PEARSON

CHEMISTRY

QUEENSLAND

UNITS 3 & 4

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Student Book

QCE 2025 Chemistry SYLLABUS

CHAPTER

02 Chemical equilibrium

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 scientists 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 is of vital importance in nature, including the metabolic processes that occur within the human body and other reactions in the biosphere. It also has serious consequences on the efficiency of many chemical manufacturing industries. You will learn how reaction conditions affect the relative quantities of reactants and products in an equilibrium system.

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

Syllabus subject matter

Topic 1 • Chemical equilibrium systems

CHEMICAL EQUILIBRIUM

- Discriminate between open or closed chemical systems. **2.1**
- Identify that physical changes are usually reversible, whereas only some chemical reactions are reversible. **2.1**
- Symbolise equilibrium equations using $\rightleftharpoons$ in balanced chemical equations. **2.1**
- Explain observable properties and the characteristics of physical and chemical systems in a state of equilibrium. **2.1**
- Explain that, over time, physical change and reversible chemical reactions reach a state of dynamic equilibrium in a closed system, with the relative concentrations of products and reactants defining the position of equilibrium. **2.1**
- Explain the reversibility of chemical reactions by considering the activation energies of the forward and reverse reactions. **2.1**
- Analyse data and interpret graphical representations of relative changes in the concentration of reactants and products against time to determine the position of equilibrium. **2.1**

FACTORS THAT AFFECT EQUILIBRIUM

- Determine the effect of temperature change on chemical systems at equilibrium by considering the enthalpy change for the forward and reverse reactions. **2.3**
- Explain the effect of changes in temperature, concentration and pressure on chemical systems at equilibrium by applying collision theory to the forward and reverse reactions. **2.2, 2.3**

- Apply Le Châtelier's principle to determine the effect changes in temperature, concentration of chemicals, pressure and the addition of a catalyst have on the position of equilibrium and on the value of the equilibrium constant. **2.4**

EQUILIBRIUM CONSTANTS

- Identify that the equilibrium constant (K_c) indicates the relationship between product and reactant concentrations at equilibrium. **2.4**
- Identify that the solubility product (K_{sp}) gives a measure of the solubility of an ionic compound. **2.4**
- Determine the equilibrium law expression for homogeneous and heterogeneous systems. **2.4**
- Determine the extent of a reaction from the magnitude of the equilibrium constant (K_c). **2.4**
- Calculate the reaction quotient (Q) for reversible reactions (Formula: $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for the reaction aA + bB $\rightleftharpoons$ cC + dD). **2.4**
- Calculate equilibrium constants (K_c) and the concentrations of reactants and products. Assume that $[\text{reactants}]_{\text{initial}} = [\text{reactants}]_{\text{equilibrium}}$ when K_c is very small, and state the assumption when used. (Formula: $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ for the reaction aA + bB $\rightleftharpoons$ cC + dD). **2.4**
- Calculate solubility products (K_{sp}) and the concentrations of ions in aqueous solutions. (Formula: $K_{sp} = [C]^c [D]^d$ for the reaction aA(s) $\rightleftharpoons$ cC(aq) + dD(aq)). **2.4**
- Infer shifts in equilibrium reactions using equilibrium constants (K_c) and reaction quotients (Q). **2.4**
- Analyse data to determine reaction quotients (Q), equilibrium constants (K_c), concentrations of reactants and products and the concentration of ions in aqueous solutions. **2.4**

Revision

In Units 1 and 2, you covered the content that forms the background required to successfully complete this chapter. To assist you in understanding the content of this chapter, the following key concepts are revisited in summary:

- energy changes in chemical reactions
- rates of reaction.

Reviewing this content should not be factored in as part of the notional hours for Chapter 2.

ENERGY CHANGES IN CHEMICAL REACTIONS

All substances have **chemical energy**. The chemical energy of a substance is the sum of its potential energy and kinetic energy. These energies result from such things as attractions between electrons and protons in atoms, repulsions between nuclei, repulsions between electrons, movement of electrons, and vibrations of and rotations around bonds. The chemical energy of a substance is also called its **enthalpy**, and is given the symbol H.

During a chemical reaction, the atoms in the reactants are rearranged into products with different chemical energies. The reaction can be **exothermic** or **endothermic** depending upon the relative energies of the reactants and products. The energy released or absorbed during a chemical reaction is called the **heat of reaction** (symbol ΔH). For exothermic reactions $\Delta H < 0$, and for endothermic reactions $\Delta H > 0$.

The energy required to break the bonds of reactants so that a reaction can proceed is called the **activation energy**.

Thermochemical equations

Thermochemical equations show the energy released or absorbed during a chemical reaction, symbol ΔH. Energy is usually measured in joules (J) or kilojoules (kJ) and the ΔH value has the units $J\,mol^{-1}$ or $kJ\ mol^{-1}$. This means that the energy shown by the ΔH value corresponds to the mole quantities specified by the coefficients in the equation. Remember:

- when the coefficients of an equation change, the ΔH value changes by the same factor
- when the equation is reversed, the sign of the ΔH value is reversed
- states of matter must be shown in thermochemical equations because changes of state involve enthalpy changes.

RATES OF REACTION

The rate of a chemical reaction can be determined by measuring the change in concentration of the reactants or products with time. As the reaction conditions change, the rate of reaction will change.

There are five main ways in which reaction rate can be increased: increasing the concentration of solutions, increasing the pressure of gases, increasing the surface area of a solid reactant, increasing the temperature and using a **catalyst**.

Collision theory

For a chemical reaction to occur, the particles involved must collide with each other with sufficient energy to overcome the activation energy 'barrier' to the reaction. This way of visualising reactions is known as **collision theory**.

Only 'successful' collisions, where the energy of collision is greater than the activation energy, allow a chemical reaction to progress. So, the rate of a chemical reaction is also dependent on the proportion of collisions that are successful.

According to collision theory, for a reaction to occur, the reactant particles must collide with each other, and have an energy that is equal to, or greater than, the activation energy so that collisions break or weaken the bonds within the reactants and allow products to form.

2.1 Dynamic equilibrium

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- distinguish between open and closed systems
- appreciate why some reactions are described as reversible
- understand how reversible reactions in a closed system reach a dynamic equilibrium
- recognise that the extent of reaction can be different for different equilibria.

In this module, you will learn that some chemical 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 individual cells in your body and the reactions carbon dioxide undergoes in the environment.

This module also describes how some reversible reactions can reach a point where they appear to 'stop'. 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 important 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—the extent of conversion of reactants into products.

Although these reactions appear to stop, they actually continue to proceed. If you could see what was occurring at the atomic scale, you would notice that as rapidly as the reactants are forming products, the products are re-forming reactants. This situation can be likened to the queue shown in Figure 2.1.1. 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 2.1.1 A queue of constant length can be likened to a reaction that appears to have stopped. People leave the queue at one end at the same rate as others join it at the other end.

OPEN AND CLOSED SYSTEMS

In Units 1 and 2, 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 system absorbs energy from the surroundings, whereas in an exothermic reaction, energy is released to the surroundings.

Figure 2.1.2 illustrates how you can distinguish between the two different types of systems:

- **open systems**
- **closed systems**.

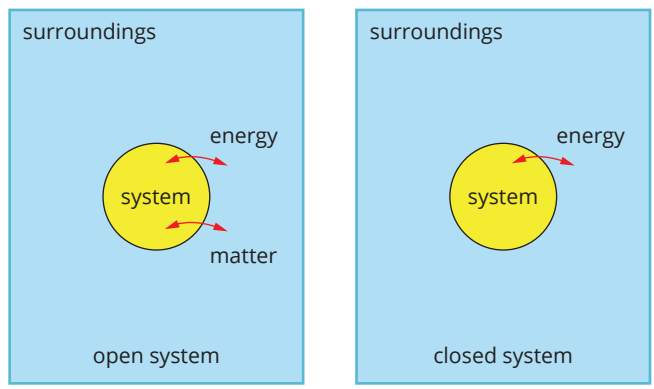


FIGURE 2.1.2 Open systems exchange energy and matter with the surroundings. Closed systems exchange only energy with the surroundings.

In a closed system, only energy can be exchanged with the surroundings.

The most common situation in everyday life is an open system. In an open system, matter and energy can be exchanged with the surroundings. In contrast, a closed system exchanges only energy with the surroundings.

Some examples of open and closed systems are illustrated in Figure 2.1.3.

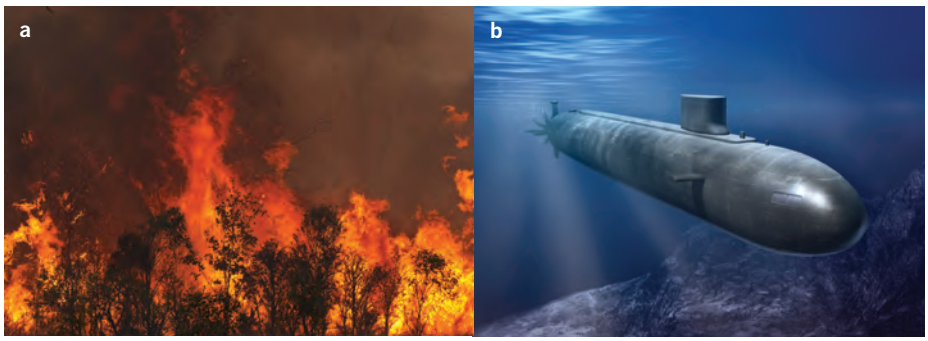


FIGURE 2.1.3 Everyday examples of open and closed systems. (a) A bushfire burning through a forest in south-west Queensland. This is an example of an open system. Carbon dioxide and water vapour produced by the burning trees are released into the atmosphere. (b) A nuclear submarine in operation under water—the carefully monitored environment of the submarine can be regarded as a closed system.

IRREVERSIBLE AND REVERSIBLE SYSTEMS

You may have thought, as a younger student, that when chemical reactions occur, the reactants form products and these products cannot be converted back to the reactants. Such reactions, which occur only in one direction, are called non-reversible or **irreversible reactions**.

Baking a cake, like the one shown in Figure 2.1.4, involves several irreversible reactions. The reactions are complex and include reactions that change the chemical structures of the protein in flour and egg, as well as reactions between protein and sugars.

FIGURE 2.1.4 Baking a cake involves a series of irreversible chemical reactions.

Combustion reactions, such as the burning of methane, are also irreversible:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Once a fuel has burnt, the products, carbon dioxide and water, do not react with each other to re-form methane and oxygen under normal conditions.

As you will see, other reactions are **reversible reactions** where the products, once formed, can react together to re-form the reactants.

Reversibility of physical and chemical changes

Four examples of systems that are reversible are:

- evaporation and condensation of water
- a saturated sugar solution
- oxygen transport in the blood
- synthesis of ammonia.

These examples are described below.

Evaporation and condensation of water

PA 3.1.1

You are familiar with the idea that a physical change, such as a state change, 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 states of solid, liquid and gas because each change of state process is reversible.

The evaporation of water can be expressed by the equation:

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

The condensation of water can be expressed by the equation:

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

Equilibrium is not achieved in an open system.

Equilibrium is achieved in a closed system when the rates of the forward and reverse processes are equal.

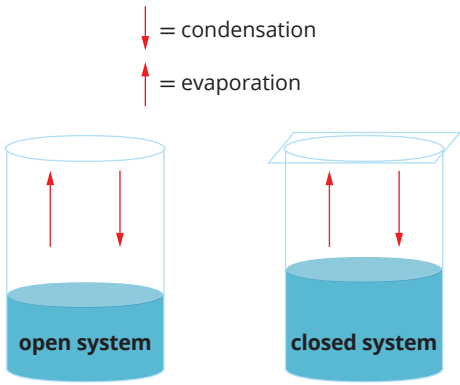


FIGURE 2.1.5 A physical change—the evaporation and condensation of water—in open and closed systems. In the open system, all the water eventually evaporates.

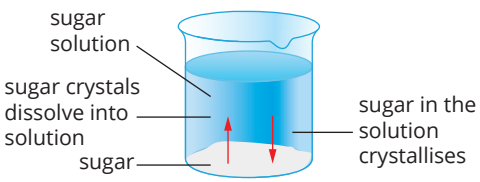


FIGURE 2.1.6 A representation of the processes occurring in a saturated sugar solution.

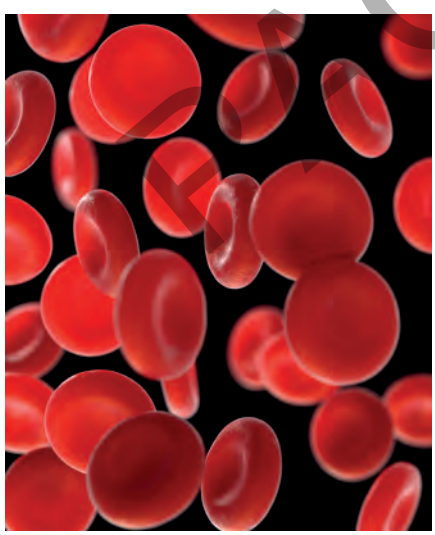


FIGURE 2.1.7 Blood cells contain a red pigment, haemoglobin, that transports oxygen from the lungs to other cells in the body.

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

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

As you can see in the diagram of water in two glasses in Figure 2.1.5, these changes of state can occur in either open or closed systems. In a closed system, the water vapour cannot escape. In general, reversible processes in a closed system eventually reach a situation where the rates of the forward and reverse processes 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

A **saturated solution** contains the maximum amount of solute that can be dissolved in a solvent. Consider a saturated solution of sugar in contact with undissolved sugar crystals at a constant temperature, as shown in Figure 2.1.6.

Even though it appears to an observer that nothing is happening, on a molecular level, the molecules are constantly in motion and exchanging between the solid and solution phases. 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:

$$C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$$

While there is no lid on the beaker, this system can still 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, as shown in Figure 2.1.7. 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:

$$\text{haemoglobin} + \text{oxygen} \rightarrow \text{oxyhaemoglobin}$$

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:

$$\text{oxyhaemoglobin} \rightarrow \text{haemoglobin} + \text{oxygen}$$

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

The reaction can therefore be written as:

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

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.

Synthesis of ammonia

The production of ammonia from nitrogen gas and hydrogen gas is known as the Haber process. (This process will be covered in more detail in Module XX.) The main reaction in the Haber process is reversible and can be represented by the equation:

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

Suppose you mix 1 mole of nitrogen gas and 3 moles of hydrogen gas in a sealed container. From the equation, you might expect that 2 moles of ammonia would eventually be formed. However, no matter how long you wait, the reaction seems to 'stop' when much less than 2 moles of ammonia is present, as shown in Figure 2.1.8.

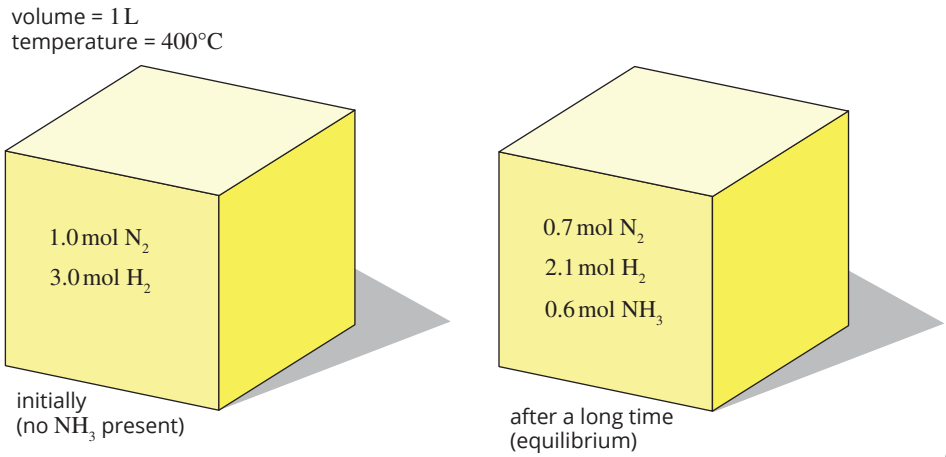


FIGURE 2.1.8 When 1 mole of nitrogen and 3 moles of hydrogen are mixed, the reaction to form ammonia appears to stop before all the reactants are consumed.

The reaction vessel in this process creates a closed system from which the reactants and products cannot escape. Once some products are formed, as a result of collisions between reactant particles, then the collisions between product particles can result in the reactants being re-formed. The reaction eventually reaches a situation where the rate of the forward reaction and the rate of the reverse reaction are equal, and an equilibrium is formed.

As for our earlier examples, when a reaction reaches equilibrium, there appears to be no further measurable change and the reaction appears to have 'stopped'. At equilibrium, significant amounts of reactants may still be present in the system.

Explaining reversibility

The reason why reversible reactions can occur can be understood by referring to **energy profile diagrams**, which represent the energy changes that occur during chemical reactions.

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 or weaken the bonds of the reactants for the reaction to occur is known as the activation energy of the reaction.

You can see from the energy profile diagram shown in Figure 2.1.9 that once products form, if these 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.

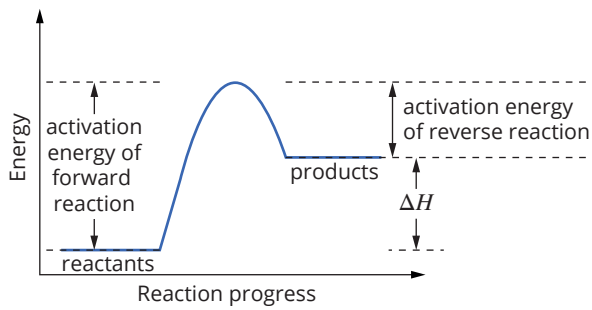


FIGURE 2.1.9 An energy profile diagram for an endothermic reaction showing the activation energy required for both the forward reaction (formation of products) and the reverse reaction (re-formation of reactants).

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

EXPLAINING EQUILIBRIUM

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

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

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

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, which can be illustrated by a plot of reaction rate versus time, as shown in Figure 2.1.10.

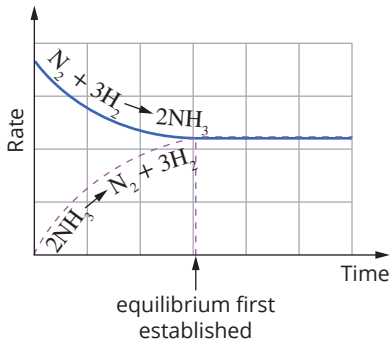


FIGURE 2.1.10 The variation of the rates of the forward and reverse reactions with time when nitrogen gas and hydrogen gas are mixed.

If you consider the graph in Figure 2.1.10, you can understand the following:

- Nitrogen gas and hydrogen gas molecules collide with each other and form ammonia. As the forward reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, 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: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$.
- 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 or measurable change.

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

The concentration versus time graph in Figure 2.1.11 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.

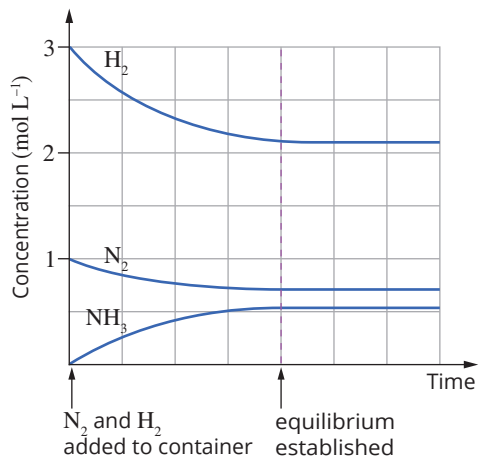


FIGURE 2.1.11 Changes in the concentrations of N_2, H_2 and NH_3 as a mixture of nitrogen gas and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every mole of N_2 that reacts, three times as much H_2 reacts and twice as much NH_3 is produced.

When considering graphs involving equilibrium systems, always check if the data is presented as a plot of concentration versus time (as in Figure 2.1.11), or as a plot of reaction rate versus time (as in Figure 2.1.10).

Dynamic state of equilibrium

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

During **dynamic equilibrium**:

- the reaction can be considered as 'incomplete' since *all* of the substances (reactants *and* products) are still 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.

The decomposition of dinitrogen tetraoxide (N_2O_4) to nitrogen dioxide (NO_2) is an example of a reversible reaction that reaches a dynamic equilibrium. The progression of this reaction from pure N_2O_4 to the equilibrium mixture containing both N_2O_4 and NO_2 can be monitored through the changing colour of the gases in the reaction vessel. N_2O_4 is colourless and NO_2 is dark brown.

The reaction occurs according to the following equation:

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

Figure 2.1.12 illustrates the observations made of a reaction vessel that is injected with some pure N_2O_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.

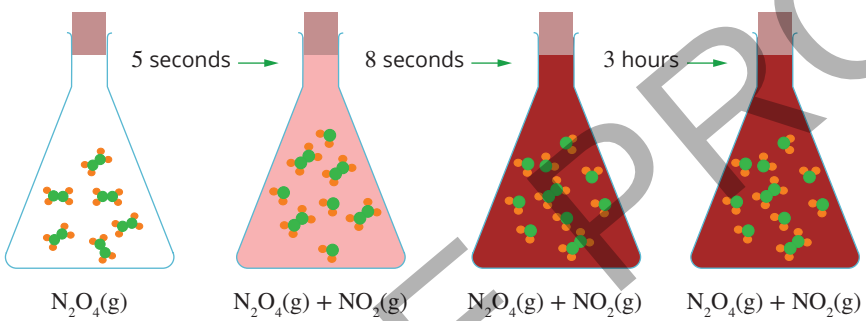


FIGURE 2.1.12 The decomposition of dinitrogen tetraoxide produces the brown gas nitrogen dioxide. As the concentration of nitrogen dioxide increases, the colour deepens until equilibrium is reached. At equilibrium (after 8 seconds), there is no further change in colour regardless of how long the reaction is allowed to proceed.

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

EXTENT OF REACTION

You have seen that reactions are reversible, but do all reactions proceed to the same extent before they reach equilibrium? This can be answered with a simple experiment.

You saw in Unit 2 (and will again see in Module 3.2), both hydrogen chloride (HCl) and ethanoic acid (CH_3COOH) react with water to form ions, according to the equations:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

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

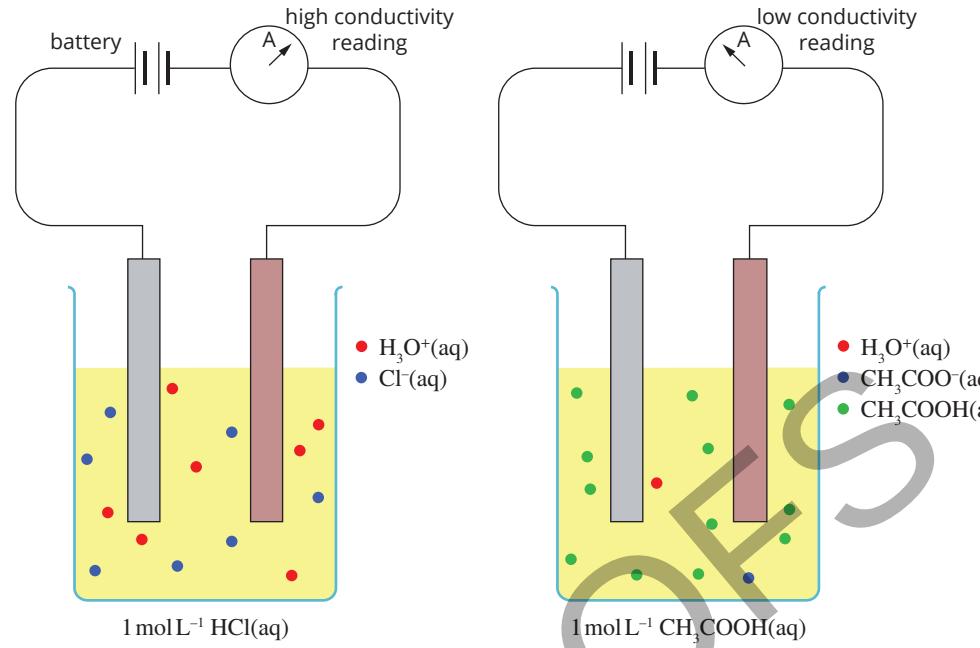


FIGURE 2.1.13 This experiment compares the electrical conductivity of 1 mol L^{-1} solutions of hydrochloric acid and ethanoic acid.

As you will remember from Unit 2, 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 us to better explain the idea of strong and weak acids by looking at the extent of the ionisation reaction (see Module 3.2).

The difference in conductivity observed in the experiment arises because these reactions occur to remarkably different extents. At equilibrium in a 1 mol L^{-1} solution, at 25°C, almost all the HCl molecules are ionised, whereas only approximately 1% of the CH_3COOH molecules are ionised.

We can conclude that 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.

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.

2.1 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 react together to be converted back to the reactants.
- An irreversible reaction is a reaction in which the products cannot react together to be converted back to the reactants.
- A double arrow (⇌) is used when writing a chemical equation to show a reversible process.
- Reversible reactions in a closed system will reach a point where the rate of the forward reaction and the rate of the reverse reaction are equal. At this point, a dynamic equilibrium has been achieved.
- Equilibrium can be achieved in closed systems but not in open systems.
- Different reactions proceed to different extents.
- The relative ratio of reactants to products when equilibrium is reached is 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 the concentrations of the reactants and products with time.

KEY QUESTIONS

Describe

1 Select the correct response in the statements about chemical equilibria.

a An **open/closed** system occurs when both matter and energy are exchanged between the system and the surroundings.

b Chemical equilibria can occur in **open/closed** systems.

c In some circumstances, a reversible reaction can form a **dynamic/static** equilibrium.

d The extent of reaction for chemical equilibria is **constant/different** for different equilibria.

2 Indicate whether each of the following statements about the extent of reaction is true or false.

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.

Apply

3 Hydrogen gas is mixed with iodine gas in a sealed container. A reaction occurs according to the equation:

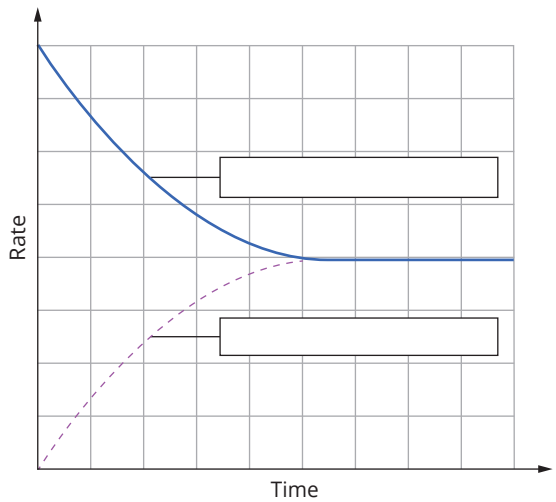
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Refer to the rate–time graph for this system shown below. Determine and label the following items on the graph.

a the forward reaction with the appropriate chemical equation

b the reverse reaction with the appropriate chemical equation

c the point when equilibrium is first established



4 Summarise dynamic equilibrium using the correct words to fill in the blanks below.

In a _____ system, as the concentrations of the reactants decrease, the rate of the forward reaction also _____. The collisions between

Continued over page

2.1 Review *continued*

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 reverse reactions are _____ and the concentrations of all species do not change.

Analyse

5 Classify the following systems as open or closed and explain your reasoning.

a a car engine in operation
b a can of soup
c a tree

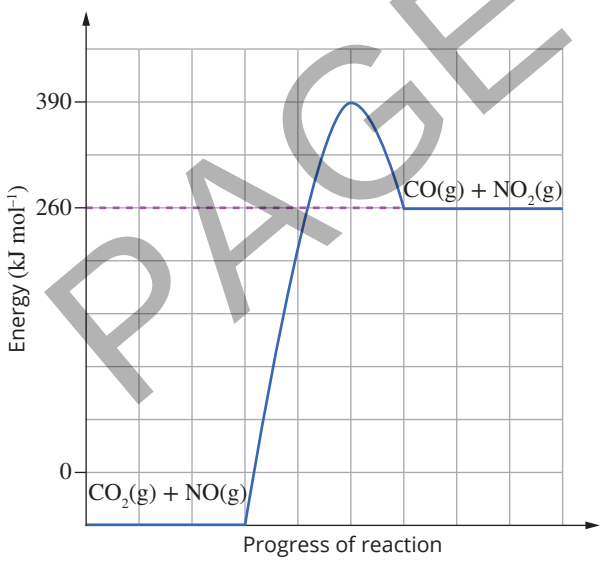
6 Determine which of the following systems are at equilibrium and explain your answer.

A a salt crystal slowly dissolving in a beaker of water
B a saturated sugar solution with sugar remaining on the bottom of the cup
C an open bottle of perfume
D the combustion of a log of wood in a campfire
E an open bottle of sparkling mineral water
F an unopened bottle of sparkling mineral water

7 The graph below shows the energy profile diagram for the reaction:

$$CO_2(g) + NO(g) \rightarrow CO(g) + NO_2(g)$$

Determine the activation energy for the reverse reaction in $kJ\,mol^{-1}$.

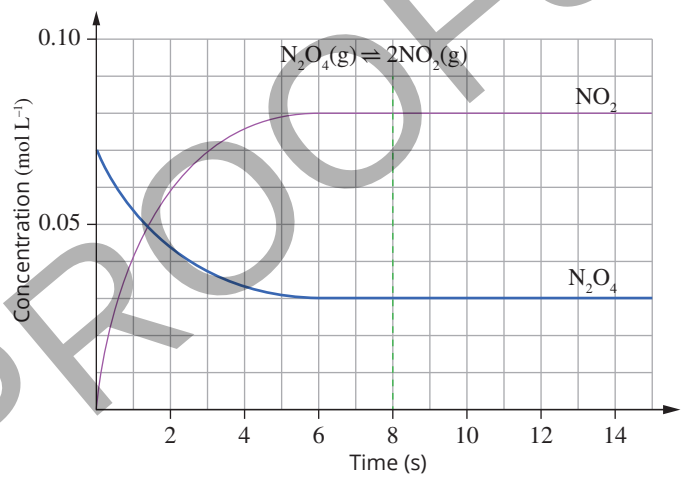


8 Consider the following equilibrium.

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

a Explain what is meant by the 'dynamic nature' of equilibrium and why wet clothes in a closed laundry bag do not dry.
b When the bag in part **a** is opened, the clothes begin to dry. Assess whether this is because of an equilibrium process. Explain your answer.

9 The graph below shows the concentration versus time plot for the decomposition of dinitrogen tetraoxide: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 100°C in a 1 L reaction vessel. N_2O_4 is a colourless gas and NO_2 is brown. Use the graph to determine the answer to the following questions.



a State the initial concentration of N_2O_4 in the flask.
b State the initial concentration of NO_2 in the flask.
c Identify the concentration of N_2O_4 at equilibrium.
d Identify the concentration of NO_2 at equilibrium.
e Calculate the number of moles of N_2O_4 that decompose during the reaction.
f State what the horizontal regions of the graph indicate.
g Identify how long it takes for equilibrium to be reached.
h Describe what a student studying this reaction will observe as the reaction proceeds.

2.2 Factors that affect equilibrium

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- explain the effect of adding extra reactant or product on a chemical equilibrium using collision theory and reaction rates
- predict the effect of adding extra reactant or product by the application of Le Châtelier's principle.

In this module, you will learn about how chemical systems at equilibrium are affected by changes in reaction conditions.

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 2.2.1. In this example, the addition of excess Cl^- ions causes a net forward reaction and the solution turns blue as more $CoCl_4^{2-}$ is formed. The addition of excess water causes a net reverse reaction and the solution returns to the original pink colour as more $[Co(H_2O)_6]^{2+}$ is formed.

You have seen in Module 2.1 that different reactions proceed to different extents. As a consequence, the relative amounts of reactants and products differ from one reaction to another at equilibrium. The relative amounts of reactants and products at equilibrium are called the **position of equilibrium**.

FIGURE 2.2.1 The effect of changes on the equilibrium: $Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

The relative amounts of substances present in equilibrium mixtures depend 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 of the sealed container (for equilibria involving gases)
- dilution (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', thereby increasing the amount of products formed.

> **i** 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 the change.

LE CHÂTELIER'S PRINCIPLE

The effect of a change in reaction conditions on an equilibrium system is summarised in a useful generalisation called **Le Châtelier's principle**. The principle is named after Henri Le Châtelier (Figure 2.2.2), a French chemist and engineer.

When a change occurs in an equilibrium system so that it is momentarily no longer at equilibrium, the system shifts to partially counteract 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.

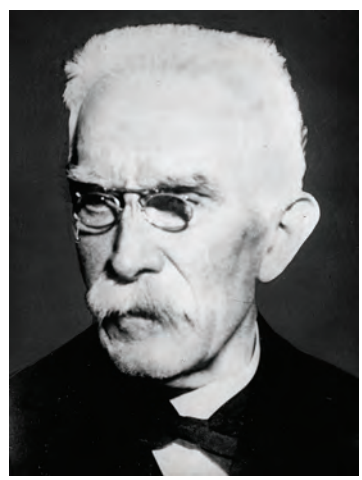


FIGURE 2.2.2 Henri Le Châtelier (1850–1936)

Adding more reactant or product

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

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

At equilibrium, the rates of the forward and reverse reactions are equal. The concentrations of the three gases are constant. If more nitrogen 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 N_2, H_2 and 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 N_2 gas to the equilibrium may be predicted simply by applying Le Châtelier's principle. According to Le Châtelier's principle, if N_2 is added to an equilibrium system, the system will shift to decrease the concentration of the added N_2, so a net forward reaction will occur.

It is important to note that, even though the concentration of N_2 gas decreases as the system moves to establish the new equilibrium, its final concentration 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.

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. The more successful collisions that occur within a specified time period, the faster is the reaction rate.

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

Instead of using Le Châtelier's principle, you can apply your knowledge of collision theory and reaction rates to understand the reasons for the effect of adding the extra N_2 gas. Because the concentration of N_2 molecules has increased, the rate of the forward reaction initially becomes greater than the rate of the reverse reaction. Then, as the concentration of N_2 and H_2 decreases and the concentration of NH_3 increases, the rate of the forward reaction 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 2.2.3 shows the effect on the rate of the forward and reverse reactions as the composition of the mixture adjusts to form a new equilibrium.

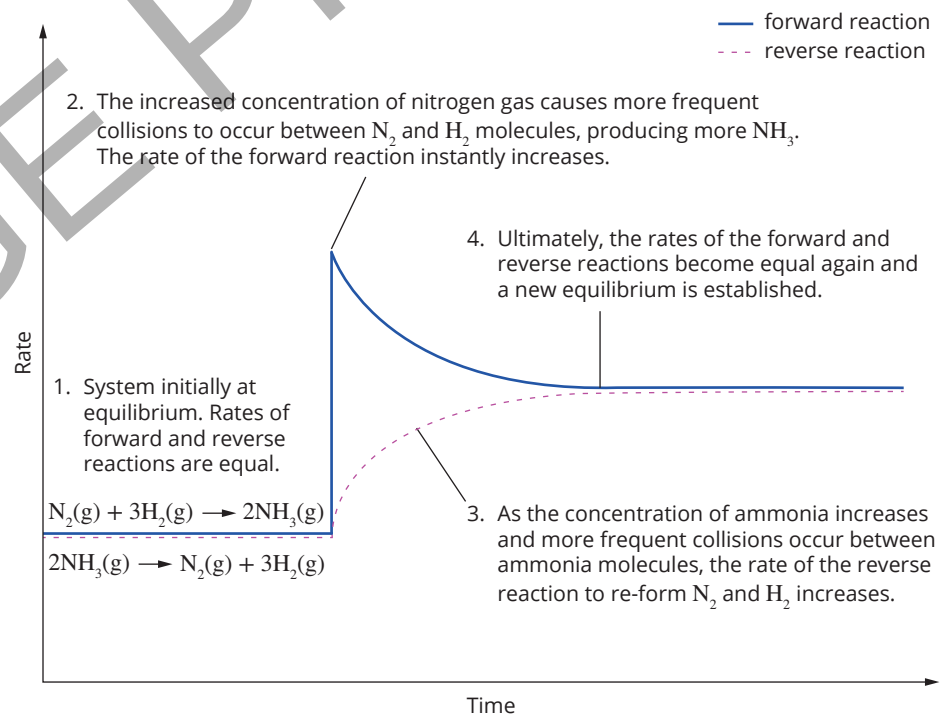


FIGURE 2.2.3 This rate–time graph shows the events that occur as a mixture of nitrogen, hydrogen and ammonia gas returns to equilibrium after the addition of extra nitrogen gas.

Once the system has re-established equilibrium, the rates of the forward and reverse reactions will again be equal. Overall, a net forward reaction has occurred with an increase in the concentration of ammonia 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. Figure 2.2.4 illustrates the effect on the system when N_2 gas is added as described.

If you follow the same reasoning as for N_2, you can see that adding extra amounts of the other reactant, H_2, to the system will also increase the concentration of ammonia produced. However, the addition of more product, NH_3, would result in a net reverse reaction and the equilibrium position shifting to the left, reducing the overall concentration of ammonia, as shown in Figure 2.2.5.

While you can apply your knowledge of collision theory and reaction rates to determine the overall effect of changes on an equilibrium as was done above, applying Le Châtelier's principle is a simpler way of predicting these effects.

Table 2.2.1 summarises how an equilibrium system acts to oppose the addition or removal of reactants and products.

TABLE 2.2.1 The general effects of a change to a system at equilibrium as predicted by Le Châtelier's principle

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
removing a reactant	formation of more reactants—a net reverse reaction; equilibrium position shifts to the left

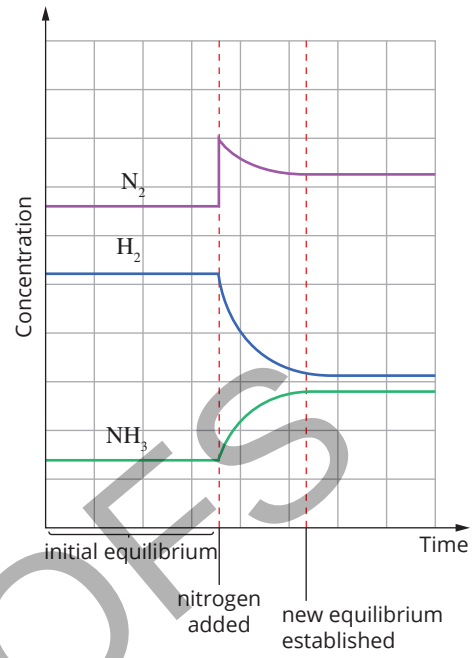


FIGURE 2.2.4 A representation of changes in concentrations that occur when additional nitrogen gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Worked example 2.2.1

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

In solution, $Co(H_2O)_6^{2+}$ ions form an equilibrium with $CoCl_4^{2-}(aq)$ ions, as shown by the equation:

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

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

Thinking	Working
Determine the initial effect of the change on the concentration of the particles.	Adding 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 $Co(H_2O)_6^{2+}$ ions and Cl^- ions become more frequent, increasing the rate of the forward reaction and reducing the concentration of $Co(H_2O)_6^{2+}$ and Cl^- ions.
Consider how the rates of the forward and reverse reactions change as the system reaches a new equilibrium.	As more product ions, $CoCl_4^{2-}$, 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 and the position of equilibrium is said to have 'shifted to the right'.

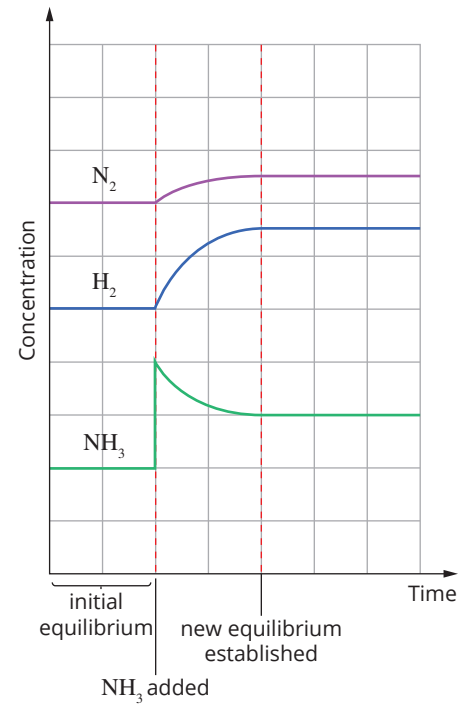


FIGURE 2.2.5 A representation of changes in concentrations that occur when additional ammonia gas is added to the equilibrium: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

➤ Try yourself 2.2.1

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

Consider the following equilibrium system:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Use the concepts of rates of reaction and collision theory to predict the effect on the position of equilibrium of the addition of CO gas on the equilibrium.

2.2 Review

SUMMARY

- Le Châtelier's principle states that if an equilibrium system is subjected to change, the system will shift to partially oppose the change.
- The effect of a change on an equilibrium system can be predicted from Le Châtelier's principle. The effects of changes can also be explained on the basis of collision theory and reaction rates.

Change to system in equilibrium	Effect of change on equilibrium position
adding more reactant	shifts to the right (net forward reaction)
adding more product	shifts to the left (net reverse reaction)
removing some reactant	shifts to the left (net reverse reaction)
removing some product	shifts to the right (net forward reaction)

KEY QUESTIONS

Describe

1 State Le Châtelier's principle.

Apply

2 Select the correct words in the paragraph below to summarise the effect of adding additional reactant to an equilibrium system.

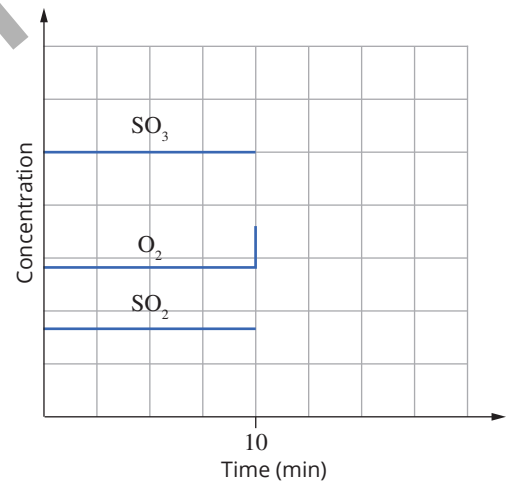
If a reactant is added to an equilibrium system, the rate of the forward reaction initially becomes **less/greater** than the rate of the reverse reaction. Then, as the concentration of reactants **increases/decreases** and the concentration of products **increases/decreases**, the rate of the forward reaction **increases/decreases** and the rate of the reverse reaction **increases/decreases** until they become equal again and a new equilibrium is formed.

3 Consider the equilibrium:

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

The following graph shows the concentrations of the three gases in an equilibrium mixture of constant volume and temperature. After 10 minutes, additional O_2 was added to the mixture.

Sketch a graph to show how concentrations would change as a consequence of the addition of O_2.



Analyse

4 Predict the effect of adding more hydrogen gas to the following equilibria using Le Châtelier's principle.

a $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

5 Predict the effect of the following changes on the position of each equilibrium.

a addition of SO_3 to the equilibrium:
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

b removal of CH_3COO^- from the equilibrium:
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

2.3 Applying Le Châtelier's principle and collision theory to equilibria

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- use your knowledge of Le Châtelier's principle, collision theory and rates of reaction to predict the impact of changes in gas pressure and solution concentration on equilibria
- describe the effect of raising and lowering temperature on an equilibrium system
- explain why the presence of a catalyst does not affect the equilibrium position of a reaction.

Le Châtelier's principle can be used to understand how changes to chemical equilibria can affect numerous natural systems, as well as to optimise yields of reactions occurring in industrial processes. In the previous module, you learnt how the addition or removal of reactants and products affected the position of chemical equilibrium.

In this module, 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.

CHANGING PRESSURE

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:

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

3 gas particles 2 gas particles

You can see that the forward reaction involves a reduction in the number of gas particles 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, a net reverse reaction causes an overall increase in pressure of the system.

As you saw in Module 2.2, a change in the position of an equilibrium can be predicted by applying either:

- Le Châtelier's principle, or
- an understanding of collision theory and the rates of reactions.

Predicting the effect of pressure change using Le Châtelier's principle

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

In the example:

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

Remember that gas 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 number of particles will change the pressure.

an increase in pressure will cause a net forward reaction to occur to reduce the overall pressure (three gaseous reactant particles become two gaseous product particles). The amount of SO_3 present at equilibrium will increase and the position of equilibrium is said to have been shifted to the right, as shown in Figure 2.3.1.

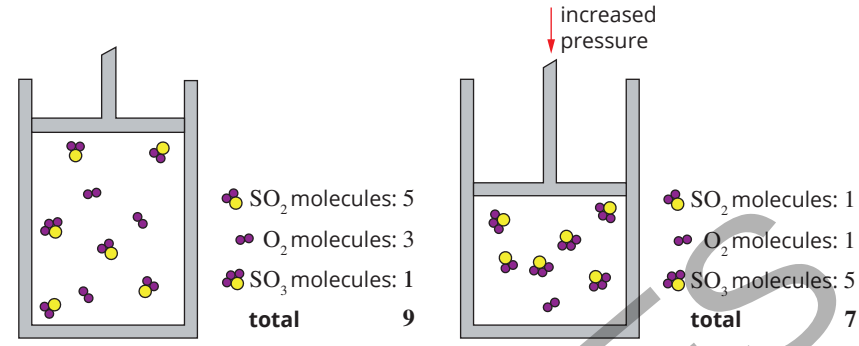


FIGURE 2.3.1 A representation of the effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

The effect of the change can also be illustrated graphically, as shown in Figure 2.3.2. When the system is initially at equilibrium and there is an increase in pressure, the concentrations of all gases increase simultaneously.

As the system adjusts, there is a gradual change in the concentration of each of the species until the new equilibrium is established. At the new equilibrium position, the individual concentrations are different to those at the first equilibrium.

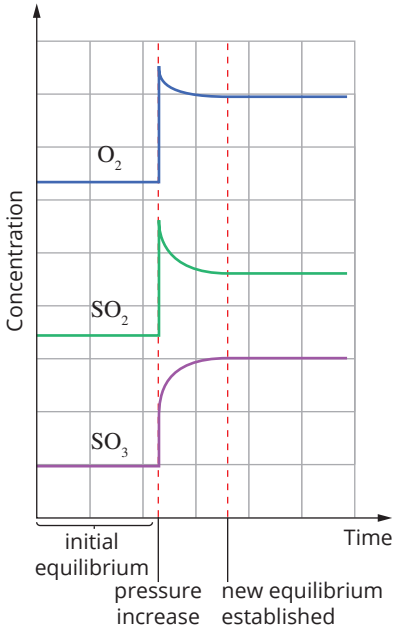


FIGURE 2.3.2 The effect of increased pressure on the equilibrium: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

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

Predicting the effect of pressure change using collision theory

The effect of a reduction in volume on the equilibrium can also be understood 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 states nor for systems in aqueous solutions. 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 position of equilibrium.

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 the balanced equation shows an equal number 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:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

2 reactant gas particles 2 product gas particles

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 change in the position of equilibrium.

In terms of collision theory, the volume decrease causes the rates of the forward and reverse reactions to be increased equally because there are equal numbers of particles on both sides of the equation.

Worked example 2.3.1

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

Consider the equilibrium:

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

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

Thinking	Working
Determine the immediate effect of the change of volume on the pressure.	Halving the volume will double the pressure of all species at equilibrium.
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 gaseous particles, and vice versa for a volume increase.) Decide how the equilibrium will respond.	There are two molecules of gas on the reactant side and four molecules of gas on the product side, so the system will shift to the left (a net reverse reaction). This decreases the amounts of the products, including CO. (Note that the CO *concentration* will still be higher than it was at the initial equilibrium position, but the *amount* will be less. The shift in equilibrium position only partially compensates for the change.)

➤ Try yourself 2.3.1

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

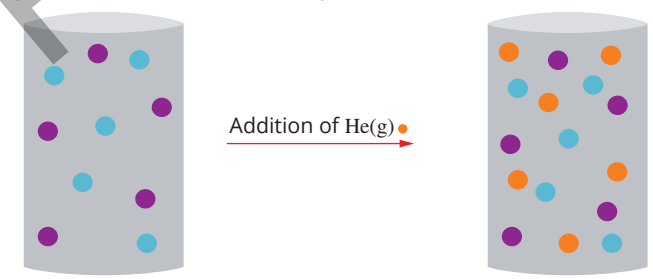
Consider the equilibrium:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Predict the shift in equilibrium position and the effect on the amount of Cl_2 when the volume is doubled at a 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. This can be seen in Figure 2.3.3.



System at equilibrium
Volume 1 L
[•] = 5 particles L^{-1}
[•] = 5 particles L^{-1}

System still in equilibrium but at higher pressure. Volume 1 L
[•] = 5 particles L^{-1}
[•] = 5 particles L^{-1}

FIGURE 2.3.3 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 the reactants or products.

WS 3.1.3

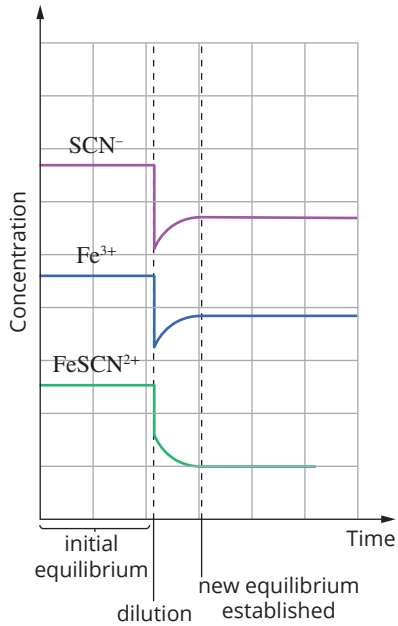


FIGURE 2.3.4 Effect of dilution on the equilibrium $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq)$. Although the equilibrium position shifts to the left, note that the concentrations of Fe^{3+} and SCN^{-} at the new equilibrium are lower than their concentrations prior to dilution, as the equilibrium shift only partially opposes the change.

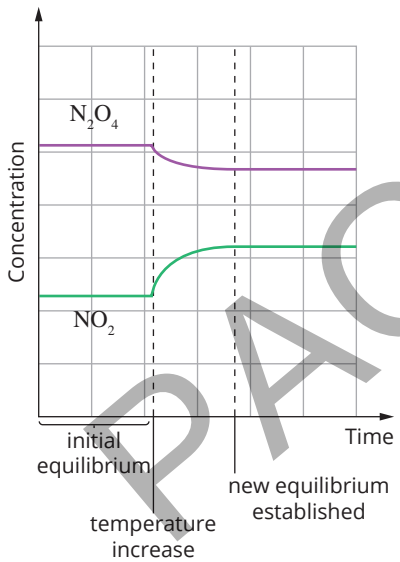


FIGURE 2.3.5 The effect of heating on the equilibrium: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

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. Using collision theory, you can see that any collisions with inert gas molecules will not produce a reaction, so no net change in equilibrium position will be observed.

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 unit of volume. 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:

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

2 particles in solution 1 particle in solution

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 number of particles in solution – the position of equilibrium is therefore shifted to the left in this example.

Figure 2.3.4 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.

CHANGING TEMPERATURE

The effect of a temperature change on an equilibrium reaction depends upon whether the reaction is exothermic or endothermic. The overall effect on equilibrium position can be predicted using Le Châtelier's principle and explained using collision theory and rates of reaction.

For example, consider the conversion of brown nitrogen dioxide gas (NO_2) to colourless dinitrogen tetraoxide gas (N_2O_4). The reaction is exothermic, releasing energy to the surroundings. You could (but would not usually) write an equation for the reaction that includes the energy released:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + \text{energy}$$

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 and the position of equilibrium will therefore shift to the left. Figure 2.3.5 shows the gradual decrease in the concentration of N_2O_4 as the system moves to produce more reactant, NO_2. Note that with a change in temperature, there is no instantaneous change in concentration.

Because the reactants and products of the system are different colours, you can monitor the change in this equilibrium visually. When a new equilibrium is attained, there is less dinitrogen tetraoxide and more nitrogen dioxide present, so the mixture appears a darker brown. This can be seen in Figure 2.3.6.

FIGURE 2.3.6 Equilibrium mixtures of NO_2 and N_2O_4 in hot water and ice. Heating the mixture favours the formation of brown 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
- net forward reaction (more products) for endothermic reactions.

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 energy to overcome the activation energy barrier 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 that there will be a greater proportion of molecules with the necessary energy to overcome the activation energy barrier 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 2.3.7, which shows the frequency distribution of molecules at different temperatures.

In this example of the equilibrium between NO_2 and N_2O_4, the reverse reaction is endothermic, and so there will be a net reverse reaction if the temperature increases. When the system re-establishes equilibrium at a higher temperature, the new equilibrium has a higher concentration of NO_2 and a lower concentration of N_2O_4. Conversely, decreasing the temperature of an equilibrium results in a net reaction in the direction of the exothermic reaction.

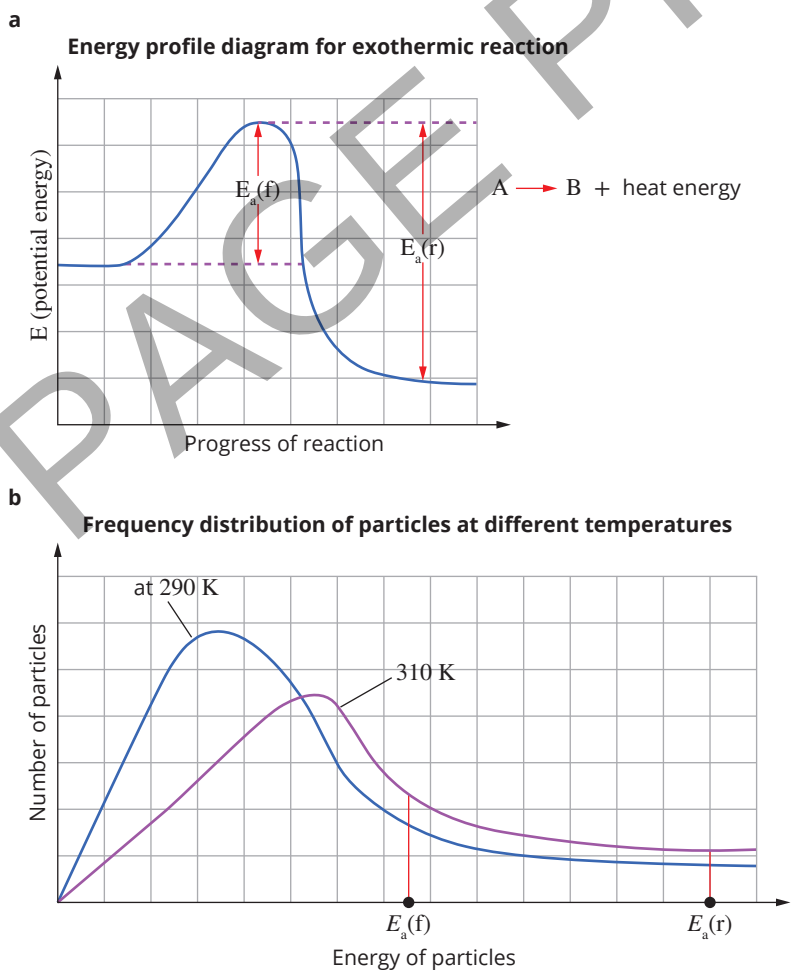


FIGURE 2.3.7 (a) Energy profile diagram for an exothermic reaction. The activation energy of the forward reaction, E_a(f), is less than the activation energy of the reverse reaction, E_a(r). (b) The frequency distribution of molecules at two different temperatures. At the higher temperature, a greater proportion of particles have the necessary energy to overcome the activation energy barrier for the endothermic reaction.

Worked example 2.3.2

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

Consider the equilibrium:

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad \Delta H = +42\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this endothermic reaction.

Thinking	Working
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 energy to overcome the activation energy barrier 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 H_2 and CO_2 react and the concentration of reactants decreases, the rate of the forward reaction will decrease. As the concentration of CO and H_2O 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, CO and H_2O, and lower concentrations of the reactants, CO_2 and H_2. The position of equilibrium is said to have shifted to the right.

➤ Try yourself 2.3.2

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

Consider the equilibrium:

$$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \quad \Delta H = -165\,kJ\,mol^{-1}$$

Using collision theory, explain the effect of an increase in temperature on this exothermic reaction.

EFFECT OF A CATALYST ON EQUILIBRIUM

A catalyst lowers the activation energy of the forward and reverse reactions by the same amount. This can be seen in the energy profile diagram shown in Figure 2.3.8.

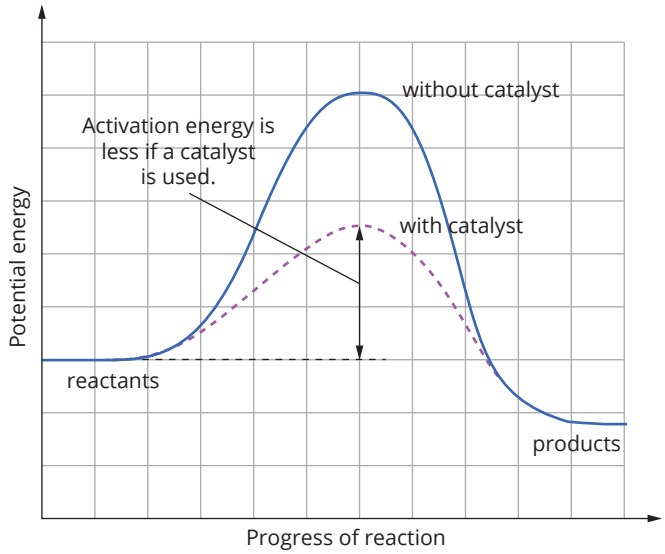


FIGURE 2.3.8 Energy changes in a catalysed and uncatalysed reaction

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.

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, and the presence of a catalyst does not change the position of equilibrium. 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.

Lowering the activation energy of a reaction by the addition of a catalyst does not change the position of equilibrium of a system. Addition of a catalyst only affects how quickly equilibrium is attained.

2.3 Review

SUMMARY

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

Summary of the effect of a change on equilibrium

Change on equilibrium	Effect of change on equilibrium position	Collision theory explanation of the effect of change on equilibrium position
increasing pressure by decreasing volume (for gases)	shifts in the direction of the lower number of gas particles in the balanced chemical equation	more frequent collisions; the reaction that is more dependent on collisions (more particles reacting) occurs to a greater extent
decreasing pressure by increasing volume (for gases)	shifts in the direction of the greater number of gas particles in the balanced chemical equation	less frequent collisions; the reaction that is less dependent on collisions (fewer particles reacting) occurs to a greater extent
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 greater number of dissolved particles in the balanced chemical equation	less frequent collisions; the reaction less dependent on collisions (fewer particles reacting) occurs to a greater extent
increasing the temperature for exothermic reactions	shifts to the left (net reverse reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in the direction of endothermic reaction, i.e. favouring the reverse direction
increasing the temperature for endothermic reactions	shifts to the right (net forward reaction)	all reactant and product molecules have more energy and move faster; increased temperature favours rate of an endothermic reaction; net reaction in the direction of endothermic reaction, i.e. favouring the forward direction
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

KEY QUESTIONS

Describe

1 State whether the following statements are true or false.

a Adding a catalyst to an equilibrium system does not affect the position of equilibrium.

b At constant volume, increasing the temperature of an exothermic reaction at equilibrium increases the amount of products.

c At constant temperature, increasing the pressure of a gaseous equilibrium system always increases the amount of products.

d If an aqueous equilibrium system is diluted at constant temperature, the position of equilibrium shifts in the direction that produces the greater number of dissolved particles.

2 Select the correct words in this paragraph to describe the effect of adding a catalyst to an equilibrium system.

A catalyst **raises/lowers** the activation energy of a reaction and increases the rate of the forward and reverse reactions **unequally/equally**. The presence of a catalyst **does/does not** change the position of equilibrium. A catalyst **will increase/does not increase** the rate at which an equilibrium is attained.

Apply

3 Summarise the effect of changes on an equilibrium system by completing the following table.

Change to equilibrium	Effect of change on equilibrium position
adding a reactant	
increasing pressure by decreasing the size of the closed container (for gases)	
adding a catalyst	
increasing the temperature for endothermic reactions	
decreasing the temperature for exothermic reactions	
adding water (dilution of solutions)	

4 The total pressure of the equilibrium system below was increased by reducing the volume at constant temperature:

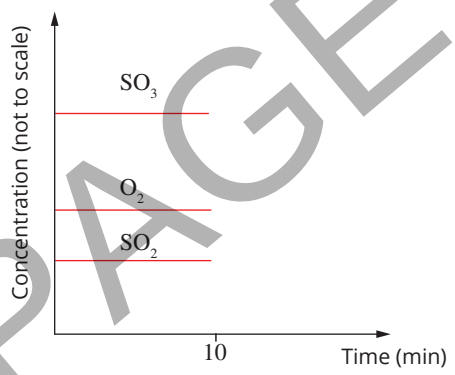
$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Explain why more N_2O_4 is formed in terms of the effect of the change on the rates of the forward and reverse reactions.

5 Consider the equilibrium:

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

The graph below shows the concentrations of the three gases in an equilibrium mixture at constant volume and temperature.



Draw graphs to show how concentrations would change with time if the following changes occurred separately at ten minutes. Your graphs should show the relative stoichiometric changes in the concentration of each gas.

a the pressure of the system was suddenly increased by reducing volume

b the temperature of the system was increased at constant volume

c a catalyst was added at constant volume and temperature.

Analyse

6 For each of the three changes to the equilibrium system described in question **5**, predict the effect of the changes in terms of collision theory and rates of reaction.

7 Predict the effect of the following changes on the position of each equilibrium.

a halving the volume (doubling the pressure) of the equilibrium:

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

b increasing the pressure of the equilibrium (by reducing volume):

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

c increasing the temperature of the endothermic equilibrium:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

8 An equilibrium mixture consists of the gases N_2O_4 and NO_2:

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

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.

a concentration of NO_2

b mass of NO_2

9 Determine how the concentration of hydrogen gas in each of the following equilibrium mixtures will change when the mixtures are cooled and kept at constant volume. Explain your answer.

a $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ $\Delta H = +138\ kJ\ mol^{-1}$

b $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$ $\Delta H = -208\ kJ\ mol^{-1}$

2.4 Equilibrium constants

BY THE END OF THIS MODULE, YOU SHOULD BE ABLE TO:

- understand that an equilibrium law expression can be written for equilibrium systems
- state equilibrium law expressions for reactions
- deduce the extent of a reaction from the value of its equilibrium constant
- solve mathematical problems using equilibrium law expressions.

In this module, you will be introduced to the equilibrium constant, K_c, and use it to investigate the relationship between the quantities of reactants and the quantities of products present when a system reaches equilibrium. The equilibrium constant allows you to:

- qualitatively predict the *relative* amounts of reactants and products in chemical equilibrium systems
- quantitatively calculate the *actual* amounts of reactants and products in chemical equilibrium systems.

Although the calculations in this section 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 2.4.1). If the populations change through 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 2.4.1 The populations of zebras and lions in Africa can be understood using the principles of equilibrium.

INTRODUCING THE REACTION QUOTIENT, Q_C, AND THE EQUILIBRIUM CONSTANT, K_C

Consider the equilibrium system you were introduced to in Module 2.1:

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

An unlimited number of different equilibrium mixtures of the three gases, nitrogen, hydrogen and ammonia, can be prepared. Table 2.4.1 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 $\frac{[NH_3]^2}{[N_2][H_2]^3}$ for each mixture are also given. Note that the coefficients of the reactants and products in the chemical equation above form the indices of the reactant and product concentrations used in this fraction.

The fraction $\frac{[NH_3]^2}{[N_2][H_2]^3}$ is called the **reaction quotient** (Q_c) or **concentration fraction** of the mixture.

TABLE 2.4.1 Concentrations of reactants and products present in equilibrium mixtures

Equilibrium mixture	$[N_2]$ (mol L^{-1})	$[H_2]$ (mol L^{-1})	$[NH_3]$ (mol L^{-1})	$\frac{[NH_3]^2}{[N_2][H_2]^3}$
1	0.25	0.75	0.074	0.052
2	0.55	0.65	0.089	0.052
3	0.0025	0.0055	4.6×10^{-6}	0.051
4	0.0011	0.0011	2.7×10^{-7}	0.051

As you can see in Table 2.4.1, the reaction quotient $\frac{[NH_3]^2}{[N_2][H_2]^3}$ has an almost constant value of 0.052 for each equilibrium mixture regardless of the concentration of each component.

You can write a reaction quotient expression for any reversible chemical reaction. For example, consider the generalised equation

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

where a, b, c and d are the stoichiometric coefficients of substances A, B, C and D. The Q_c expression can be written as

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In Q_c expressions, the products always appear on the top line of the expression (the numerator) and the reactants always appear on the bottom of the expression (the denominator). The terms $[A]$, $[B]$, $[C]$ and $[D]$ refer to the concentration of substances A, B, C and D, respectively. The Q_c expression is obtained by multiplying the concentration of products, divided by the concentrations of reactants, with each concentration term raised to a power equal to its stoichiometric coefficient in the balanced chemical equation.

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 (as in Table 2.4.1). At equilibrium, the value of the reaction quotient is equal to the **equilibrium constant**, K_c, and we can write the equilibrium law expression as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The **equilibrium law** expression is a mathematical expression of the *law of mass action* first postulated by Norwegian scientists Cato Gulberg and Peter Waage in 1864. It asserts that for a reaction at equilibrium, and at a constant temperature, the ratio of the reactant and product concentrations has a constant value, K_c.

You will note that the expressions for Q_c and K_c take exactly the same form. However, it is important to note that when writing a K_c expression, the concentration terms refer to *equilibrium concentrations only*, whereas a Q_c expression can be written for reactant and product concentrations at any time during the reaction, *before* equilibrium is reached.

In general, for reversible chemical reactions:

- a reaction quotient expression, Q_c, can be written for reactant and product concentrations at any time during the reaction
- an equilibrium constant expression, K_c, can be written for reactant and product concentrations at equilibrium (i.e. only when the reaction has been allowed to come to equilibrium)
- different chemical reactions have different values of K_c

K_c represents the equilibrium constant for a particular reaction.

The value of K_c is different for different reactions.

K_c values are constant for a fixed temperature and will change with changes in temperature.

K_c values should therefore be reported for a particular reaction at a particular temperature.

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

- 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
- K_c is temperature dependent, so the value of K_c for a particular reaction will change with changes in temperature.

A useful way of remembering the equilibrium law expression 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.

Worked example 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

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

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

Determine the expression for the equilibrium constant K_c.

Thinking	Working
Identify the coefficients of the products and the reactants in the equation.	The product, NO_2, has a coefficient of 2 and the reactant, N_2O_4, has a coefficient of 1.
Write the expression for K_c, noting that: • the concentration of products is written in the numerator • the concentration of reactants is written in the denominator • each concentration term is raised to a power equal to its stoichiometric coefficient $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$

Try yourself 2.4.1

WRITING AN EQUILIBRIUM LAW EXPRESSION

Determine the equilibrium expression for K_c for the reversible reaction:

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

Calculating equilibrium constants and equilibrium concentrations

An equilibrium constant, K_c, can be calculated from the molar concentrations of reactants and products at equilibrium, as shown in Worked example 2.4.2.

Worked example 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 2.00 L vessel contains a mixture of 0.0860 mol of H_2, 0.124 mol of I_2 and 0.716 mol of HI in equilibrium at 460°C according to the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Calculate the value of the equilibrium constant, K_c, at 460°C.

Thinking	Working
Find the molar concentrations for all species at equilibrium. Convert the number of moles to mol L^{-1} using $c = \frac{n}{V}$.	The volume of the vessel = 2.00 L $[H_2] = \frac{n(H_2)}{V}$ $= \frac{0.0860}{2.00} = 0.0430\,\text{mol}\,L^{-1}$ $[I_2] = \frac{n(I_2)}{V}$ $= \frac{0.124}{2.00} = 0.0620\,\text{mol}\,L^{-1}$ $[HI] = \frac{n(HI)}{V}$ $= \frac{0.716}{2.00} = 0.358\,\text{mol}\,L^{-1}$
State the expression for K_c.	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
Substitute into the expression for K_c to determine the value of K_c.	$K_c = \frac{0.358^2}{0.0430 \times 0.0620}$ $= 48.1$ Note that the there are no units for K_c (see below for an explanation).

➤ Try yourself 2.4.2

CALCULATING AN EQUILIBRIUM CONSTANT

A 3.00 L vessel contains a mixture of 0.120 mol of N_2O_4 and 0.500 mol of NO_2 in equilibrium at 460°C according to the equation:

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

Calculate the value of the equilibrium constant, K_c, at 460°C.

You can also calculate the equilibrium concentration of a reactant or product, if you know the value of the equilibrium constant K_c. To do this, you will have to 'work backwards' and substitute the magnitude of K_c into the equilibrium law expression, as shown in Worked example 2.4.3.

Worked example 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium where $K_c = 0.400$ at 250°C:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

An equilibrium mixture contains 0.0020 mol L^{-1} PCl_5 and 0.0010 mol L^{-1} PCl_3 at 250°C. Determine the equilibrium concentration of Cl_2 in this mixture.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$
Substitute the known values into the expression for K_c.	$0.400 = \frac{0.0010 \times [Cl_2}{0.0020}$
Rearrange the expression to make $[Cl_2]$ the subject of the equation and calculate the concentration of this species.	$[Cl_2] = \frac{0.400 \times 0.0020}{0.0010}$ $= 0.80\,\text{mol}\,L^{-1}$

➤ Try yourself 2.4.3

CALCULATING AN EQUILIBRIUM CONCENTRATION

Consider the following equilibrium where $K_c = 0.720$ at 250°C:

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

An equilibrium mixture contains 0.040 mol L^{-1} N_2O_4 at 250°C. Determine the equilibrium concentration of NO_2 in this mixture.

Units of *Kc*

You will note in the worked examples above that the values of K_c are dimensionless, even though concentration values that substitute into the equilibrium expression have the unit of molarity (M). This is because the concentration terms in the equilibrium expression are actually ratios of concentrations, referenced to a standard concentration of exactly 1 mol L^{-1}. By dividing each concentration term by 1 mol L^{-1}, the individual concentration units disappear, and we get a dimensionless K_c value.

In this text, the reference concentration of 1 mol L^{-1} will not be included in K_c expressions, as it will not explicitly change the magnitude of the K_c value. Instead, we will simply use the concentration values provided, while remembering that K_c values have no units.

It is also important to note that K_c values are always positive, since we cannot have negative concentration values. Depending on the reaction, K_c values can vary over enormous ranges, typically from $\sim 10^{-30}$ up to $\sim 10^{50}$.

DEPENDENCY OF AN EQUILIBRIUM CONSTANT ON THE EQUATION

The equilibrium law expression 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 given. Values of K_c for this system at 25°C are also shown.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 6.2 \times 10^{-4}$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = \frac{[N_2O_4]}{[NO_2]} = \frac{1}{6.0 \times 10^{-4}} = 1.6 \times 10^{3}$$

$$2N_2O_4(g) \rightleftharpoons 4NO_2(g) \qquad K_c = \frac{[NO_2]^4}{[N_2O_4]^2} = (6.2 \times 10^{-4})^2 = 3.8 \times 10^{-7}$$

$$\frac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g) \qquad K_c = \frac{[NO_2]}{[N_2O_4]^{\frac{1}{2}}} = (6.2 \times 10^{-4})^{\frac{1}{2}} = 2.5 \times 10^{-2}$$

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

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.

INTERPRETING 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 number of moles of products present at equilibrium).

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

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

The relationship between the value of K_c and the relative proportions of reactants and products at equilibrium is shown in Table 2.4.2.

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

TABLE 2.4.2 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. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.052$ at 400°C
very large; $>10^{4}$	Almost complete reaction occurs. The concentrations of products are much higher than the concentrations of reactants at equilibrium. e.g. $HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$ $K_c = 10^7$ at 25°C
very small; $<10^{-4}$	Negligible reaction occurs. The concentrations of reactants are considerably higher than the concentrations of products at equilibrium. e.g. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ $K_c = 1.8 \times 10^{-5}$ at 25°C

Using K_c and Q_c to predict the direction of chemical reactions

You have seen that a value for the equilibrium constant, K_c, can be calculated for any chemical reaction at equilibrium. You have also noted that a value for the reaction quotient, Q_c, can be calculated for any mixture of reactants and products at any time during a reaction. For the generalised reaction

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

K_c is calculated using $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ and is calculated for reactions at equilibrium, while Q_c is calculated using $Q_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ and is calculated for reactions that have not yet reached equilibrium.

The value for K_c for a particular reaction, at a particular temperature, can only have one positive value; this is because the concentration values of all reactants and products do not change once equilibrium has been reached. By contrast, the value for Q_c can take on any positive value since the concentration values of reactants and products are changing with time up to the point at which equilibrium is established.

When $Q_c = K_c$, the reaction is at equilibrium. When $Q_c \neq K_c$, we can compare the values to determine in which direction the reaction must proceed to reach equilibrium. For example, if $Q_c > K_c$, then, relatively speaking, the numerator (or products) term is dominant compared to the equilibrium case. This means that, relatively speaking, the ratio of products to reactants is too high and the reaction will proceed to the left, consuming more products, to establish equilibrium.

By contrast, if $Q_c < K_c$, then the opposite will occur – the reaction will proceed to the right because, relatively speaking, the denominator (or reactants) term is dominant and the ratio of reactants to products is too high compared to the equilibrium case.

So, if the reaction quotient, Q_c, is:

- greater than K_c, the system 'shifts to the left' to achieve equilibrium and more reactants are formed

- smaller than K_c, the system 'shifts to the right' to achieve equilibrium and more products are formed
- equal to K_c, the system is at equilibrium.

The relationship between Q_c and K_c is illustrated in Figure 2.4.2. By comparing the value of Q_c for a reaction to K_c at a given temperature, it is possible to predict the direction a reaction will proceed in order to reach equilibrium.

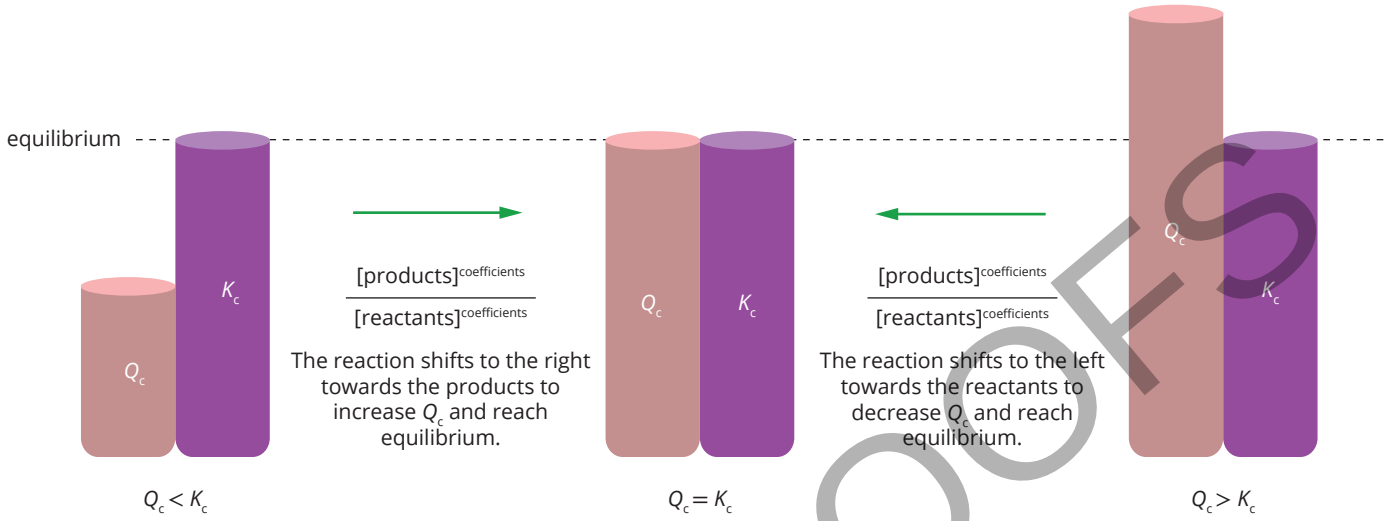


FIGURE 2.4.2 For any reversible reaction at equilibrium $K_c = Q_c$, so comparing these two values for a reaction can indicate which way a reaction must progress to reach equilibrium.

Worked example 2.4.4

PREDICTING THE DIRECTION OF A REACTION

The value of the equilibrium constant, K_c, for the following reaction is 3.07×10^{-4} at 25°C.

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

If the initial concentrations of reacting species are [NOBr] = 0.16 M, [NO] = 0.010 M and $[Br_2]$ = 0.010 M, decide in which direction the reaction will proceed.

Thinking	Working
The concentrations given are not necessarily the equilibrium concentrations. If you calculate the reaction quotient, Q_c, for concentrations given, you can then compare the value of Q_c to the value of K_c to determine which direction the reaction will proceed. Write the Q_c expression for the reaction using the general expression as a guide $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$	For this reaction, the Q_c expression is $Q_c = \frac{[NO]^2[Br]}{[NOBr]^2}$ Noting that the concentration terms for each substance are raised to the power indicated by the stoichiometric coefficient of each substance in the balanced chemical equation.
Substitute the given concentration values into the Q_c expression.	$Q_c = \frac{0.010^2 \times 0.010}{0.16^2}$ $= 3.9 \times 10^{-5}$

Compare the calculated Q_c value with the K_c value given in the question.	$Q_c = 3.9 \times 10^{-5}$; $K_c = 3.07 \times 10^{-4}$ Therefore, $Q_c < K_c$ and the reaction will proceed to the right.

➤ Try yourself 2.4.4

PREDICTING THE DIRECTION OF A REACTION

The value of the equilibrium constant, K_c, for the following reaction is 3.07×10^{-4} at 25°C.

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

If the initial concentrations of reacting species are $[H_2] = 0.50\,M$, $[N_2] = 0.40\,M$ and $[NH_3] = 0.30\,M$, decide in which direction the reaction will proceed.

In summary, we can gain very useful information from the values of K_c and Q_c as follows:

- If $K_c >> 1$, the equilibrium mixture will be dominated by products.
- If $K_c << 1$, the equilibrium mixture will be dominated by reactants.
- If $Q_c > K_c$, the reaction will proceed to the left.
- If $Q_c = K_c$, the reaction is at equilibrium.
- If $Q_c < K_c$, the reaction will proceed to the right.

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.

As you learnt in Module 2.2, the effect of a change in temperature on reactions at equilibrium depends on whether the reaction is exothermic or endothermic. Changes in K_c values with changes in temperature also depend 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 2.4.3 summarises the effect on K_c when temperature increases. The opposite is true when temperature decreases.

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

TABLE 2.4.3 The effect on the value of K_c when the temperature of a system increases

ΔH	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.

STOICHIOMETRIC CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT AND CONCENTRATIONS

Calculating K_c values

K_c values can be calculated directly from the molar concentrations of reactants and products at equilibrium, as was shown in Worked example 2.4.2 on page XX. In that example, all equilibrium concentrations in the reaction mixture were known, making the calculation straightforward – simply substituting all concentration values into the K_c expression for the reaction given. In practice, however, it is rare to have complete knowledge of the equilibrium concentrations of all reacting substances in

An ICE table (reaction table) sets up the steps for working out equilibrium calculations where the equilibrium concentration of one or more species is unknown. The first letter of each word corresponds to the information that is recorded in each row of the table: Initial, Change, Equilibrium.

an equilibrium mixture. Typically, the concentration of only one reactant or product will be monitored and measured at equilibrium.

Fortunately, this is usually sufficient, as the stoichiometric coefficients in the balanced chemical equation can be used to deduce the equilibrium concentrations of the other substances in the reaction. Once these are known, the equilibrium constant can then be calculated, as shown in Worked example 2.4.2 on page XX.

A popular way to set out calculations of this type is with the use of a **reaction table** (also known as an ICE table). The reaction table shows the *initial* amounts (or concentrations) of reactants and products, the *changes* that occur as the system reaches equilibrium and the final values at *equilibrium*, as Worked example 2.4.5 illustrates.

Worked example 2.4.5

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

An equilibrium is established between A and B at a specified temperature according to the following equation:

$$A(g) \rightleftharpoons 2B(g)$$

0.540 mol of A was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.280 mol of B was present. Calculate the value of the equilibrium constant at this temperature.

Thinking

Construct a reaction table using each species in the balanced equation as the headings for the columns in the table. Insert three rows in the table labelled 'I' (initial), 'C' (change) and 'E' (equilibrium):

	Reactants ⇌ Products	
I		
C		
E		

Enter the data provided above in the table.

When a species is consumed, the change is negative; when a species is produced, the change is positive.

Working

Initially, there is:

- 0.540 mol of A(g)
- 0.0 mol of the product B(g).

Let x mol of A react; from the coefficients of the equation $2x$ mol of B is produced.

At equilibrium, there is 0.280 mol of B(g).

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x$ mol	$+2x$ mol
E	$0.540 - x$ mol	$2x = 0.280$ mol

Using the coefficients from the equation, calculate the moles of all species at equilibrium.

Initially, no B was present, so because 0.280 mol of B has been produced at equilibrium:

$2x = 0.280$ mol

$x = 0.140$ mol

We can enter these values in the table:

	A(g) ⇌ 2B(g)	
I	0.540 mol	0.0 mol
C	$-x = -0.140$ mol	$+2x = 0.280$ mol
E	$0.540 - x$ $= 0.540 - 0.140$ $= 0.400$ mol	$2x = 0.280$ mol

Using the volume of the vessel, calculate the concentrations for all species at equilibrium. Use the formula $c = \frac{n}{V}$.	The volume of the vessel is 2.00 L. $[A] = \frac{n}{V}$ $= \frac{0.400}{2.00}$ $= 0.200\ \text{mol L}^{-1}$ $[B] = \frac{n}{V}$ $= \frac{0.280}{2.00}$ $= 0.140\ \text{mol L}^{-1}$
State the expression for K_c and substitute the equilibrium concentrations. Calculate the equilibrium constant, K_c.	$K_c = \frac{[B]^2}{[A]}$ $= \frac{0.140^2}{0.200}$ $= 0.0980$

➤ Try yourself 2.4.5

USING STOICHIOMETRY TO CALCULATE AN EQUILIBRIUM CONSTANT

At one step during the synthesis of nitric acid, nitrogen dioxide (NO_2) is in equilibrium with dinitrogen tetraoxide (N_2O_4) at 60°C:

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

0.350 mol of N_2O_4 was placed in an empty 2.00 L vessel. When equilibrium was achieved, 0.120 mol of NO_2 was present. Calculate the value of the equilibrium constant at 60°C.

Calculations for reactions with small K_c values

If the equilibrium constant for a reaction is very low (less than about 10^{-4}), at equilibrium, the concentrations of products will be much less than the concentrations of the reactants. For reactions of this type, it is possible to calculate the concentration of the products by assuming that the equilibrium concentrations of the reactants are the same as their initial concentrations. Worked example 2.4.6 demonstrates this approach.

Although an ICE table can be used for these calculations, it is often unnecessary. Note that you must state any assumptions you make when doing calculations.

Worked example 2.4.6

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_c

The following equilibrium has a K_c of 1.6×10^{-6} at 200°C:

$$A(g) \rightleftharpoons B(g) + C(g)$$

0.48 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentrations of B and C at equilibrium.

Thinking	Working
State the expression for K_c.	$K_c = \frac{[B][C]}{[A]}$

Decide if any assumptions can be made in the calculation.	Initially, there is: • 0.48 mol of A(g) • 0.0 mol of the products B(g) and C(g). From the equation, the equilibrium concentration of C will be equal to the concentration of B, i.e. [C] = [B] Since K_c is very small, the amount of reactant A converted into products will be very small, and we assume the amount of A at equilibrium is 0.48 mol. While this assumption will introduce a small amount of error to our calculations, it is a valid assumption since the moles of A at equilibrium can be expressed as $n_A = 0.48 - x$ ≈ 0.48 when x is very small
Calculate the concentration of the reactant.	$[A] = \frac{n}{V}$ $= \frac{0.48}{2.0}$ $= 0.24\,\text{mol L}^{-1}$
Substitute into the expression for K_c.	$1.6 \times 10^{-6} = \frac{[B][C]}{0.24}$ Since [C] = [B] $= \frac{[B] \times [B]}{0.24}$
Calculate the unknown concentration, stating the assumption you made in the calculation.	$1.6 \times 10^{-6} = \frac{[B]^2}{0.24}$ So, $3.84 \times 10^{-7} = [B]^2$ Taking the square root of both sides (use your calculator): $[B] = 6.2 \times 10^{-4}$ So, $[B] = 6.2 \times 10^{-4}\,\text{mol L}^{-1}$ and $[C] = 6.2 \times 10^{-4}\,\text{mol L}^{-1}$ Since K_c is very small, the concentration of A at equilibrium was assumed to be the same as its initial concentration.

➤ Try yourself 2.4.6

CALCULATING AN EQUILIBRIUM CONCENTRATION FOR REACTIONS WITH LOW K_C

The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$X(g) \rightleftharpoons 2Y(g)$$

0.30 mol of X was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of Y at equilibrium.

HETEROGENEOUS EQUILIBRIA

The chemical reactions discussed so far in this module have involved **homogeneous reactions**, in which all reactants and products are in the same phase – for example, where all reactants and products exist in the gaseous state or as dissolved solutes in an aqueous solution. However, some equilibria involve **heterogeneous reactions**, in which reactants and products are in different phases.

The important feature of the equilibrium law expression for heterogeneous reactions is that the concentration of a pure solid or a pure liquid is assigned a 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 the 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:

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

the expression for the equilibrium constant is $K_c = [CO_2]$. CaO and $CaCO_3$ are both solids and do not appear in the equilibrium law expression.

The same is true for reactions involving pure liquids. For example, the decomposition of hydrogen peroxide (H_2O_2) in the gaseous state, producing liquid water, can be represented by the following chemical equation:

$$2H_2O_2(g) \rightleftharpoons 2H_2O(l) + O_2(g)$$

Based on the balanced chemical equation you might expect the K_c expression to be given by

$$K_c = \frac{[H_2O]^2\,[O_2]}{[H_2O_2]}$$

However, since this is a heterogeneous equilibrium where H_2O exists in the liquid state, you omit the H_2O term. The K_c expression is therefore

$$K_c = \frac{[O_2]}{[H_2O_2]^2}$$

For heterogeneous equilibria in solutions where the solvent is involved in the chemical reaction, its concentration can also be excluded from the equilibrium expression, provided the reactants and products are present at much lower concentrations than the solvent. In the case of *aqueous* solutions, the amount of water is extremely high compared to the amount of dissolved solute. As a result, even if water takes part in the reaction, we can exclude it from the equilibrium expression because, for all intents, its concentration will not change with time, and it can be considered a pure liquid.

As an example, the reaction between the carbonate ion (CO_3^{2-}) and water (H_2O) to produce the hydrogen carbonate ion (HCO_3^-) and the hydroxide ion (OH^-) can be written as follows:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

The equilibrium expression for this equilibrium process is given by

$$K_c = \frac{[HCO_3^-]\quad[OH^-]}{[CO_3^{2-}]}$$

Note how the pure liquid, H_2O, denoted with the (l) subscript, has been left out of the equilibrium expression. This approach to writing equilibrium expressions for reactions in aqueous solutions becomes very important in the next chapter where you consider equilibrium processes of weak acids and weak bases.

In summary:

- Pure liquids, pure solids and solvents are not included in the equilibrium expression.
- Only the molar concentrations of gases and molar concentrations of dissolved solutes are written into the equilibrium expression.

Worked example 2.4.7

WRITING K_c EXPRESSIONS FOR HETEROGENEOUS EQUILIBRIA

Write equilibrium expressions for the following chemical reactions.

a) $2CuS(s) + 3O_2(g) \rightleftharpoons 2CuO(s) + 2SO_2(g)$

b) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

c) $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$

Thinking	Working
Identify the coefficients of the products and the reactants in the equation. These will be the indices of the concentration terms in the equilibrium expression. Write the expression for K_c. $\frac{[\text{products}]^{\text{coefficients}}}{[\text{reactants}]^{\text{coefficients}}}$ Only gases and dissolved substances should be included in the equilibrium expressions. Leave out pure solids, pure liquids and solvents.	a) $K_c = \frac{[SO_2]^2}{[O_2]^3}$ b) $K_c = \frac{[C_2H_3O_2^-][H_3O^+]}{[HC_2H_3O_2]}$ c) $K_c = [Pb^{2+}][I^-]^2$ or $K_{sp} = [Pb^{2+}][I^-]^2$ N.B. when the equilibrium reaction involves the dissolution of a sparingly soluble salt like PbI_2, the equilibrium constant is given a special name (the solubility product) and symbol (K_{sp}). This is explained in detail in the following section.

➤ Try yourself 2.4.7

WRITING K_c EXPRESSIONS FOR HETEROGENEOUS EQUILIBRIA

Write equilibrium expressions for the following chemical reactions.

a) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

b) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

c) $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$

Quantifying solubility: the solubility constant, K_{sp}

In part C of Worked example 2.4.7, you were shown how to determine the K_c expression for the ionic solid, lead(II) iodide (PbI_2), in equilibrium with its ions in aqueous solution:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \qquad K_C = [Pb^{2+}]\,[I^-]^2$$

In Unit 2, you learnt that ionic compounds are generally classified as either 'soluble', 'insoluble' or 'slightly soluble' in water, with PbI_2 categorised as insoluble. While this classification suggests that 'insoluble' salts, such as PbI_2, do not dissolve in water at all, this is not entirely accurate.

Figure 2.4.3 shows the precipitation of 'insoluble' lead(II) iodide when aqueous solutions of sodium iodide and lead(II) nitrate are combined. The chemical equation for this reaction can be represented as:

$$2NaI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$$

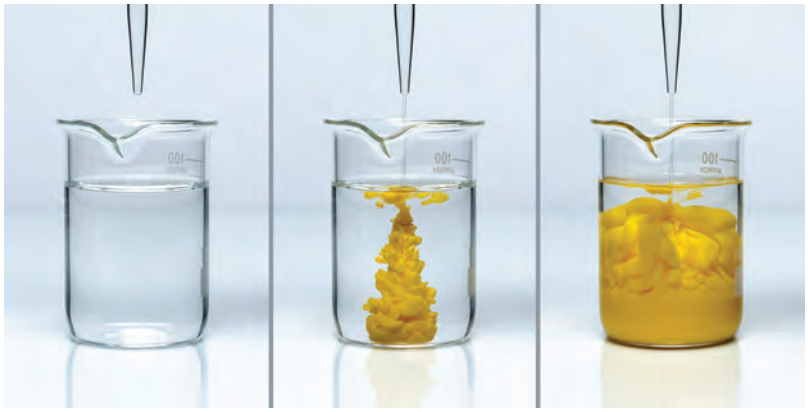


FIGURE 2.4.3 Precipitation of 'insoluble' lead(II) iodide (PbI_2) upon mixing aqueous solutions of sodium iodide (NaI) and lead(II) nitrate ($Pb(NO_3)_2$)

A close analysis of the solution after precipitation will reveal trace amounts of dissolved $Pb^{2+}(aq)$ cations and $I^{-}(aq)$ anions. This indicates that PbI_2, though considered insoluble, has limited solubility in water (approximately 0.056 g per 100 mL). We refer to salts that are only slightly soluble in water as **sparingly soluble salts**.

When sparingly soluble salts such as PbI_2 are added to water, they dissolve until the solution becomes saturated. At this point, a dynamic equilibrium is established between the undissolved solid and the ions in the solution. Barium sulfate ($BaSO_4$) is another example of a sparingly soluble salt, and establishes the following equilibrium when dissolved in water:

$$Ba(SO_4)(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$$

In this saturated solution at equilibrium, the rate of dissolution of $BaSO_4$ (forward reaction) equals the rate of precipitation (backward reaction), and the concentrations of $Ba^{2+}(aq)$ and $SO_4{}^{2-}(aq)$ ions remain constant. Because this equilibrium describes the dissolution of a solid, the equilibrium constant is given a special name, the **solubility-constant product** (or simply the **solubility product**) with the symbol K_{sp} – where 'sp' stands for 'solubility product'. The equilibrium expression for the $BaSO_4$ equilibrium shown above is therefore written as:

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

You should note that this equilibrium process is a heterogeneous equilibrium, so the solid $BaSO_4$ term is omitted from the K_{sp} expression. You should further note that the K_c expression for the dissolution of PbI_2 written above (and in Worked example 2.4.7 on page XX) should be correctly expressed as a K_{sp} expression, i.e.:

$$K_{sp} = [Pb^{2+}]\,[I^{-}]^2$$

You can write a K_{sp} expression for any solid salt in equilibrium with its dissolved ions. The generalised equilibrium equation for this process can be written as:

$$aA(s) \rightleftharpoons cC(aq) + dD(aq)$$

where A(s) represents the solid, C(aq) represents the dissolved cation, D(aq) represents the dissolved anion and the lower-case a, c, and d represent the stoichiometric coefficients of substances A, C and D, respectively. The K_{sp} expression for this generalised equation is written as:

$$K_{sp} = [C]^c\,[D]^d$$

Table 2.4.4 shows balanced chemical equations and K_{sp} expressions for the dissolution of some common sparingly soluble salts. Also included are the magnitudes of the K_{sp} values for these processes at 25°C.

TABLE 2.4.4 Equilibrium equations, K_{sp} expressions and K_{sp} values for some common salts

Salt	Equilibrium equation	K_{sp} expression	K_{sp} value (25°C)
AgCl (silver chloride)	$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$	$K_{sp} = [Ag^+][Cl^-]$	1.77×10^{-10}
$BaSO_4$ (barium sulfate)	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$	1.08×10^{-10}
$CaCO_3$ (calcium carbonate)	$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$	3.36×10^{-9}
CuS (copper(II) sulfide)	$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Cu^{2+}][S^{2-}]$	6.3×10^{-36}
FeS (iron(II) sulfide)	$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Fe^{2+}][S^{2-}]$	6.3×10^{-18}
PbI_2 (lead(II) iodide)	$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$	$K_{sp} = [Pb^{2+}][I^-]^2$	9.8×10^{-9}
ZnS (zinc sulfide)	$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$	$K_{sp} = [Zn^{2+}][S^{2-}]$	1.6×10^{-24}

Relationship between K_{sp} and solubility

The very small K_{sp} values (i.e. $K_{sp} << 1$) shown for all salts in Table 2.4.4 indicate that the position of equilibrium for each salt lies very much to the left, in favour of the solid salt rather than the dissolved ions. This is confirmation of the small extent of ionisation and the very low solubility of these salts. The sulfide salts, in particular, have extremely small K_{sp} values and are therefore considerably more 'insoluble' compared to the other salts listed. In this way, K_{sp} values can be used to qualitatively compare the relative solubility of sparingly soluble salts.

K_{sp} values are the mathematical product of the equilibrium concentrations of dissolved ions in water at 25°C, and they quantify the extent to which the solid dissolves. The K_{sp} value can therefore be used to quantify the solubility of sparingly soluble salts. An example of calculating the solubility of a sparingly soluble salt is shown in Worked example 2.4.8.

Worked example 2.4.8

CALUCLATING MOLAR SOLUBILITY FROM K_{SP} VALUES

Use the K_{sp} values in Table 2.4.4 to calculate the molar solubility of barium sulfate, $BaSO_4$, at 25°C.

Thinking	Working
Write the balanced chemical equation of the dissolution of $BaSO_4$. Write the K_{sp} expression and equate it to K_{sp} value from Table 2.4.4.	$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ $K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right] = 1.08 \times 10^{-10}$

<table>
<tr>
<td>Construct an ICE table with three rows in the table labelled ‘I’ (initial), ‘C’ (change) and ‘E’ (equilibrium):
<table><tr><th></th><th colspan="2">Reactants ⇌ Products</th></tr><tr><td>I</td><td></td><td></td></tr><tr><td>C</td><td></td><td></td></tr><tr><td>E</td><td></td><td></td></tr></table>In this case, we note the solid reactant is irrelevant (i.e. not applicable – N/A) since the solid term does not appear in the K_{sp} expression.
We therefore only need to consider the concentrations of the products.</td>
<td>The initial concentration of the products is zero.
Let $+x$ mol L^{-1} represent the change in concentration of Ba^{2+} as the dissolution process comes to equilibrium.
Since there is a 1:1 ratio between Ba^{2+} ions and SO_4^{2-} ions, the change in the concentration for SO_4^{2-} will also be $+x$ mol L^{-1}.
At equilibrium, the concentrations of Ba^{2+} and SO_4^{2-} are both x mol L^{-1}.
<table><tr><th></th><th>$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq)$ +</th><th>$SO_4^{2-}(aq)$</th></tr><tr><td>I</td><td>N/A</td><td>0.0 mol L^{-1}</td><td>0.0 mol L^{-1}</td></tr><tr><td>C</td><td>N/A</td><td>$+x$ mol L^{-1}</td><td>$+x$ mol L^{-1}</td></tr><tr><td>E</td><td>N/A</td><td>x mol L^{-1}</td><td>x mol L^{-1}</td></tr></table></td>
</tr>
<tr>
<td>Substitute the equilibrium concentration values into the K_{sp} expression and solve for x.</td>
<td>$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$
$x \times x = 1.08 \times 10^{-10}$
$x^2 = 1.08 \times 10^{-10}$
$x = \sqrt{1.08 \times 10^{-10}}$
$x = 1.04 \times 10^{-5}$
Therefore, $[Ba^{2+}] = 1.04 \times 10^{-5}$ mol L^{-1}</td>
</tr>
<tr>
<td>Determine the molar solubility.</td>
<td>Since Ba^{2+} and $BaSO_4$ are in a 1:1 ratio in the balanced chemical equation, the molar solubility of $BaSO_4$ is therefore 1.04×10^{-5} mol L^{-1}.</td>
</tr>
</table>

➤ Try yourself 2.4.8

CALCULATING MOLAR SOLUBILITY FROM K_{SP} VALUES

Use the K_{sp} values in Table 2.4.4 to calculate the molar solubility of zinc sulfide, ZnS, at 25°C.

Worked example 2.4.8 shows that the K_{sp} not only describes the equilibrium behaviour of sparingly soluble salts but also enables precise quantification of their solubility.

2.4 Review

SUMMARY

- The equilibrium constant, K_c, is a constant for a particular chemical reaction at a particular temperature.
- The equilibrium law expression for the equation:

$$aA + bB \rightleftharpoons cC + dC$$

$$\text{is } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- A reaction quotient (concentration fraction) can be calculated at any time during a chemical reaction. The reaction quotient, Q_c, has the same mathematical expression as the equilibrium law expression.
- When a reaction system at a particular temperature has reached equilibrium, the magnitude of the reaction quotient is equal to the magnitude of the equilibrium constant.
- The value of K_c provides a measure of the extent of reaction and the relative concentrations of reactants and products at equilibrium.

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

- When an equation is reversed, the new equilibrium constant is the reciprocal, or inverse, of the original K_c.
- When coefficients are doubled, K_c is squared.
- As temperature increases, the value of K_c increases for endothermic reactions and decreases for exothermic reactions.
- An equilibrium constant for a particular temperature can be calculated from the concentrations of the reactants and products at equilibrium and the expression for the equilibrium constant.
- At equilibrium, the concentration of a reactant or product can be calculated if the concentrations of the other reactants and products and the equilibrium constant are known.
- Stoichiometry may be used to calculate equilibrium concentrations of reactants and products, and hence the value of the equilibrium constant using a reaction (ICE) table.
- For heterogeneous equilibrium processes, pure liquids, pure solids and solvents are not included in the equilibrium expression – only the molar concentrations of gases and dissolved solutes are written into the equilibrium expression.
- The solubility product, K_{sp}, represents the equilibrium constant for the dissolution of a sparingly soluble ionic compound.
- The magnitude of K_{sp} can used qualitatively to compare the solubilities of sparingly soluble salts; it can also be used quantitatively to calculate the molar solubility of these salts.

KEY QUESTIONS

Describe

1 Define the following terms.
- **a** homogeneous system
- **b** reaction quotient
- **c** equilibrium constant

Apply

2 Determine an expression for the reaction quotient for the reaction of hydrogen and chlorine with the equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

3 Determine the expression for the equilibrium constant for the following chemical equations.
- **a** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- **b** $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$
- **c** $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$
- **d** $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$

4 A chemist investigated three different reactions and determined the value of the equilibrium constant for each. Select the reaction in which there would be substantially more products produced compared to reactants.
- **A** Reaction 1: $K_c = 0.0057$
- **B** Reaction 2: $K_c = 2.5 \times 10^9$
- **C** Reaction 3: $K_c = 3.1 \times 10^{-3}$

Analyse

5 At a particular temperature, the equilibrium constant for the reaction represented by the following equation is 0.667:

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

At a specific point in the reaction, the reaction quotient is found to be 0.234. Predict which way the reaction will shift in order to reach equilibrium with reference to the concentration of the products.

6 Consider the reaction represented by the equation:

$$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

At 25°C, the equilibrium constant is determined to be $K_c = 0.46$. At a particular time during the reaction, the reaction quotient is 1.2.

State an expression for the reaction quotient for this reaction and predict what will happen to the system as it moves to equilibrium.

7 The equilibrium constant for the decomposition of ammonia is 100 at 255°C for the equation:

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

a State an expression for the equilibrium constant for the equation:

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

b Calculate the equilibrium constant for the equation given in part **a**.

c State an expression for the equilibrium constant for the equation:

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

d Calculate the equilibrium constant for the equation qiven in part **c**.

e Use your answers to parts **a**–**d** to determine the effect on the value of an equilibrium constant when the:

i equation is reversed

ii coefficients of the equation are halved.

8 Water reacts with chlorine according to the equation:

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$$

At a particular temperature, the value of the equilibrium constant for this reaction is determined to be 4.0×10^{-4}. Determine the value for the equilibrium constant for the reaction if it is represented by the following equations, assuming no change in temperature.

a $H_2O(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + \frac{1}{2}O_2(g)$

b $2HCl(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

9 For the chemical reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant is 1.70 at 250°C.

For each equation, calculate the value of K_c at the same temperature.

a $4PCl_5(g) \rightleftharpoons 4PCl_3(g) + 4Cl_2(g)$

b $\frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons \frac{1}{2}PCl_5(g)$

c $\frac{1}{2}PCl_5(g) \rightleftharpoons \frac{1}{2}PCl_3(g) + \frac{1}{2}Cl_2(g)$

d $2PCl_3(g) + 2Cl_2(g) \rightleftharpoons 2PCl_5(g)$

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

a $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $\quad \Delta H = +91\,kJ\,mol^{-1}$

b $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$ $\quad \Delta H = -113\,kJ\,mol^{-1}$

c $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\quad \Delta H = +42\,kJ\,mol^{-1}$

d $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\quad \Delta H = -564\,kJ\,mol^{-1}$

11 Calculate the equilibrium constant for the reaction represented by the equation $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if an equilibrium mixture in a 2.0 L container was found to consist of 0.80 mol of N_2O_4 and 0.40 mol of NO_2.

12 Phosgene is a poisonous gas that was used during World War I. It can be formed by the reaction of carbon monoxide with chlorine gas in the equilibrium reaction:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The reaction was allowed to proceed at 74°C until equilibrium was reached. The equilibrium concentrations of each species were determined and recorded as follows: $[CO] = 2.4 \times 10^{-2}\,mol\,L^{-1}$, $[Cl_2] = 0.108\,mol\,L^{-1}$ and $[COCl_2] = 0.280\,mol\,L^{-1}$. Determine the equilibrium constant for the reaction at this temperature.

13 The following reaction was allowed to reach equilibrium at a temperature of 230°C:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The value of the equilibrium constant was determined to be 6.44×10^5.

If the equilibrium concentration of $[NO_2] = 15.50\,mol\,L^{-1}$ and $[NO] = 0.0542\,mol\,L^{-1}$, determine the concentration of O_2 in the equilibrium mixture.

14 4.45 mol of PCl_3 and 5.50 mol of Cl_2 were mixed in a 2.00 L vessel. They reacted according to the equation:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

When equilibrium was reached, it was found that 0.350 mol of PCl_5 had been formed. Calculate the value of the equilibrium constant.

15 5.89 mol of N_2 and 8.23 mol of H_2 were mixed in a 5.00 L vessel. They reacted according to the equation:

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

When equilibrium was reached, it was found that 0.480 mol of NH_3 had been formed. Calculate the value of the equilibrium constant.

Continued over page

2.4 Review *continued*

16 The equilibrium constant for the following reaction is 48.8 at 455°C:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

An equilibrium mixture in a 2.00 L vessel at this temperature contains 0.220 mol of H_2 and 0.110 mol of I_2.

a Calculate the concentration of HI in this mixture.

b Another mixture was prepared by placing 4.00 mol of HI in a 2.00 L vessel at 330°C. At equilibrium, 0.440 mol of H_2 and 0.440 mol of I_2 were present. Determine the value of the equilibrium constant at this temperature.

c A third mixture consisted of 1.00 mol of HI, 0.240 mol of H_2 and 0.320 mol of I_2 in a 2.00 L container at 330°C. Deduce if the mixture is at equilibrium and, if not, predict the direction the reaction will shift to reach equilibrium.

17 A mixture of 0.100 mol of NO, 0.051 mol of H_2 and 0.100 mol of H_2O was added to a reaction vessel with a volume of 1.00 L at 300°C. The reaction at equilibrium is given by the equation:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

After equilibrium was established, the concentration of NO was found to be 0.062. Determine the equilibrium constant, K_c, for the reaction at 300°C.

18 The following equilibrium has a K_c of 4.4×10^{-8} at 200°C:

$$A(g) \rightleftharpoons 2B(g)$$

0.50 mol of A was placed in an empty 2.0 L vessel at 200°C. Determine the concentration of B at equilibrium.

Chapter review

02

KEY TERMS

activation energy
catalyst
chemical energy
closed system
collision theory
concentration fraction
dynamic equilibrium
endothermic
energy profile diagram
enthalpy
equilibrium
equilibrium constant
equilibrium law
equilibrium yield
exothermic
extent of reaction
heat of reaction
heterogeneous reaction
homogeneous reaction
irreversible reaction
Le Châtelier's principle
open system
position of equilibrium
rate of reaction
reaction quotient
reaction table
reversible reaction
saturated solution
solubility-constant product
solubility product (K_{sp})
sparingly soluble salt
system
thermochemical equation

KEY QUESTIONS

Describe

1 Identify which one of the following statements about a closed system is correct.

A Energy cannot enter or leave a closed system.
B In a closed system, only products remain when the reaction is complete.
C A closed system must be completely sealed to stop reactants or products from escaping.
D In a closed system, the reactants and products cannot be exchanged with the surroundings.

2 Select which one of the following statements about a chemical equilibrium is correct.

A The reaction has stopped.
B The rate of reaction is negligible.
C The rates of the forward and reverse reactions are equal.
D At least one of the reactants has been completely consumed.

3 Hydrogen iodide formed an equilibrium with hydrogen and iodine in a sealed vessel of constant volume, according to the equation:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Additional iodine gas was added and the system was allowed to reach a new equilibrium at constant temperature. Compared to the initial equilibrium, at the new equilibrium the:

A concentration of HI would be unchanged.
B concentration of H_2 would be unchanged.
C concentration of HI would have increased.
D concentration of H_2 would have increased.

4 A closed vessel at constant temperature contains H_2 and CO_2 in equilibrium with H_2O and CO, as shown by the following equation:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \quad \Delta H = +42 \text{ kJ mol}^{-1}$$

Select which one of the following procedures will shift the equilibrium position to the right.

A addition of CO gas
B addition of a catalyst to the system
C decreasing the volume of the system
D increasing the temperature of the system

5 SO_2, O_2 and SO_3 were mixed and formed the equilibrium system:

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

Indicate which one of the following ratios is constant at a fixed temperature, irrespective of the initial amounts of gases.

A $\dfrac{[SO_3]}{[SO_2][O_2]}$
B $\dfrac{[SO_3]}{[SO_2]+[O_2]}$
C $\dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$
D $\dfrac{[SO_2]+[O_2]}{[SO_3]}$

6 Deduce which one of the equations below has the following expression for the equilibrium constant.

$$K_c = \frac{[H_2]^2[CO]}{[CH_3OH]}$$

A $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$
B $4H_2(g) + 2CO(g) \rightleftharpoons 2CH_3OH(g)$
C $2CH_3OH(g) \rightleftharpoons 4H_2(g) + 2CO(g)$
D $CH_3OH(g) \rightleftharpoons 2H_2(g) + CO(g)$

7 Select the correct answers from the list to complete the following paragraph about equilibrium.
concentration, 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 _____. There will be no observable change in the _____ of the reactants or products.

Apply

8 Determine whether the following systems are open or closed and explain your reasoning.
- **a** a lit candle
- **b** a refrigerator with a door that is shut
- **c** a human being
- **d** a weather balloon

9 Suppose CO gas and Cl_2 gas are added to a sealed container at constant temperature. A reaction occurs according to the following equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

Explain how equilibrium is established by sorting the following statements into the correct order.
- **i** Equilibrium has been reached and the concentrations of CO, Cl_2 and $COCl_2$ will now remain constant.
- **ii** When the rates of the forward and reverse reactions become equal, $COCl_2$ is formed at the same rate as it is breaking down.
- **iii** The forward reaction will occur and, as the concentrations of CO and Cl_2 decrease, the rate of the production of $COCl_2$ decreases.
- **iv** As $COCl_2$ is formed, some $COCl_2$ molecules decompose to re-form CO and Cl_2.

10 Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium of increasing the concentration of hydrogen by adding more hydrogen gas to the equilibrium system:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

11 The total pressure of the following equilibrium system was increased by reducing the volume at constant temperature:

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

Use the concepts of rates of reaction and collision theory to explain the effect on the position of equilibrium.

12 Explain the difference between the terms 'reaction quotient' (Q_c) and 'equilibrium constant' (K_c).

13 State the expression for the equilibrium constant for the following chemical equations.
- **a** $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
- **b** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- **c** $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$
- **d** $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

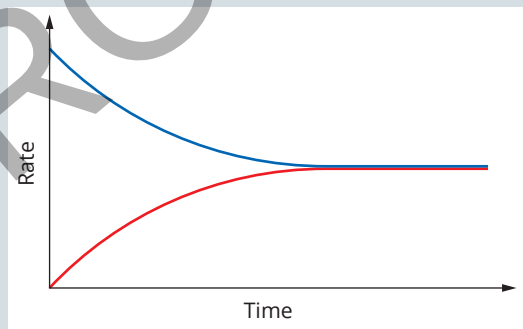
Analyse

14 Determine whether the following processes occur in open or closed systems.
- **a** a saturated solution of salt in a glass: $NaCl(s) \rightleftharpoons NaCl(aq)$
- **b** solid $(NH_4)_2SO_4$ reacting with NaOH solution in a beaker: $(NH_4)_2SO_4(s) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2NH_3(g) + 2H_2O(l)$
- **c** a beaker containing a solution of CH_3COOH that dissociates: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
- **d** burning toast

15 SO_2 and O_2 react to form an equilibrium with SO_3, according to the equation:

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

Analyse, using collision theory, the shape of the rate–time graph below that was obtained when SO_2 and O_2 were mixed in a container at constant temperature.



16 Elderly people, especially women, can become very susceptible to bone breakages. It is thought that as people age, they absorb 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:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Deduce why inefficient absorption of Ca^{2+} ions could cause weakness in bones using your understanding of equilibrium.

17 Determine in which of following reactions the position of the equilibrium is not affected by a change of volume at constant temperature, and justify your answer using collision theory.
- **A** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- **B** $Cl_2(g) + H_2(g) \rightleftharpoons 2HCl(g)$
- **C** $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
- **D** $2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(g)$

18 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.
- **a** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H = -91\ kJ\ mol^{-1}$

b $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
$\Delta H = +208\,kJ\,mol^{-1}$

19 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.

a $C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$
b $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
c $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

20 Deduce the balanced equations for the reactions with the following equilibrium equations.

a $K_c = \dfrac{[H_2]^2[CO]}{[CH_3OH]}$

b $K_c = \dfrac{[H_2S]^2}{[S_2][H_2]^2}$

c $K_c = \dfrac{[N_2O_4]^{\frac{1}{2}}}{[NO_2]}$

21 The value of K_c for the following reaction is equal to 4 at 25°C:

$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

At time t, the reaction quotient, Q_c, for a mixture of ethanol, water, ethyl ethanoate ($CH_3COOC_2H_5$) and ethanoic acid is equal to 6. Assuming that the mixture is also at 25°C, and referring to the values of K_c and Q_c, predict what will happen to the concentration of ethyl ethanoate as the system reaches equilibrium.

22 Apply your knowledge about the equilibrium constant K_c to complete the following statements.

a If $K_c = 0.0001$ for a particular reaction, at equilibrium the concentrations of products will be _____ the concentrations of reactants.
b For the reaction with the equation:
$2H_2(g) + 2NO(g) \rightleftharpoons 2H_2O(g) + N_2(g)$
the expression for the equilibrium constant, K_c, is _____.
c When the reaction quotient is smaller than K_c, the reaction _____ to establish equilibrium.

23 The equilibrium constant for the following reaction at 25°C is 10^{-10}:

$2Fe^{2+}(aq) + Sn^{4+}(aq) \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$

a Identify if a significant reaction would occur when solutions of tin(IV) chloride and iron(II) chloride are mixed.
b Determine the value of the equilibrium constant for the reaction:
$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$
c Explain whether a significant reaction would occur when solutions of tin(II) chloride and iron(III) chloride are mixed.

24 Consider the following equilibrium at 227°C:

$2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

a State the expression for K_c for the equilibrium system.
b Given that the value of K_c at 227°C for the expression in part **a** is 32, deduce the equilibrium constant for each of the following.

i $BrCl(g) \rightleftharpoons \frac{1}{2}Br_2(g) + \frac{1}{2}Cl_2(g)$
ii $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$
iii $4BrCl(g) \rightleftharpoons 2Br_2(g) + 2Cl_2(g)$
iv $\frac{1}{2}Cl_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons BrCl(g)$

25 The reaction used to manufacture ammonia is represented by the equation:

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

The equilibrium constant for the reaction is 0.052 at 400°C.
A gas mixture contains 1.00 mol of N_2 gas, 1.00 mol of H_2 gas and 0.250 mol of NH_3 gas in a 1.00 L vessel at 400°C. Determine if the mixture is at equilibrium and, if not, predict the direction it will shift to reach equilibrium.

26 An equilibrium mixture contains 0.020 mol of H_2O gas, 0.030 mol of H_2 gas, 0.040 mol of CO gas and 0.050 mol of CO_2 gas in a 2.00 L vessel. The gases react according to the equation:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$

Calculate the equilibrium constant at 900°C.

27 At a specified temperature, the reaction between solutions of Sn^{2+} and Fe^{3+} reaches equilibrium according to the equation:

$2Fe^{3+}(aq) + Sn^{2+}(aq) \rightleftharpoons 2Fe^{2+}(aq) + Sn^{4+}(aq)$

a Determine the expression for K_c.
b If the equilibrium concentrations are 0.30 mol L^{-1} Fe^{3+}, 0.40 mol L^{-1} Fe^{2+}, 0.20 mol L^{-1} Sn^{4+} and 0.10 mol L^{-1} Sn^{2+} at a particular temperature, calculate the equilibrium constant at that temperature.

28 Propan-2-one (C_3H_6O) is used to remove nail polish. It can be prepared from propan-2-ol (C_3H_8O) using a copper–zinc catalyst, according to the equation:

$C_3H_8O(g) \rightleftharpoons C_3H_6O(g) + H_2(g)$

If an equilibrium mixture of these gases consists of 0.018 mol of propan-2-ol, 0.082 mol of propan-2-one and 0.082 mol of hydrogen in a 20.0 L vessel, calculate the value of the equilibrium constant.

29 Consider the equilibrium:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

A 3.00 L vessel contained 6.00 mol of PCl_3, 4.50 mol of PCl_5 and 0.900 mol of Cl_2 at equilibrium at 250°C.

a State an expression for the equilibrium constant for this reaction.
b Calculate the equilibrium constant for the reaction at 250°C.
c Another equilibrium mixture contains 0.002 mol L^{-1} of PCl_5 and 0.001 mol L^{-1} of PCl_3 at 250°C. Determine the concentration of Cl_2 in this mixture.
d Calculate the equilibrium constant at 250°C for the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

30 Consider the reaction:

$$A + 3B \rightleftharpoons 2C + D$$

Analysis of an equilibrium mixture in a 2.00 L container shows that 2.00 mol of A, 0.500 mol of B and 3.00 mol of D are present. If the equilibrium constant of the reaction is 0.024, calculate the:
a concentration of A, B and D at equilibrium
b concentration of C in the equilibrium mixture
c number of moles of C in the equilibrium mixture.

31 Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at 1000°C.
a Predict what will happen to the equilibrium position as a result of:
i a decrease in temperature
ii the addition of a catalyst
iii the addition of more oxygen.
b Predict 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, what conclusion can you make about the magnitude of the equilibrium constant for the reaction?

32 a The equilibrium constant is 0.670 at a particular temperature for the reaction:

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

A mixture of 0.100 mol L^{-1} of CO, 0.200 mol L^{-1} of H_2, 0.300 mol L^{-1} of CH_4 and 0.400 mol L^{-1} of H_2O is heated to this temperature. Predict whether the concentration of the following would increase, decrease or not change.
i CO
ii H_2
iii CH_4
iv H_2O
b When the temperature of the reaction mixture is increased by 10°C, the equilibrium constant for the reaction becomes 0.71. Determine what the enthalpy change of this reaction will be.

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

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = -114\,kJ\,mol^{-1}$$

Nitrogen dioxide is a brown gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1.0 L container at 350°C. Copy the following table, and for each of the changes listed, predict if the reaction mixture would become darker or lighter. Give a reason for your choice.

	Colour change (lighter or darker)	**Explanation**
a The temperature is increased to 450°C at constant volume.		
b The volume of the container is increased at constant temperature.		
c A catalyst is added at constant volume and temperature.		
d More oxygen is added at constant volume and temperature.		

34 Ethene gas is produced from ethane gas in an endothermic reaction represented by the equation:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \quad \Delta H = +138\,kJ\,mol^{-1}$$

a Predict whether the following changes will result in the equilibrium percentage yield of ethene increasing, decreasing or not changing.
i The volume is reduced at constant temperature.
ii More hydrogen gas is added at constant temperature and volume.
iii The temperature is increased at constant volume.
iv A catalyst is added.
v Argon gas is added at constant temperature and volume.
b Assess how each of the changes in part **a** will affect the rate at which the reaction achieves equilibrium.

35 The reaction used to manufacture ammonia is represented by:

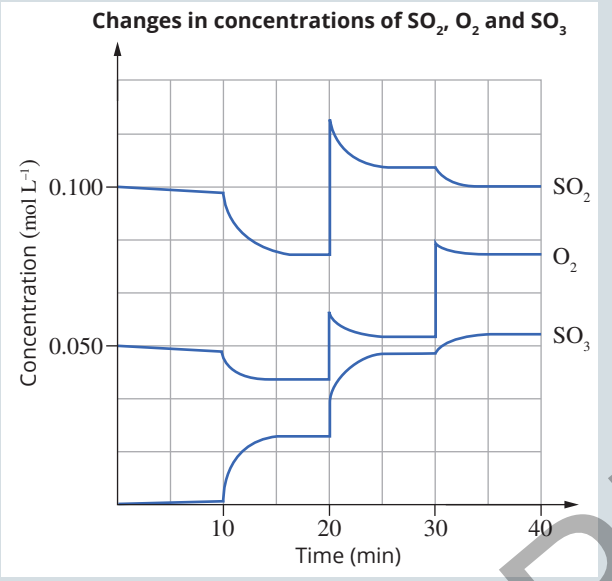
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant for the reaction is 0.052 at 400°C.
Each of the following gas mixtures is contained in a 1.00 L vessel at 400°C. Determine if each mixture is in equilibrium. If not, predict the direction the reaction will shift in order to reach equilibrium.
a 0.200 mol of N_2, 0.200 mol of H_2, 0.200 mol of NH_3
b 0.050 mol of N_2 and 0.500 mol of H_2

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

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

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



a State an expression for the equilibrium constant, K_c, of the reaction.

b Determine at what time intervals the reaction was at equilibrium.

c Calculate the value of K_c at 18 minutes.

d Determine at what time was the catalyst added. Explain your reasoning.

e Calculate the value of K_c at 25 minutes.

f Deduce what changes were made to the system at 20 minutes.

Interpret

37 Methanol is manufactured for use as a fuel for racing cars. It can be made by the following reaction between carbon monoxide and hydrogen:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -103\,kJ\,mol^{-1}$$

a Predict what conditions of temperature and pressure would be required for a:

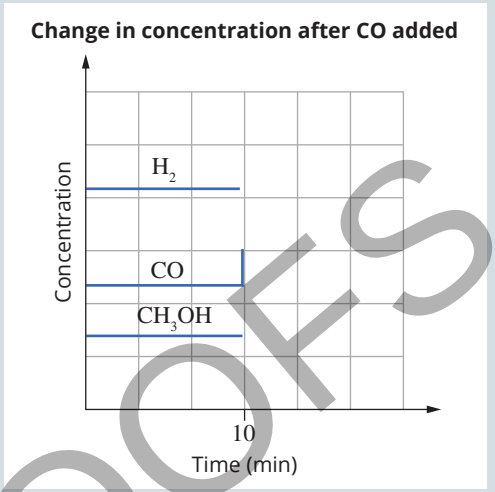
i fast reaction rate

ii high equilibrium yield of methanol.

b State whether a compromise will be needed in the choice of temperature or pressure.

c Propose another method that could be employed at a manufacturing plant to increase the rate of methanol production.

d As part of an investigation of this process, the concentration of a mixture of CO, H_2 and CH_3OH was monitored continuously. The mixture was initially at equilibrium at 400°C and constant volume. After 10 minutes, additional CO was added to the mixture, as shown in the following figure.



i Draw a graph to indicate how concentrations would change as a consequence of the addition of CO.

ii Following the addition of the CO, the mixture again reaches equilibrium. Draw a second graph to show the effect on the concentrations if the temperature was then increased to 450°C.

38 During the process for sulfuric acid manufacture, sulfur dioxide is converted to sulfur trioxide at temperatures of 400–500°C:

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

a Predict the effect of increasing the pressure on:

i reaction rate

ii equilibrium yield.

b In practice, this step is usually performed at atmospheric pressure. Propose a reason why.

c During the process, sulfur trioxide is removed from the reaction mixture by converting it to sulfuric acid. The remaining gases are then recycled to the reaction vessel. Explain the reason for recycling the gases.

d Assess what factors would have influenced the choice of the reaction temperature.

39 Carbon disulfide gas (CS_2) is used in the manufacture of rayon. $CS_2(g)$ can be made in an endothermic gas-phase reaction between sulfur trioxide gas (SO_3) and carbon dioxide. Oxygen gas is also produced in the reaction.

a Construct a balanced chemical equation for the reaction.

b State an expression for the equilibrium constant of the reaction.

c An equilibrium mixture of these gases was made by mixing sulfur trioxide and carbon dioxide. The equilibrium mixture consisted of 0.028 mol of CS_2, 0.022 mol of SO_3, 0.014 mol of CO_2 and an unknown amount of O_2 in a 20.0 L vessel. Determine the:
- **i** number of moles of O_2 present in the equilibrium mixture
- **ii** value of the equilibrium constant at that temperature.

d Predict how each of the following changes to an equilibrium mixture would affect the yield of CS_2.
- **i** removing O_2 (at constant total volume)
- **ii** increasing the temperature
- **iii** adding a catalyst
- **iv** increasing the pressure by decreasing the volume of the reaction vessel (at constant temperature)
- **v** increasing the pressure by introducing argon gas into the reaction vessel (at constant volume).

Data analysis

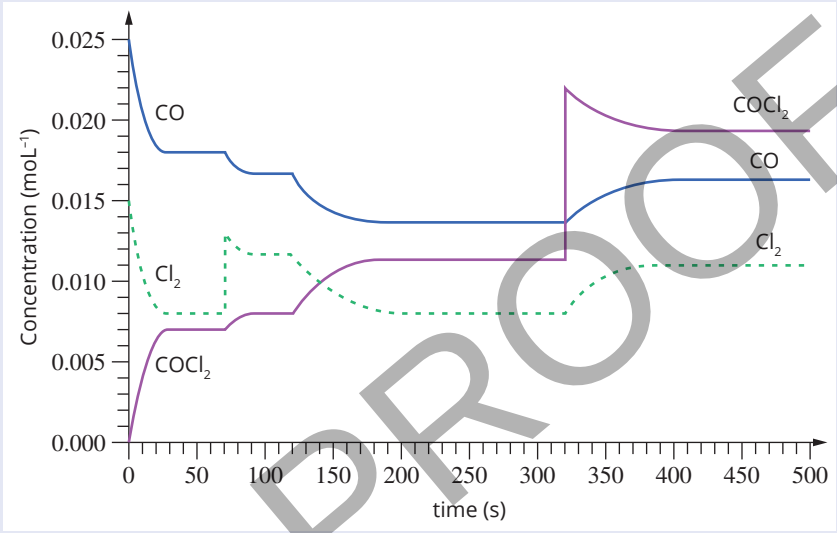
DATA SET 1

The information below applies to Questions 1–5.

The reaction between chlorine gas and carbon monoxide gas to produce phosgene is an exothermic reaction and is shown in the following equation:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

When chlorine gas and carbon monoxide gas are mixed in a closed 1.00 L container, the concentration of each species is measured during experimentation. The graph below shows this data over time.



Question 1 (1 mark)

Identify the number of times that the system establishes equilibrium between 0 and 500 seconds.

Question 2 (2 marks)

The volume of the container is increased at 450 seconds. Explain the changes occurring to concentrations as a new equilibrium is established.

Question 3 (3 marks)

Predict the change that was applied to the system at 120 seconds and describe its effect on the equilibrium constant (K_c). Show your reasoning.

Question 4 (2 marks)

Calculate K_c for the above reaction when equilibrium is first established. Show your working.