{3+}$  ions reacts with a colourless solution containing  $\text{SCN}^-$  ions to form a blood-red solution containing  $\text{FeSCN}^{2+}$  ions, according to the equilibrium reaction:



An appreciable amount of the product  $\text{FeSCN}^{2+}$  is present in an equilibrium mixture, so the mixture appears blood red (Figure 2.3.3).

This equilibrium reaction is used in theatrical productions to make fake blood. A layer of colourless  $\text{SCN}^-$  solution can be painted onto an actor's hand prior to the scene. If a plastic knife that has been previously dipped in pale yellow  $\text{Fe}^{3+}$  solution is used to make a fake cut across the hand, a blood-red 'cut' appears due to the production of red  $\text{FeSCN}^{2+}$ .



**FIGURE 2.3.3** Chemicals needed to make fake blood. From left to right: a solution containing  $\text{Fe}^{3+}$ , a solution containing  $\text{SCN}^-$ , and an equilibrium mixture of  $\text{Fe}^{3+}$ ,  $\text{SCN}^-$  and  $\text{FeSCN}^{2+}$ .

## HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

The chemical reactions discussed so far have involved **homogeneous reactions**, in which all reactants and products are in the same state or phase. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different states or phases.

The important feature of the equilibrium law for heterogeneous reactions is that the concentration of a pure solid or a pure liquid is assigned the value of 1. This is because these concentrations do not depend on how much of the pure substance is present.

Because the concentration of the solid in a heterogeneous system is considered a constant, it is removed from the equilibrium expression. As a result, the expression for the equilibrium of a heterogeneous system is often much simpler.

For example, for the equation:

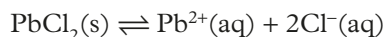


the expression for the equilibrium constant is:

$$K_c = [\text{CO}_2]$$

Since  $\text{CaO}$  and  $\text{CaCO}_3$  are both solids, they do not appear in the equilibrium law.

The dissolution of a solid to form an aqueous solution is another example of a heterogeneous equilibrium system. Consider the dissociation of lead chloride ( $\text{PbCl}_2$ ) into lead and chloride ions in solution:



Because the concentration of the solid lead chloride is constant, it is assigned the value of 1 and not written in the expression for the equilibrium law. This results in the expression:

$$K_c = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$

## 2.3 Review

### SUMMARY

- The equilibrium constant,  $K_c$ , is a constant for a particular chemical reaction at a particular temperature.
- The equilibrium law for the equation:  
 $aW + bX \rightleftharpoons cY + dZ$   
is:  
$$K_c = \frac{[Y]^c [Z]^d}{[W]^a [X]^b}$$
- A reaction quotient,  $Q_c$ , can be calculated for any stage of a chemical reaction. The reaction quotient has the same mathematical expression as the equilibrium constant.
- When a reaction system at a particular temperature has reached equilibrium, the reaction quotient is equal to the equilibrium constant.
- An expression for the equilibrium law can be written for both homogeneous and heterogeneous systems. For heterogeneous systems, the concentration of a pure solid or a pure liquid is assigned as 1.

### KEY QUESTIONS

- Write an expression for the equilibrium constant for the reaction of hydrogen and chlorine with the equation:  
$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$
- Match each of the terms in **a–d** with the appropriate statement (1–4) from the box.

1	a system where some of the species are in different states
2	is always equal to $K_c$
3	a system where all the species are in the same state
4	is equal to $K_c$ at equilibrium

  - Homogeneous system
  - Heterogeneous system
  - Reaction quotient
  - Equilibrium constant
- For each of the following reactions, write the correct expression for the equilibrium constant,  $K_c$ .
  - $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
  - $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
  - $2Ag^+(aq) + CO_3^{2-}(aq) \rightleftharpoons Ag_2CO_3(s)$
  - $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
- Which one of the equations below has the following expression for the equilibrium constant?  
$$K_c = \frac{[H_2]^2 [CO]}{[CH_3OH]}$$
  - $4H_2(g) + 2CO(g) \rightleftharpoons 2CH_3OH(g)$
  - $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
  - $2CH_3OH(g) \rightleftharpoons 4H_2(g) + 2CO(g)$
  - $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

## 2.4 Working with equilibrium constants

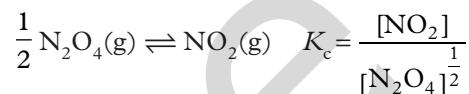
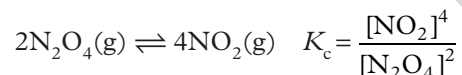
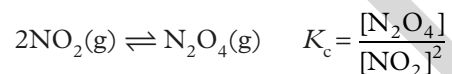
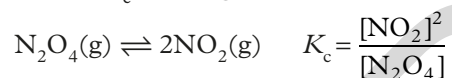
In section 2.3, you learnt that an equilibrium law can be written for a chemical reaction at equilibrium. The mathematical expression for the equilibrium law is a fraction involving the concentrations of the reactants and products, which has a value equal to  $K_c$ , the equilibrium constant for the reaction at equilibrium.

The value of an equilibrium constant indicates the extent of a reaction or how far a reaction will proceed towards the products. In this section, you will learn how to interpret these values in terms of the relative amounts of reactants and products present at equilibrium.

You will also discover how temperature affects an equilibrium constant and what happens to the value of an equilibrium constant when an equation is reversed or the coefficients of the equation are changed.

### DEPENDENCY OF AN EQUILIBRIUM CONSTANT ON THE EQUATION

The equilibrium law depends upon the chemical equation used for a particular reaction. For example, the equilibrium between the gases  $N_2O_4$  and  $NO_2$  can be represented by several equations. For each equation provided below, the expression for the equilibrium constant,  $K_c$ , is also given.



You can see from these expressions that if:

- one equation is the reverse of another, the equilibrium constants are the inverse (or reciprocal) of each other
- the coefficients of an equation are doubled, the value of  $K_c$  is squared
- the coefficients of an equation are halved, the value of  $K_c$  is the square root of the original value of  $K_c$ .

Therefore, it is important to specify the equation when quoting an equilibrium constant.

### THE MEANING OF THE VALUE OF AN EQUILIBRIUM CONSTANT

The value of an equilibrium constant is based on the equilibrium concentrations of the products divided by the equilibrium concentrations of the reactants. Therefore, it indicates the extent of reaction at equilibrium (how far the forward reaction proceeds before equilibrium is established) and the **equilibrium yield** (the amount of products present at equilibrium).

**i** When comparing values of  $K_c$ , it is important to know the equation associated with the equilibrium constant.

**i** The concentrations used to determine  $K_c$  must be the concentration of each component of the mixture at equilibrium.

The relationship between the value of  $K_c$  and the relative proportions of reactants and products at equilibrium is shown in Table 2.4.1.

**TABLE 2.4.1** The relationship between the value of  $K_c$  and the extent of a reaction provides information on the relative amounts of reactants and products in the reaction mixture at equilibrium

Value of $K_c$	Extent of reaction
Between about $10^{-4}$ and $10^4$	The extent of reaction is significant. Appreciable concentrations of both reactants and products are present at equilibrium. e.g. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $K_c = 0.52$ at $400^\circ\text{C}$
Very large; $>10^4$	Almost complete reaction occurs. The concentrations of products are much higher than the concentrations of the reactants at equilibrium. e.g. $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ $K_c = 10^7$ at $25^\circ\text{C}$
Very small; $<10^{-4}$	Negligible reaction occurs. The concentrations of reactants are considerably higher than the concentrations of products at equilibrium. e.g. $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$ $K_c = 1.8 \times 10^{-5}$ at $25^\circ\text{C}$

When  $K_c$  is very large, the numerator of the equilibrium expression must be large compared to the denominator, which means there is a large amount of products relative to the amount of reactants.

When  $K_c$  is very small, the numerator of the equilibrium expression must be very small compared to the denominator, which means there must be a large amount of reactants relative to the amount of products.

## EFFECT OF TEMPERATURE ON AN EQUILIBRIUM CONSTANT

It has been shown experimentally that the value of the equilibrium constant,  $K_c$ , for a particular reaction depends only upon temperature. It is not affected by the addition of reactants or products, changes in pressure, or the use of catalysts.

The effect of a change in temperature on an equilibrium constant depends on whether the reaction is exothermic or endothermic. As temperature increases, for:

- exothermic reactions, the value of  $K_c$  decreases and so the amount of products present at equilibrium decreases
- endothermic reactions, the value of  $K_c$  increases and so the amount of products present at equilibrium increases.

Table 2.4.2 summarises the effect on  $K_c$  when temperature increases. The opposite is true when temperature decreases.

**TABLE 2.4.2** The effect on the value of  $K_c$  when the temperature of the system increases

$\Delta H$	$T$	$K_c$
Exothermic (-)	Increases	Decreases
Endothermic (+)	Increases	Increases

Because the value of  $K_c$  depends on temperature, it is essential to specify the temperature at which an equilibrium constant has been measured.

**i** Only a change in temperature will change the value of  $K_c$  for a given reaction.

## 2.4 Review

### SUMMARY

- The expression for the equilibrium constant,  $K_c$ , is dependent on the equation for the reaction.
- The value of  $K_c$  provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium (Table 2.4.3).
- As temperature increases, the value of  $K_c$  increases for endothermic reactions and decreases for exothermic reactions.

**TABLE 2.4.3** Summary of the relationship between the value of  $K_c$  and the extent of a reaction

Value of $K_c$	Extent of reaction
Between about $10^{-4}$ and $10^4$	Indicates significant reaction occurs
$>10^4$	Indicates an almost complete reaction occurs
$<10^{-4}$	Indicates negligible reaction occurs

### KEY QUESTIONS

- 1 Complete the sentences to describe equilibrium by selecting terms from the box below.

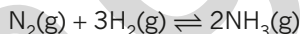
a significant	an extensive	equal to
greater than	the products	less than
negligible	the reactants	
both the reactants and the products		

Equilibrium occurs when the rate of the forward reaction is \_\_\_\_\_ the rate of the reverse reaction. The value of the equilibrium constant,  $K_c$ , is dependent upon the equilibrium concentrations of \_\_\_\_\_. If, at a particular temperature,  $K_c$  for a reaction is  $10^{-6}$ , this reaction will produce \_\_\_\_\_ amounts of product at equilibrium.

- 2 The equilibrium constant for the decomposition of ammonia is 100 at  $255^\circ\text{C}$  for the equation:

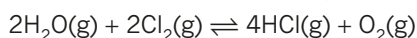


- a Write an expression for the equilibrium constant for the equation:

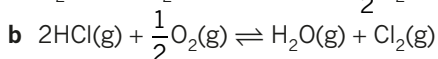
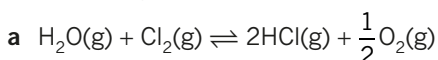


- b Based on the stated value of the equilibrium constant in the question, suggest why, at the same temperature, the value of the equilibrium constant for the equation in part a will be less than 1.

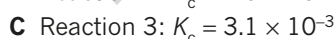
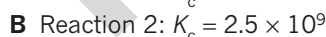
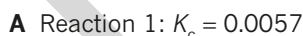
- 3 Water reacts with chlorine according to the equation:



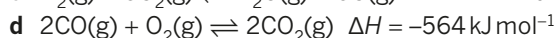
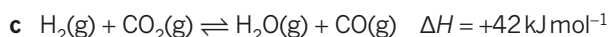
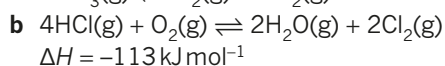
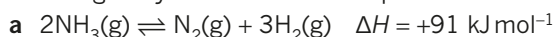
At a particular temperature, the value of the equilibrium constant for this reaction is determined to be  $4.0 \times 10^{-4}$ . Assuming no change in temperature, write the expression for the equilibrium constant for the following reactions:



- 4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. In which of the reactions would there be substantially more products produced compared to reactants?



- 5 State whether the equilibrium constants for each of the following would be increased, decreased or unchanged by an increase in temperature:



## 2.5 Le Châtelier's principle



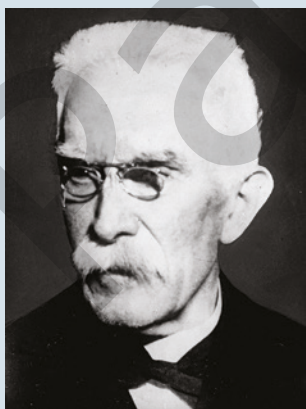
**FIGURE 2.5.1** The effect of changes on the equilibrium:  $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$ . The addition of excess  $\text{Cl}^-$  ions causes a net forward reaction and the solution turns blue as more  $\text{CoCl}_4^{2-}$  is formed. The addition of excess water causes a net reverse reaction and the solution returns to the original pink colour as more  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is formed.

### CHEMFILE

#### Henri Le Châtelier

Henri Le Châtelier (Figure 2.5.2), was a French chemist and engineer. He is best known for developing the principle of chemical equilibrium, which is now named after him.

Le Châtelier made an early attempt at synthesising ammonia from nitrogen and hydrogen, but an error in the design of the experiment resulted in an explosion that nearly killed one of his laboratory assistants. Le Châtelier also developed the oxyacetylene welding torch and the thermocouple for accurate temperature measurement.



**FIGURE 2.5.2** Henri Le Châtelier (1850–1936)

In this section, you will learn about some of the effects of changes on chemical systems at equilibrium.

Your understanding of the underlying principles of chemical equilibrium will enable you to predict the impact of changes when a reactant or product is added or removed from an equilibrium system, as seen in the system shown in Figure 2.5.1.

The effect of changes on a chemical equilibrium is very important to the chemical industry. Conditions must be carefully selected to ensure that optimum yields of products are obtained within a reasonable timeframe.

### CHANGES TO AN EQUILIBRIUM SYSTEM

Different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products at equilibrium differ from one reaction to another. The relative amounts of reactants and products at equilibrium is called the **position of equilibrium** and it depends upon reaction conditions.

For any equilibrium system, the position of equilibrium may be changed by:

- adding or removing a reactant or product
- changing the pressure by changing the volume (for equilibria involving gases)
- diluting (for equilibria in solution)
- changing the temperature.

Careful control of the reaction conditions allows chemists to maximise the equilibrium yield of a desired product by moving the position of equilibrium to the right (and therefore increasing the amount of products formed).

**i** The position of equilibrium should not be confused with  $K_c$ . The value of  $K_c$  is only ever changed by a change in temperature.

### LE CHÂTELIER'S PRINCIPLE

The effect of a change in conditions on an equilibrium system is summarised in a useful generalisation called **Le Châtelier's principle**.

*Le Châtelier's principle states that if an equilibrium system is subjected to a change, the system will adjust itself to partially oppose the effect of that change.*

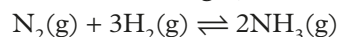
When a change occurs to an equilibrium system so that it is momentarily no longer at equilibrium, a net reaction occurs that partially counteracts the effect of the change. The system will establish a new equilibrium.

As a result, the position of equilibrium will change. There may be an increase in the amount of either products or reactants, depending on the nature of the change. By understanding Le Châtelier's principle, you can predict the effect of a change to an equilibrium system.

You will now consider the effect of different changes on equilibrium systems.

#### Adding extra reactant or product

A sealed reaction vessel of hydrogen and nitrogen gases at a particular temperature will establish an equilibrium with ammonia gas, according to the equation:



At equilibrium, the rates of the forward and reverse reactions are equal. The concentrations and partial pressures of the three gases are constant. If extra  $\text{N}_2$  gas were added to the container without changing the volume or temperature, the mixture would momentarily not be in equilibrium. The system would then adjust to form a new equilibrium with different concentrations and partial pressures of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$ .

You can predict the change in the position of the equilibrium by using Le Châtelier's principle. The underlying basis for this prediction can be understood by applying the principles of **collision theory** and the rates of reactions.

### Predicting the effect of a change using Le Châtelier's principle

The effect of adding the  $\text{N}_2$  gas to the equilibrium may be predicted simply by applying Le Châtelier's principle. According to Le Châtelier's principle, if  $\text{N}_2$  is added to an equilibrium system, the system will adjust to decrease the concentration (and partial pressure) of the added  $\text{N}_2$ , so a net forward reaction will occur.

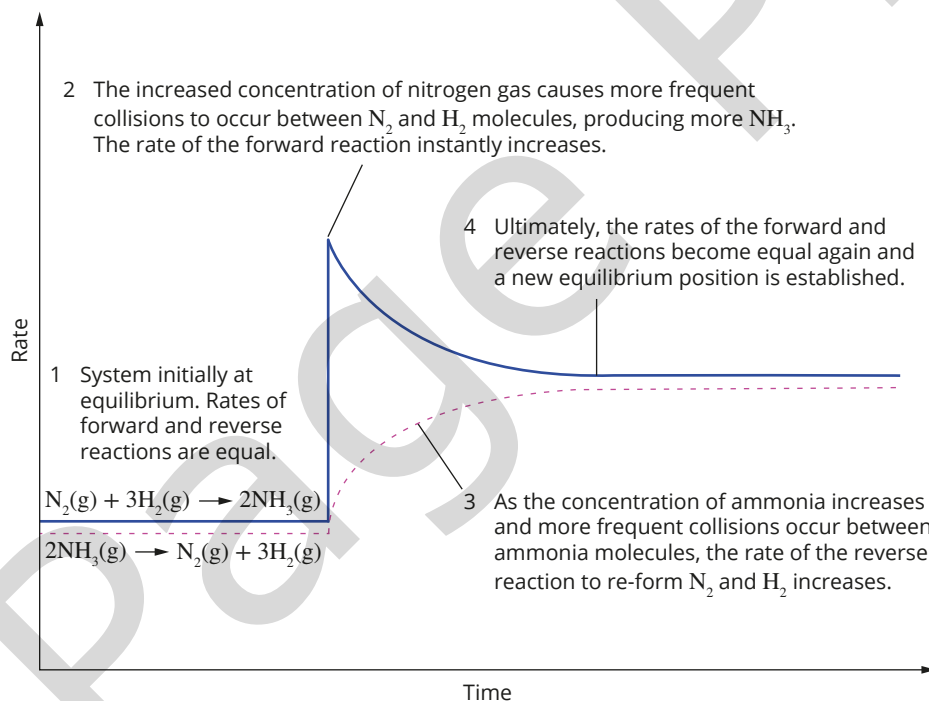
It is important to note that, even though the concentration (and partial pressure) of  $\text{N}_2$  gas decreases as the system moves to establish the new equilibrium, its final concentration (and partial pressure) is still higher than in the original equilibrium. Le Châtelier's principle states that the change is *partially* opposed. The system does not return to the initial equilibrium position following the change in conditions.

### Explaining the effect of a change using collision theory and reaction rates

You can apply your knowledge of collision theory and reaction rates to understand the effect of adding the extra  $\text{N}_2$  gas. Because the concentration of  $\text{N}_2$  molecules has increased, the rate of the forward reaction initially becomes greater than the rate of the reverse reaction.

Then, as the concentrations of  $\text{N}_2$  and  $\text{H}_2$  decrease and the concentration of  $\text{NH}_3$  increases, the rate of the forward reaction rate decreases and the rate of the reverse reaction increases until they become equal again. A new equilibrium is formed. The rate-time graph in Figure 2.5.3 show the effects on the rate of the forward and reverse reactions as the composition of the mixture adjusts to form a new equilibrium.

**i** Collision theory is used to explain the different rates of chemical reactions. It states that for a reaction to occur, the reactant particles must collide with sufficient energy and the correct orientation. The more successful collisions that occur within a specified time period, the faster is the reaction rate.



**FIGURE 2.5.3** This rate-time graph shows the events that occur as a mixture of nitrogen and hydrogen gas returns to equilibrium after the addition of extra nitrogen gas.

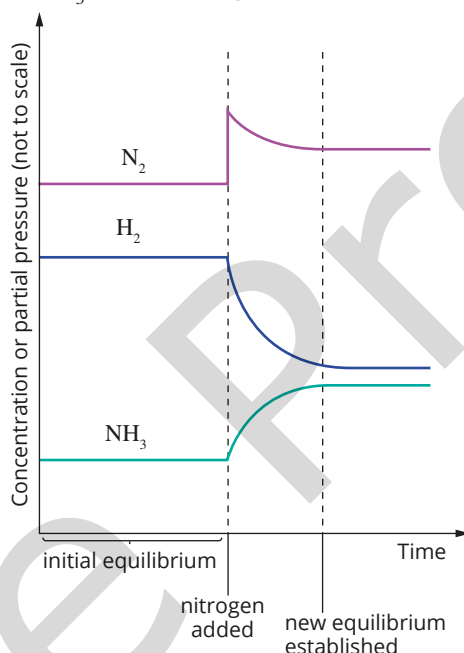
Once the system has re-established equilibrium, the rates of the forward and reverse reactions will again be equal. Overall though, a net forward reaction has occurred with an increase in the concentration and partial pressure of  $\text{NH}_3$  at equilibrium. The equilibrium position is said to have shifted to the right.

The changes occurring to the system can also be shown on a concentration–time graph or a pressure–time graph. Figure 2.5.4 illustrates the effect on the system when  $\text{N}_2$  gas is added as described.

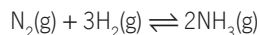
Note that the value of  $K_c$  for the equilibrium reaction remains unchanged as the temperature has not changed.

If you follow the same reasoning as for the addition of  $\text{N}_2$ , you can see that adding extra amounts of the other reactant,  $\text{H}_2$ , to the system will also increase the concentration and partial pressure of  $\text{NH}_3$  produced. However, the addition of more product,  $\text{NH}_3$ , would result in a net reverse reaction and the equilibrium position shifting to the left, reducing the overall concentration and partial pressure of  $\text{NH}_3$  as seen in Figure 2.5.5.

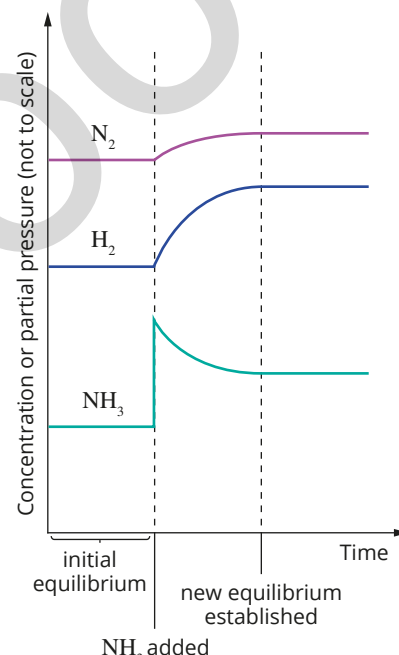
**i** Only temperature changes the value of  $K_c$  for an equilibrium system.



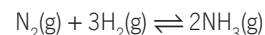
**FIGURE 2.5.4** A representation of changes in concentrations and partial pressures that occur when additional nitrogen gas is added to the equilibrium:



Note that the vertical axis does not show the rate of reaction.



**FIGURE 2.5.5** A representation of changes in concentrations and partial pressures that occur when additional ammonia gas is added to the equilibrium:



The reaction shifts to the left, forming more  $\text{N}_2$  and  $\text{H}_2$ .

Table 2.5.1 summarises how an equilibrium system acts to oppose the addition or removal of reactants and products.

**TABLE 2.5.1** The general effects of a change to a system at equilibrium

Change to equilibrium	Effect
Adding a reactant	Formation of more products—a net forward reaction Equilibrium position shifts to the right
Adding a product	Formation of more reactants—a net reverse reaction Equilibrium position shifts to the left
Removing a product	Formation of more products—a net forward reaction Equilibrium position shifts to the right

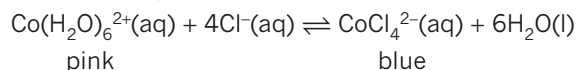


Worked Example 2.5.1 shows the use of collision theory to explain how an equilibrium system is affected by the addition of a reactant or product.

### Worked example 2.5.1

#### USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

In solution, pink-coloured  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions form an equilibrium with blue-coloured  $\text{CoCl}_4^{2-}(\text{aq})$  ions, as shown by the equation:



Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of  $\text{Cl}^-$  ions on the equilibrium.

Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding $\text{Cl}^-$ ions increases the concentration of these ions.
Use collision theory to determine the initial effect on the rate of the forward (or reverse) reaction.	Collisions between $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ions and $\text{Cl}^-$ ions become more frequent, increasing the rate of the forward reaction and reducing the concentration of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cl}^-$ ions.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more product ions, $\text{CoCl}_4^{2-}$ , are formed, the rate of the reverse reaction increases, until the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Predict the overall effect of the change on the position of equilibrium.	A net forward reaction has occurred.

### Worked example: Try yourself 2.5.1

#### USING COLLISION THEORY TO EXPLAIN THE EFFECT OF ADDITION OF A REACTANT OR PRODUCT ON AN EQUILIBRIUM SYSTEM

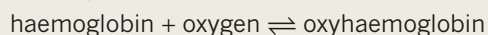
Consider the following equilibrium system:



Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of  $\text{CO}$  gas on the equilibrium.

## Competing equilibria—carbon monoxide poisoning

Haemoglobin in red blood cells transports oxygen from your lungs to the cells in your body. The haemoglobin complex combines with oxygen to form an equilibrium system with oxyhaemoglobin:



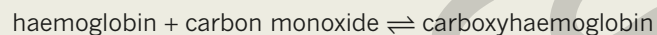
In the lungs, oxygen from the air combines with haemoglobin. According to Le Châtelier's principle, the higher concentration of oxygen in this environment will cause a net forward reaction, producing greater amounts of oxyhaemoglobin. Most of the haemoglobin is converted to oxyhaemoglobin as a result of the continual addition of oxygen from each breath you take.

Carbon monoxide is a colourless, odourless and tasteless gas that is formed as a product in the incomplete combustion of fuels. Carbon monoxide is present in cigarette smoke and in the exhaust gases from car engines (Figure 2.5.6).



**FIGURE 2.5.6** Carbon monoxide gas is formed when hydrocarbon fuels, such as petrol, are burnt in limited supplies of oxygen.

The high toxicity of carbon monoxide is a result of its reaction with haemoglobin:



The equilibrium constant for the reaction between carbon monoxide and haemoglobin is nearly 20 000 times greater than for the reaction between oxygen and haemoglobin. The larger equilibrium constant means that the forward reaction is much more likely to occur. Even small concentrations of carbon monoxide shift the position of equilibrium well to the right.

The formation of carboxyhaemoglobin reduces the concentration of haemoglobin, causing the reverse reaction of oxyhaemoglobin formation to occur. In extreme cases, almost no oxyhaemoglobin is left in the blood and carbon monoxide poisoning occurs.

Symptoms of carbon monoxide poisoning include drowsiness, dizziness, headaches, shortness of breath and loss of intellectual skills. Loss of consciousness and even death can result from carbon monoxide concentrations as low as 200 ppm.

The reactions of oxygen and carbon monoxide with haemoglobin are described as **competing equilibria**, because both oxygen and carbon monoxide 'compete' for the same substance, haemoglobin. The equilibrium reaction with the larger equilibrium constant has a significant effect on the extent of reaction of the other reaction.

## 2.5 Review

### SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will adjust itself to partially oppose the change.
- The effect of a change on an equilibrium can be predicted from Le Châtelier's principle. The effects of changes can also be explained by the use of collision theory and the equilibrium law (Table 2.5.2).

**TABLE 2.5.2** Summary of effect of change on equilibrium using Le Châtelier's principle and collision theory

Change to system in equilibrium	Le Châtelier's principle prediction: effect of change on equilibrium position	Collision theory explanation: effect of change on equilibrium position
Adding extra reactant	Shifts to the right (net forward reaction)	Increased reactant concentration causes more frequent collisions, initially increasing the rate of the forward reaction. As reactants are consumed and more products form, the rate of the forward reaction decreases and the rate of the reverse reaction increases. A new equilibrium forms when the rates become equal. However, since the rate of the forward reaction was initially increased, this results in a net forward reaction.
Adding product	Shifts to the left (net reverse reaction)	Increased product concentration causes more frequent collisions, initially increasing the rate of the reverse reaction. As products are consumed and more reactants form, the rate of the reverse reaction decreases and the rate of the forward reaction increases. A new equilibrium forms when the rates become equal. However, since the rate of the reverse reaction was initially increased, this results in a net reverse reaction.

### KEY QUESTIONS

- Use Le Châtelier's principle to predict the effect on the position of equilibrium of adding more hydrogen gas to the following systems.
  - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
  - $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
  - $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$
- Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium of increasing the partial pressure of hydrogen by adding more hydrogen gas to the following systems.
  - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
  - $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
- Predict the effect of the changes on the position of each of the following equilibrium.
  - Addition of  $\text{SO}_3$  to the equilibrium:  
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
  - Removal of  $\text{CH}_3\text{COO}^-$  from the equilibrium:  
 $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
- Consider the equilibrium:  
$$\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$$
Which one of the following correctly describes a change that would cause an increase in the amount of  $\text{Cu}(\text{NH}_3)_4^{2+}$  present?
  - $\text{OH}^-(\text{aq})$  is added, to react with  $\text{Cu}^{2+}$ , and the reaction shifts to the left.
  - More  $\text{NH}_3$  is added, and the reaction shifts to the right.
  - $\text{H}^+(\text{aq})$  is added, to react with the  $\text{NH}_3$  and the reaction shifts to the left.
  - None of the above reactions increase the amount  $\text{Cu}(\text{NH}_3)_4^{2+}$ .

## 2.6 Further applications of Le Châtelier's principle



**FIGURE 2.6.1** Cuttlefish have an internal shell made of calcium carbonate. Cuttlefish and other marine animals could be affected by the decreasing pH of oceans.

Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect many natural systems.

For example, in the oceans, carbon dioxide gas is involved in equilibria that provide the carbonate ions needed for the growth of seashells, coral reefs and other marine organisms. Using Le Châtelier's principle, scientists predict that increasing levels of carbon dioxide in the atmosphere will affect the pH of the Earth's oceans. This will put marine ecosystems and organisms at risk, including the cuttlefish in Figure 2.6.1, whose shells are made of calcium carbonate.

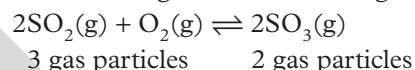
In this section, you will continue your study of the effects of changes on chemical systems at equilibrium. Your understanding of chemical equilibrium, Le Châtelier's principle, collision theory and rates of reaction will enable you to predict the impact of changes in gas pressure, solution concentration and temperature, and the addition of a catalyst on an equilibrium system.

Later in the course, you will learn how the principles of equilibrium can be applied to predict the optimum conditions for the industrial production of chemicals, by considering both rate and yield as well as costs and energy requirements.

### CHANGING PRESSURE BY CHANGING VOLUME

The pressure of a gas is inversely proportional to the volume of its container. So the pressure of gases in an equilibrium mixture can be changed by increasing or decreasing the volume of the container while keeping the temperature constant.

Consider the effect of increasing the pressure on the equilibrium between sulfur dioxide gas, oxygen and sulfur trioxide gas for the following reaction:



You can see that the forward reaction involves a reduction in the number of particles of gas from three to two. The formation of products would cause an overall reduction in pressure of the system. The reverse reaction involves an increase in the number of gas particles from two to three. So the reverse reaction causes an overall increase in pressure of the system.

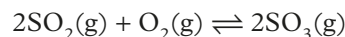
As you saw in the section 2.5, a change in the position of an equilibrium can be predicted by applying:

- Le Châtelier's principle
- your knowledge of collision theory and the rates of reactions.

### Predicting the effect of a change using Le Châtelier's principle

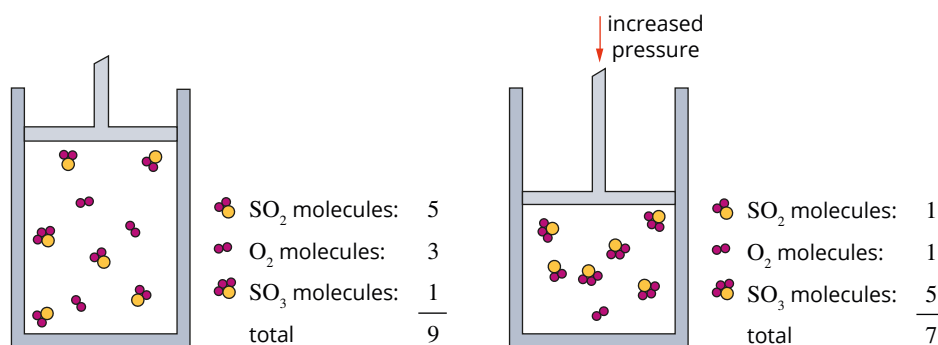
Le Châtelier's principle tells you that an equilibrium system will respond to an increase in pressure by adjusting to reduce the pressure. Therefore, the position of equilibrium will move in the direction of the fewest gas particles.

In the example:



an increase in pressure will cause a net forward reaction to occur in order to reduce the overall pressure (three gaseous reactant particles become two gaseous product particles). The amount of  $\text{SO}_3$  present at equilibrium will increase, as represented in Figure 2.6.2.

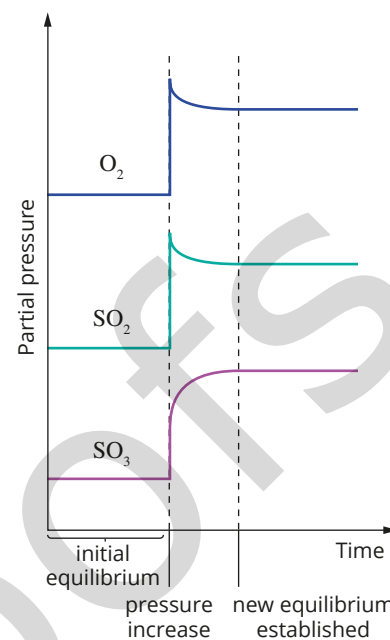
**i** Remember that pressure is a measure of the force per unit area, which is proportional to the number and frequency of collisions with the sides of the container. A change in the overall number of particles will change the pressure.



**FIGURE 2.6.2** A representation of the effect of increased pressure on the equilibrium:  
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

The effect of the change can also be illustrated graphically (Figure 2.6.3). When the system is initially at equilibrium and there is an increase in pressure, the partial pressures of all gases increase simultaneously, as do the concentrations.

As the system adjusts, there is a gradual change in concentration and partial pressure of each of the species until the new equilibrium is established. At the new equilibrium position, the individual partial pressures and concentrations are different from those at the first equilibrium. However, the equilibrium constant,  $K_c$ , has not changed. The ratio of products to reactants in the equilibrium law still equals  $K_c$  at the new equilibrium position.



**FIGURE 2.6.3** The effect of increased pressure on the equilibrium:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

**i** An increase in pressure will favour the side of the reaction with the least number of particles.

## Explaining the effect of a change using collision theory and rates of reaction

The effect of a reduction in volume on the equilibrium can also be understood by using collision theory. Because the overall volume occupied by the gases is smaller, the gas molecules are closer to each other and collisions between molecules become more frequent. The rate of the reaction involving the greater number of molecules (the forward reaction in this case) becomes greater than the rate of the reaction between the smaller number of molecules (the reverse reaction). Then, as more product is formed, the rate of the reverse reaction increases and the rate of the forward reaction decreases.

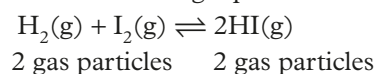
Eventually the rates of the forward and reverse reactions become equal and a new equilibrium is established. Because the forward reaction occurred to a greater extent initially, there has been a net forward reaction.

Pressure changes do not affect the equilibrium position of systems in the liquid or solid phases. Particles in these systems are too tightly packed for an increase in pressure to have a noticeable effect on volume. This means that there is negligible change in the concentration of the species involved and no effect on the concentration fraction.

## Further examples

The effect of a change of pressure or concentration, by changing the container volume, depends on the relative number of particles on both sides of the equation.

When there are equal numbers of reactant and product particles, a change in pressure will not shift the position of equilibrium. This is the case for the reaction between hydrogen and iodine in the following equilibrium:

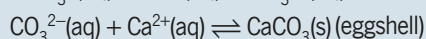
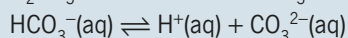
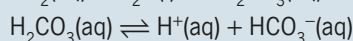
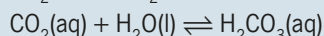
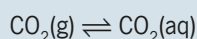


## CHEMFILE

### Chickens lay eggs with thinner shells in the summer

Chickens, like dogs, do not perspire. Therefore, in hot weather chickens have to pant to try to maintain a healthy temperature. This means that they exhale more carbon dioxide gas than when they are breathing normally.

This affects the following series of competing equilibria, which produce eggshells made from calcium carbonate:



Removing  $\text{CO}_2$  gas shifts each equilibrium, in turn, to the left. This ultimately results in less  $\text{CaCO}_3$  being made. So, in summer, chickens lay eggs with thinner shells (Figure 2.6.4). This means eggs are more easily broken, at great economic cost to farmers and supermarkets.

Scientists solved the problem by giving the chickens carbonated water to drink. This increases the concentration of aqueous carbon dioxide and pushes the equilibria to the right, increasing the amount of calcium carbonate.

Apparently the chickens like the carbonated water and they produce eggs with thicker, stronger shells. Another victory for chemistry and Le Châtelier!



**FIGURE 2.6.4** The eggshell dilemma is solved with the aid of Le Châtelier's principle.

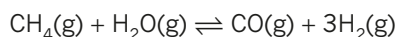
According to Le Châtelier's principle, it does not matter which way the system shifts; the number of particles in the container will remain constant (two particles of reactants and two particles of products). Therefore, the system is unable to oppose the change applied and there is no overall net reaction.

In terms of collision theory, the volume decrease causes the rates of the forward and back reactions to be increased equally.

### Worked example 2.6.1

#### USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME DECREASE

Consider the equilibrium:



Predict the shift in equilibrium position and the effect on the amount of CO when the volume is halved at constant temperature.

#### Thinking

Determine the immediate effect of the change of volume on the pressure.

The system will try to partially oppose the change in pressure by reducing or increasing the pressure of the system. (For a volume decrease, the system will shift in the direction of the fewest particles, and vice versa for a volume increase.)

Decide how the equilibrium will respond.

#### Working

Halving the volume will double the pressure of all species at equilibrium.

There are 2 molecules of gas on the reactant side and 4 molecules of gas on the product side, so the system will shift to the left.

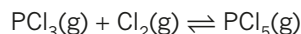
This decreases the amounts of the products, including CO.

(Note that the concentration and partial pressure of the CO will still be higher than it was at the initial equilibrium. The shift in equilibrium position only partially compensates for the change.)

### Worked example: Try yourself 2.6.1

#### USING LE CHÂTELIER'S PRINCIPLE TO DETERMINE THE SHIFT IN EQUILIBRIUM POSITION FOR A VOLUME INCREASE

Consider the equilibrium:

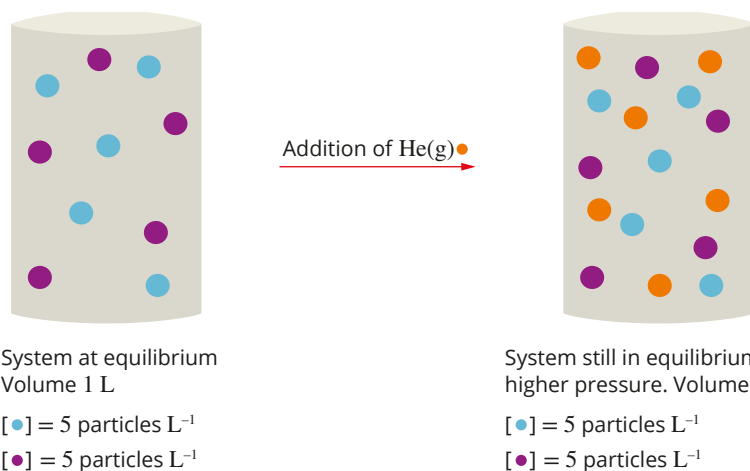


Predict the shift in equilibrium position and the effect on the amount of  $\text{Cl}_2$  when the volume is doubled at constant temperature.

### CHANGING PRESSURE BY ADDING AN INERT GAS

The total pressure of an equilibrium mixture of gases may also be changed, without changing the volume of the container, by adding a non-reacting gas such as helium, neon or argon (Figure 2.6.5).

Because the presence of the additional gas does not change any of the concentrations of the reactants and products, there is no effect on the position of equilibrium or the equilibrium constant. Using collision theory, you can see that any collisions with inert gas molecules will not produce a reaction, so no net reaction occurs.



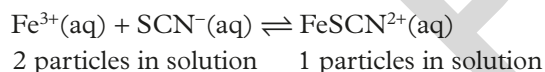
**FIGURE 2.6.5** The equilibrium of a gaseous system is unaffected by the addition of an inert gas. The total pressure of the system increases without changes in concentrations of reactants or products, so there is no change to the reaction quotient according to the equilibrium law.

## DILUTION

For equilibria in solution, the situation is similar to the one you saw with pressure and gases. The focus is on the number of particles per volume of solvent.

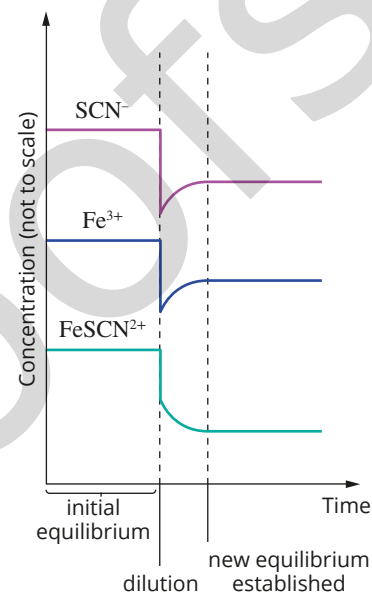
For an equilibrium occurring in solution, dilution by adding water reduces the number of particles per volume. Le Châtelier's principle shows that this results in a shift in the position of equilibrium towards the side that produces the greater number of dissolved particles.

For example, consider the equilibrium system:



The addition of water momentarily lowers the concentration of each species. In terms of Le Châtelier's principle, a net reverse reaction will occur, increasing the total concentration of particles in solution.

Figure 2.6.6 shows the changes of concentrations that occur. Note that there is an instantaneous decrease in the concentration of all species at the time of dilution.



**FIGURE 2.6.6** Effect of dilution on the equilibrium  $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{FeSCN}^{2+}(\text{aq})$ . Although the equilibrium position shifts to the left, note that the concentrations of  $\text{Fe}^{3+}$  and  $\text{SCN}^{-}$  at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

**i** Dilution of an aqueous equilibrium system has no effect on the value of  $K_c$  for the reaction.

## CHANGING TEMPERATURE

In section 2.4, you saw that the effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic, as shown in Table 2.6.1.

**TABLE 2.6.1** The effect on the value of  $K_c$  when the temperature of a system is increased

$\Delta H$	$T$	$K_c$
Exothermic (-)	Increase	Decrease
Endothermic (+)	Increase	Increase

**i** Changing the temperature of an equilibrium in a closed system affects both the equilibrium position and the value of the equilibrium constant.

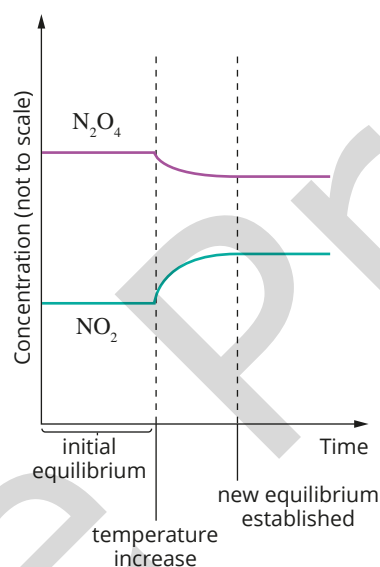
The overall effect on equilibrium position due to temperature can also be predicted from Le Châtelier's principle and explained using collision theory and rates of reaction.

For example, consider the conversion of brown nitrogen dioxide gas ( $\text{NO}_2$ ) to colourless dinitrogen tetroxide gas ( $\text{N}_2\text{O}_4$ ). The reaction is exothermic, releasing energy to the environment. You could (but wouldn't usually) write an equation for the reaction that includes the energy released:



Increasing the temperature of the system increases the energy of the substances in the mixture. Applying Le Châtelier's principle, you can see that the reaction can 'oppose' an increase in energy by absorbing energy. As the reverse reaction is endothermic, this favours a net reverse reaction. Figure 2.6.7 shows the gradual decrease in the concentration of  $\text{N}_2\text{O}_4$  as the system moves to produce more reactants,  $\text{NO}_2$ . Note that with a change in temperature, there is no instantaneous change in concentration.

Because the reactants and products of this system are different colours, you can monitor the change in this equilibrium visually. When a new equilibrium is attained, there is less dinitrogen tetroxide and more nitrogen dioxide present so the mixture appears a darker brown (Figure 2.6.8).



**FIGURE 2.6.7** The effect of heating on the equilibrium  $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$



**FIGURE 2.6.8** Equilibrium mixtures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in hot water and ice. Heating the mixture favours the formation of brown  $\text{NO}_2$  gas.

Heating an endothermic reaction causes the opposite result to occur. Applying Le Châtelier's principle, you can see that the reaction opposes an increase in energy by absorbing energy, resulting in a net forward reaction.

In summary, increasing the temperature of an equilibrium mixture results in a:

- net reverse reaction (fewer products) for exothermic reactions, and a decrease in  $K_c$
- net forward reaction (more products) for endothermic reactions, and an increase in  $K_c$ .

Decreasing the temperature has the opposite effect.

Predictions using Le Châtelier's principle of the effect of temperature on equilibria can be explained by collision theory. When there is an increase in temperature, molecules move faster and there are more frequent and more energetic collisions. More molecules now have the necessary activation energy to undergo successful collisions.

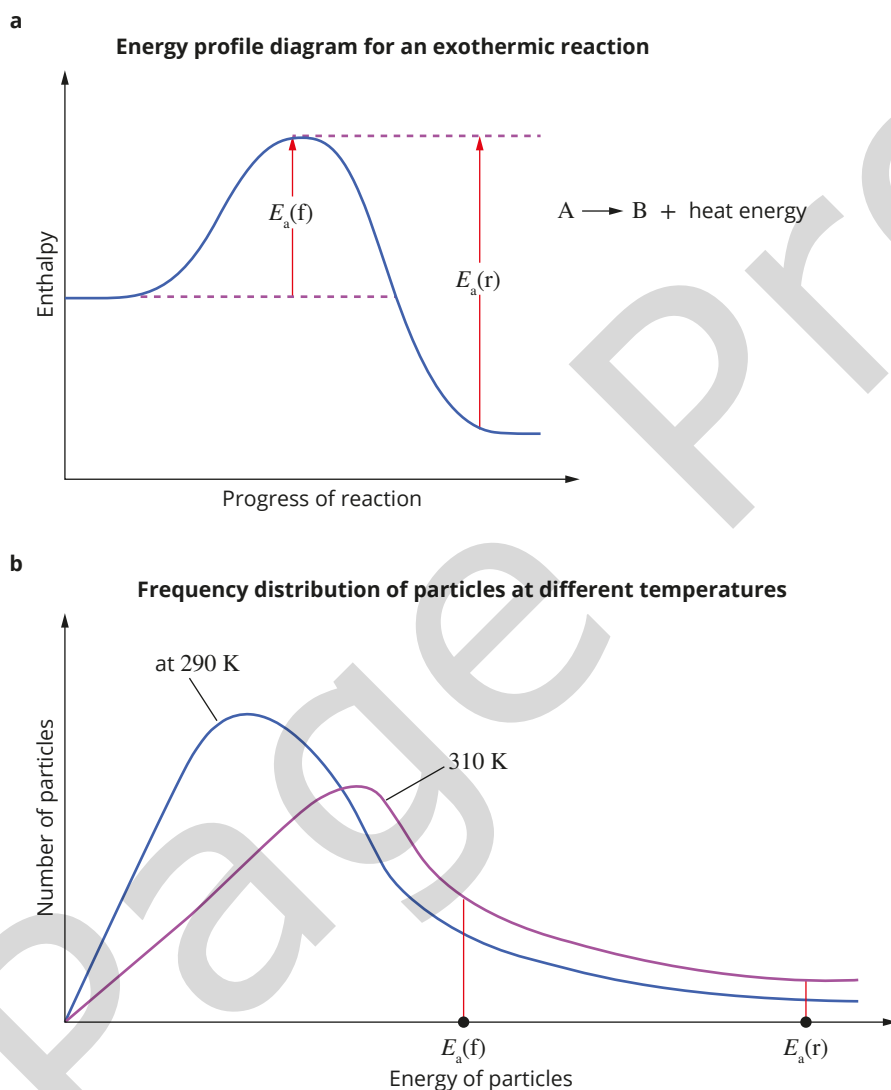


At the higher temperature, the rates of both the forward and reverse reactions increase. One of these reactions is endothermic and the other is exothermic. Because the activation energy for the endothermic reaction is greater than for the exothermic reaction, the increased energy will mean there will be a greater proportion of molecules with the necessary activation energy for the endothermic reaction. The rate of this reaction will increase more than the rate of the exothermic reaction.

This can be seen from the graph in Figure 2.6.9, which shows the frequency distribution of molecules at different temperatures.

In this example of the equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , the reverse reaction is endothermic and so there will be a net reverse reaction. When the system re-establishes equilibrium at a higher temperature, the new equilibrium has a higher concentration of  $\text{NO}_2$  and a lower concentration of  $\text{N}_2\text{O}_4$ .

Conversely, decreasing the temperature of an equilibrium results in a net reaction in the direction of the exothermic reaction.



**FIGURE 2.6.9** (a) Energy profile diagram for an exothermic reaction. The activation energy of the forward reaction,  $E_a(f)$ , is less than the activation energy of the reverse reaction,  $E_a(r)$ . (b) The frequency distribution of molecules at two different temperatures. At the higher temperature, a greater proportion of particles have the necessary activation energy for the endothermic reaction.

### Worked example 2.6.2

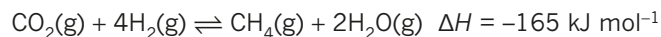
#### USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium: $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ Explain, using collision theory, the effect of an increase in temperature on this endothermic reaction.	
<b>Thinking</b>	<b>Working</b>
Decide what effect the temperature change has on the initial rates of reaction. Remember that, for an equilibrium system, an increase in temperature increases the proportion of molecules with the necessary activation energy for the endothermic reaction to a greater extent than for the exothermic reaction, and so the endothermic reaction will be favoured.	With the temperature increase, all reactant and product molecules have more energy and move faster. Since the forward reaction is endothermic, its rate initially increases more than the rate of the reverse reaction.
Using collision theory, consider what happens to the rates of the forward and reverse reactions.	As $\text{H}_2$ and $\text{CO}_2$ react and the concentration of reactants decreases, the rate of the forward reaction will decrease. As the concentration of $\text{CO}$ and $\text{H}_2\text{O}$ increases, the rate of the reverse reaction will increase. Ultimately, the rates of the forward and reverse reactions become equal and a new equilibrium is established.
Determine the overall effect of the change on the equilibrium.	This results in a net forward reaction, with higher concentrations of the products, $\text{CO}$ and $\text{H}_2\text{O}$ and lower concentrations of the reactants, $\text{CO}_2$ and $\text{H}_2$ .

### Worked example: Try yourself 2.6.2

#### USING COLLISION THEORY TO DETERMINE THE EFFECT OF TEMPERATURE ON AN EQUILIBRIUM SYSTEM

Consider the equilibrium:



Explain, using collision theory, the effect of an increase in temperature on this reaction.

## EFFECT OF A CATALYST ON EQUILIBRIUM

A catalyst lowers the activation energy of both the forward and reverse reactions by the same amount (see Chapter 1). This can be seen in the energy profile diagram shown in Figure 2.6.10.

The lower activation energy causes an increase in the number of effective collisions. As a result, there is an increase in the rate of both forward and reverse reactions. This occurs because more particles have energies greater than the activation energy barrier of the reaction.

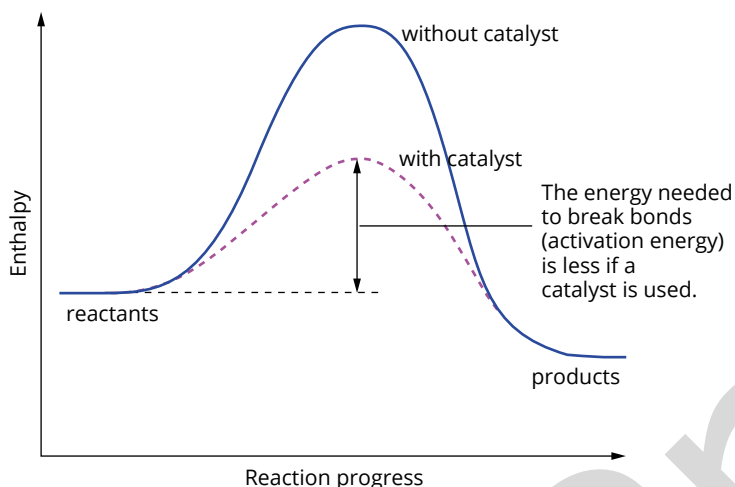


FIGURE 2.6.10 Energy changes in a catalysed and uncatalysed reaction.

A catalyst increases the rate of the forward and reverse reactions equally. Therefore, it will not change the relative concentrations of the reactants and products at equilibrium. Consequently the presence of a catalyst does not change the position of equilibrium or the value of the equilibrium constant,  $K_c$ . A catalyst will increase the rate at which an equilibrium is attained. It is for this reason that catalysts are used in many industrial and biological systems.

**i** Addition of a catalyst does not change the position of equilibrium of a system, just how quickly equilibrium is attained.

## OPTIMISING THE YIELD OF INDUSTRIAL PROCESSES

The chemical industry is central to the world economy. The companies in this sector convert raw materials (such as oil, natural gas, air, water, metals and minerals) into tens of thousands of different products, including dyes and pigments, ammonia, chlorine, caustic soda, sulfuric and nitric acids, and organic chemicals.

The extent of the reactions in these industrial processes and the rate of conversion of reactants to products are influenced by reaction conditions such as temperature, pressure and concentration. In order to avoid waste and reduce costs, conditions are carefully selected to ensure that acceptable yields of product are obtained.

It is essential to select the optimum conditions for an efficient reaction process to make the production of useful chemicals economically viable.

Later in the course, you will learn how industrial chemists maximise the rate and yield of chemical reactions by manipulating the position of equilibrium and by controlling reaction rate.

## CHEMISTRY IN ACTION

### Equilibria in a swimming pool

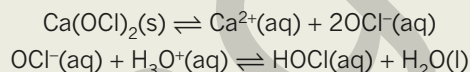
The water in swimming pools is used many times. Even though it is filtered, the water can quickly become contaminated with microscopic algae and bacteria. Some interesting chemistry involving chemical equilibria is involved in keeping swimming pools clean, clear and safe to swim in (Figure 2.6.11).



**FIGURE 2.6.11** Chemical equilibria are responsible for keeping the water in backyard swimming pools hygienic and safe for swimmers.

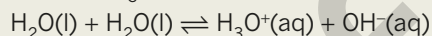
Swimming pools are ‘chlorinated’ to prevent the growth of harmful microorganisms. Chlorination produces hypochlorous acid (HOCl), which is a very efficient antibacterial agent and algicide.

Commercially available ‘pool chlorine’ powder (Figure 2.6.12) consists of calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ), which dissolves in water to release hypochlorite ions ( $\text{OCl}^-$ ). The hypochlorite ions then react with hydronium ions in the water to form hypochlorous acid:

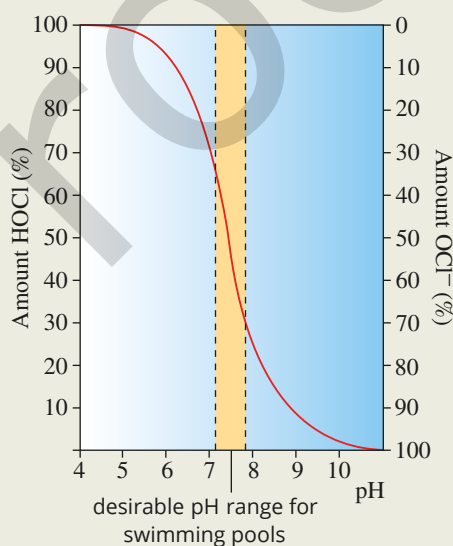


**FIGURE 2.6.12** Commercial ‘pool chlorine’ contains the hypochlorite ion ( $\text{OCl}^-$ ), which forms an equilibrium with  $\text{H}_3\text{O}^+$  ions in water.

The  $\text{H}_3\text{O}^+$  is available from the self-ionisation of water, another equilibrium reaction, this time between water molecules, forming  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions:



The relative amounts of HOCl,  $\text{OCl}^-$  and  $\text{H}_3\text{O}^+$  in a swimming pool need to be controlled carefully. This is done by monitoring the pH of the swimming pool and adding either more pool chlorine or more acid as needed to maintain a pH in the range 7.2–7.8. Figure 2.6.13 shows the relationship between the three substances. Remember, pH measures the concentration of  $\text{H}_3\text{O}^+$  ions.



**FIGURE 2.6.13** The effect of pH on the proportion of HOCl and  $\text{OCl}^-$  in water means that the position of the equilibrium can be monitored by changes in pH of the water.

As pH increases, the concentration of  $\text{H}_3\text{O}^+(\text{aq})$  decreases. Le Châtelier’s principle tells you that the position of equilibrium will move to the left, consuming some of the HOCl. If the pH rises above about 7.8, the concentration of HOCl will be insufficient to control the growth of bacteria and algae.

On the other hand, as pH falls, the concentration of  $\text{H}_3\text{O}^+(\text{aq})$  increases. The position of equilibrium will move to the right and more HOCl will be formed. Although pH values below around 7.2 result in greater amounts of HOCl in the pool, if the pool is too acidic, the water can irritate eyes and skin.

Thus, maintaining a pool so that it is hygienic and comfortable for swimmers involves carefully maintaining an optimum equilibrium position in the reaction mixture.

## 2.6 Review

### SUMMARY

- The effect of a change on an equilibrium can be predicted using Le Châtelier's principle and the equilibrium law (Table 2.6.2).
- Alternatively, the effects of changes on an equilibrium can be explained on the basis of collision theory and rates of reaction (Table 2.6.2).

**TABLE 2.6.2** Summary of the effect of a change on equilibrium

Change on equilibrium	Le Châtelier's principle prediction: effect of change on equilibrium position	Collision theory explanation: effect of change on equilibrium position
Decreasing pressure by increasing volume (for gases)	Shifts in the direction of the most particles	Less frequent collisions; the reaction that is less dependent on collisions (fewer particles reacting) occurs to a greater extent.
Adding a catalyst	No change	Increases rates of forward and reverse reactions to the same extent; an equivalent change in the number of successful collisions in both directions; no net reaction.
Adding an inert gas (container volume remains constant)	No change	No change in concentration of the reacting gases so no change to the rate of the forward and reverse reactions.
Adding water (dilution of solutions)	Shifts in the direction of the most dissolved particles	Less frequent collisions; the reaction less dependent on a collision (fewer particles reacting) occurs to a greater extent.
Increasing the temperature for exothermic reactions	Shifts to the left	All reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in direction of endothermic reaction, i.e. favouring the reverse direction.
Increasing the temperature for endothermic reactions	Shifts to the right	All reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in direction of endothermic reaction, i.e. favouring the forward direction.

### KEY QUESTIONS

- In which one the following systems will the position of equilibrium be unaffected by a change of volume at constant temperature? Explain your answer using collision theory.
  - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
  - $\text{Cl}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$
  - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
  - $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightleftharpoons 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- Predict the effect of the following changes on the position of each equilibrium.
  - Halving the volume (doubling the pressure) of the equilibrium:
 
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
  - Increasing the pressure of the equilibrium:
 
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
  - Increasing the temperature of the endothermic equilibrium:
 
$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$
- For the reactions in Question 2, explain the effect of the changes, in terms of collision theory and rates of reaction.
- Consider the following equilibria:
  - $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \quad \Delta H = +42 \text{ kJ mol}^{-1}$
  - $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad \Delta H = +58 \text{ kJ mol}^{-1}$
  - $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g}) \quad \Delta H = -536 \text{ kJ mol}^{-1}$   
How would you alter the:
    - temperature of each equilibrium mixture in order to shift the position of equilibrium to the right?
    - volume of each equilibrium mixture in order to shift the position of equilibrium to the right?
- An equilibrium mixture consists of the gases  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ :
 
$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$

The volume of the container is increased at constant temperature and a new equilibrium is established. Predict how each of the following quantities would change at the new equilibrium compared with the initial equilibrium.

  - Partial pressure of  $\text{NO}_2$
  - Mass of  $\text{NO}_2$
- The International Space Station uses waste hydrogen and the carbon dioxide released by astronauts during respiration to form water according to the reaction:
 
$$\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \quad \Delta H = -165 \text{ kJ mol}^{-1}$$
  - How would you alter the temperature in order to increase the yield of the reaction?
  - How would you alter the volume in order to increase the yield of the reaction?

## Chapter review

### KEY TERMS

activation energy	equilibrium constant	Le Châtelier's principle	
closed system	equilibrium law	macroscopic property	
collision theory	equilibrium yield	open system	
competing equilibria	exothermic	partial pressure	saturated solution
concentration fraction	extent of reaction	position of equilibrium	surroundings
dynamic equilibrium	heterogeneous reaction	rate of reaction	system
endothermic	homogeneous reaction	reaction quotient	
equilibrium	irreversible reactions	reversible reaction	

### KEY QUESTIONS

#### Chemical systems

- Which one of the following statements about an open system is correct?
  - In an open system, only energy can be exchanged with the surroundings.
  - In an open system, the reactants and products cannot be exchanged with the surroundings.
  - In an open system, matter and energy can be exchanged with the surroundings.
  - In an open system, some reactants and products must always remain when the reaction is complete.
- Consider a saturated solution of salt in contact with undissolved salt crystals at a constant temperature. Which one of the following statements is correct?
  - It is an example of a closed system, which is non-reversible.
  - It is an example of an open system, which is non-reversible.
  - It is an example of a closed system, which is reversible.
  - It is an example of an open system, which is reversible.
- Draw an energy profile diagram for the theoretical exothermic reaction:  $P + Q \rightleftharpoons R + S$ . Label  $\Delta H$ , activation energy of forward reaction, activation energy of reverse reaction, enthalpy of reactants and enthalpy of products.
  - Use the diagram to explain why it is possible for the reverse reaction  $R + S \rightleftharpoons P + Q$  to occur.

#### Dynamic equilibrium

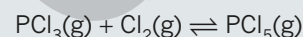
- What are the characteristics of a homogeneous reaction system at equilibrium?
- Consider the following equilibrium.
$$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$$
  - Explain what is meant by the 'dynamic nature' of equilibrium and why wet clothes in a closed laundry bag do not dry.

Le Châtelier's principle  
macroscopic property  
open system  
partial pressure  
position of equilibrium  
rate of reaction  
reaction quotient  
reversible reaction

saturated solution  
surroundings  
system

- When the bag in part **a** is opened, the clothes begin to dry. Is this because of an equilibrium process? Explain your answer.

- $\text{PCl}_3$  gas is mixed with  $\text{Cl}_2$  gas in a sealed container. A reaction occurs according to the equation:



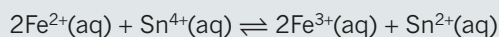
Sketch a graph to show how the rate of the forward reaction and the rate of the reverse reaction change with time. Label the lines for the forward and reverse reactions with the appropriate chemical equation. Also label the point when equilibrium is first established.

#### The equilibrium law

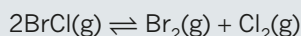
- Write the expression for  $K_c$  for the following equilibrium system:
$$2\text{Fe}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$$
- Write balanced equations for the reactions with the following equilibrium laws.
  - $K_c = \frac{[\text{H}_2]^2[\text{CO}]}{[\text{CH}_3\text{OH}]}$
  - $K_c = \frac{[\text{H}_2\text{S}]^2}{[\text{S}_2][\text{H}_2]^2}$
  - $K_c = \frac{[\text{N}_2\text{O}_4]^{\frac{1}{2}}}{[\text{NO}_2]}$
- Write the expression for the equilibrium constant for the following chemical equations.
  - $\text{Cu}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{CuCO}_3(\text{s})$
  - $\text{CuCO}_3(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$
  - $\text{P}_4(\text{s}) + 10\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{PCl}_5(\text{g})$
  - $8\text{PCl}_5(\text{g}) \rightleftharpoons 2\text{P}_4(\text{s}) + 20\text{Cl}_2(\text{g})$
- Explain the difference between the terms 'reaction quotient' ( $Q_c$ ) and 'equilibrium constant' ( $K_c$ ).

### Working with equilibrium constants

- 11** Complete the following statements about the equilibrium constant  $K_c$ .
- If  $K_c = 0.0001$  for a particular reaction, at equilibrium the concentrations of products will be \_\_\_\_\_ the concentrations of reactants.
  - For the reaction with the equation:  
$$2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$$
the expression for the equilibrium constant,  $K_c$ , is \_\_\_\_\_.
  - When the reaction quotient is smaller than  $K_c$ , the reaction \_\_\_\_\_ to establish equilibrium.
- 12** The equilibrium constant for the following reaction at  $25^\circ\text{C}$  is  $10^{-10}$ .



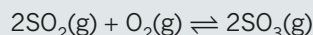
- Explain whether a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.
  - Determine the value of the equilibrium constant for the reaction:  
$$2\text{Fe}^{3+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$$
  - Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.
- 13** Consider the following equilibrium at  $227^\circ\text{C}$ :



- Write the expression for  $K_c$  for the equilibrium system.
- Given that the value of  $K_c$  at  $227^\circ\text{C}$  for the expression in part **a** is 32. Deduce the equilibrium constant for each of the following.
  - $\text{BrCl}(\text{g}) \rightleftharpoons \frac{1}{2}\text{Br}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g})$
  - $\text{Cl}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{BrCl}(\text{g})$
  - $4\text{BrCl}(\text{g}) \rightleftharpoons 2\text{Br}_2(\text{g}) + 2\text{Cl}_2(\text{g})$
  - $\frac{1}{2}\text{Cl}_2(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g}) \rightleftharpoons \text{BrCl}(\text{g})$

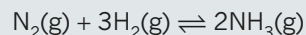
### Le Châtelier's principle

- 14** State Le Châtelier's principle. Write an equilibrium equation in terms of reactants A and B in equilibrium with products C and D. Use the principle to explain what occurs when the products are gradually removed.
- 15** Predict the effect of the following changes on the position of equilibrium in the system:



- Addition of  $\text{SO}_2$  to the equilibrium system
- Removal of  $\text{O}_2$  from the equilibrium system
- Removal of  $\text{SO}_3$  from the equilibrium system

- 16** The following equilibrium system is present in a sealed container of fixed volume:



What change in the partial pressure of hydrogen gas can cause the following changes to the system at constant temperature?

- The partial pressure of the product increased.
- There was a net reverse reaction.

### Further applications of Le Châtelier's principle

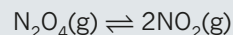
- 17** The reaction represented by the following equation is exothermic:



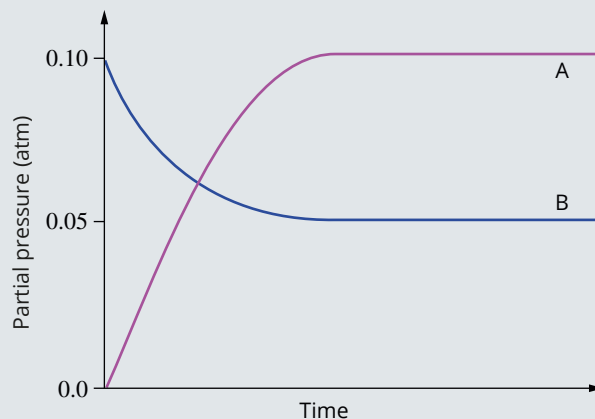
At equilibrium at constant temperature, the volume is halved by increasing the pressure. Which one of the following statements is correct?

- The new equilibrium concentration of CO will be less than the initial concentration.
- The value of  $K_c$  will increase.
- The amount of  $\text{COCl}_2$  will increase.
- A net reverse reaction will occur.

- 18** Dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , and nitrogen dioxide,  $\text{NO}_2$ , coexist according to the equilibrium reaction:

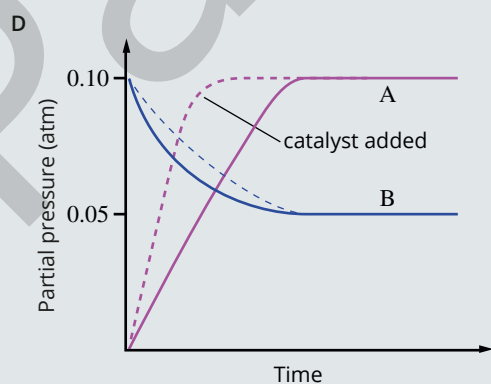
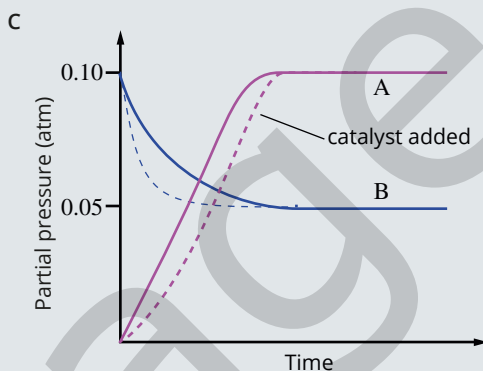
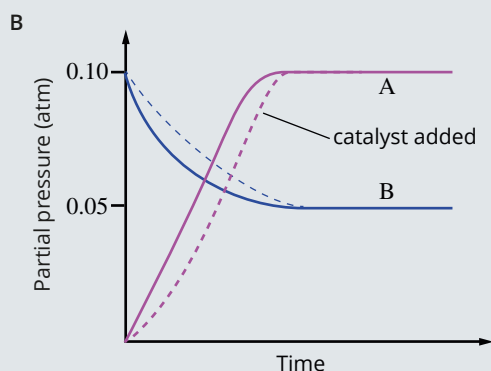
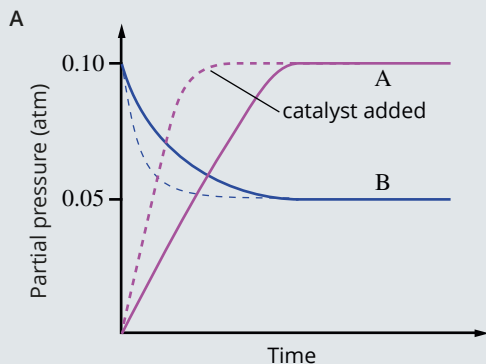


- The graph below shows the change of the partial pressures of the two gases with time as they reach equilibrium at constant temperature. Identify labels A and B as  $\text{N}_2\text{O}_4(\text{g})$  or  $\text{NO}_2(\text{g})$ .



**FIGURE 2.7.1** Change in partial pressures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$

- b** Which one of the following graphs correctly shows the effect on the partial pressures of A and B when a catalyst is added? The dashed lines indicate their pressures when the catalyst is added.

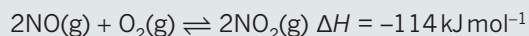


- 19** Which one of the following statements about equilibrium is true?
- A catalyst increases the rates of the forward and reverse reactions equally because it decreases the temperature.
  - Dilution of an aqueous equilibrium system never causes any change to the position of equilibrium of the system.
  - Increasing the pressure of a gaseous equilibrium system, by reducing the volume, causes the value of  $K_c$  to increase.
  - An increase in temperature of an endothermic equilibrium system increases the value of  $K_c$ .
- 20 a** Use Le Châtelier's principle to predict how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are heated and kept at constant volume?
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -91 \text{ kJ mol}^{-1}$
  - $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}) \quad \Delta H = +208 \text{ kJ mol}^{-1}$
- b** Use collision theory to explain the effect of heating the equilibrium mixtures in part **a**.
- 21** The following equations represent reactions that are important in industrial processes. Predict the effect on the equilibrium position if each reaction mixture were compressed at constant temperature.
- $\text{C}_3\text{H}_8\text{O}(\text{g}) \rightleftharpoons \text{C}_3\text{H}_6\text{O}(\text{g}) + \text{H}_2(\text{g})$
  - $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
  - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
- 22** Elderly people, especially women, can become very susceptible to bone breakages. It is thought that as people age they absorb  $\text{Ca}^{2+}$  from food inefficiently, reducing the concentration of these ions in body fluids. An equilibrium exists between calcium phosphate in bone and calcium ions in body fluids:
- $$\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$$
- Use your understanding of equilibrium to explain why inefficient absorption of  $\text{Ca}^{2+}$  ions could cause weakness in bones.
- 23** Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:
- $$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$$
- In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at  $1000^\circ\text{C}$ .
- Predict what will happen to the equilibrium position as a result of:
    - a decrease in temperature
    - addition of a catalyst
    - addition of more oxygen.
    - decreasing the partial pressure of carbon monoxide (at constant volume).



- b What will happen to the equilibrium constant as a result of each of the changes in part a?
- c If carbon monoxide can be used as a fuel, comment on the magnitude of the equilibrium constant for the reaction.

**24** A step during nitric acid production is the oxidation of nitrogen oxide to nitrogen dioxide:



Nitrogen dioxide is a brown gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1 L container at 350°C. Copy the following table and, for each of the changes listed, indicate if the reaction mixture would become darker or lighter. Give a reason for your choice.

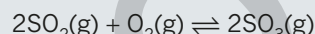
	Colour change (lighter or darker)	Explanation using Le Châtelier's principle and collision theory
<b>a</b> The temperature is increased to 450°C at constant volume.		
<b>b</b> The volume of the container is increased at constant temperature.		
<b>c</b> A catalyst is added at constant volume and temperature.		
<b>d</b> More oxygen is added at constant volume and temperature.		

### Connecting the main ideas

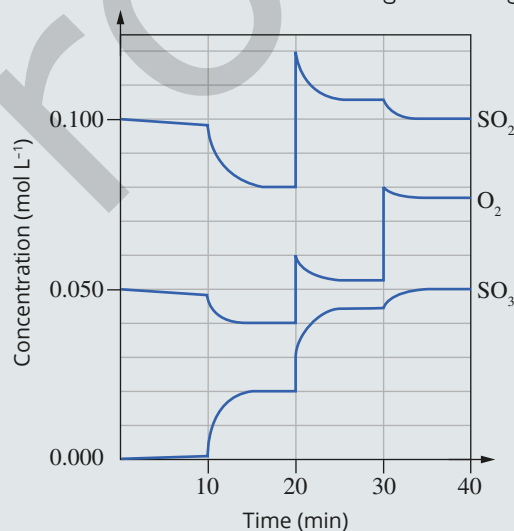
- 25** Carbon disulfide gas ( $\text{CS}_2$ ) is used in the manufacture of rayon.  $\text{CS}_2(\text{g})$  can be made in an endothermic gas-phase reaction between sulfur trioxide gas ( $\text{SO}_3$ ) and carbon dioxide. Oxygen gas is also produced in the reaction.
- Write a balanced chemical equation for the reaction.
  - Write an expression for the equilibrium constant of the reaction.

- c Predict how each of the following changes to an equilibrium mixture would affect the yield of  $\text{CS}_2$ .
- Decreasing the partial pressure of  $\text{O}_2$  (at constant total volume)
  - Increasing the temperature
  - Adding a catalyst
  - Increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)
  - Increasing the pressure by introducing argon gas into the reaction vessel (at constant volume)

**26** Sulfur dioxide gas and oxygen gas were mixed at 600°C to produce a gaseous equilibrium mixture:



A number of changes were then made, including the addition of a catalyst, resulting in the formation of new equilibrium mixtures. The graph in Figure 2.7.2 shows how the concentrations of the three gases changed.



**FIGURE 2.7.2** Concentrations of  $\text{SO}_2(\text{g})$ ,  $\text{O}_2(\text{g})$  and  $2\text{SO}_3(\text{g})$

- Write an expression for the equilibrium constant,  $K_c$ , of the reaction.
- During which time intervals was the reaction at equilibrium?
- At what time was the catalyst added? Explain your reasoning.
- What change was made to the system at 20 minutes if temperature is constant?
- What change was made to the system at 30 minutes if temperature is constant?