07

Equilibrium

Essential ideas

7.1 Many reactions are reversible. These reactions will reach a state of equilibrium when the rates of the forward reaction and reverse reaction are equal. The position of equilibrium can be controlled by changing the conditions.

17.1 The position of equilibrium can be quantified by the equilibrium law. The equilibrium constant for a particular reaction only depends on the temperature.

Imagine that you are part way along an escalator (a moving staircase) that is moving up and you decide to run down. If you can run down at exactly the same speed as the escalator is moving up, you will have no *net* movement. So, if someone were to take a picture of you at regular time intervals, it would seem as if you were not moving at all. Of course, in reality both you and the escalator *are* moving, but because there is no net change neither movement is observable. In chemical reactions a similar phenomenon occurs when a reaction takes place at the same rate as its reverse reaction, so no net change is observed. This is known as the **equilibrium state**.

In this chapter, we explore some of the features of the equilibrium state and learn how to derive and use the equilibrium constant expression. Application of the **equilibrium law** enables us to quantify reaction components and to predict how far reactions will proceed under different conditions. Industrial processes rely significantly on this type of study to determine the conditions that will maximize the yield of product. Equilibrium studies are also important in many biochemical and environmental processes, such as predicting the solubility of gases in the blood and knowing how certain chemicals in the atmosphere may react together to form pollutants that contribute to climate change. By the end of this chapter, you will be ready to tackle some of these applications in subsequent chapters.

Electron micrograph of a section through human lung tissue, showing air spaces called alveoli. Equilibrium considerations help us to understand how oxygen and carbon dioxide are exchanged between the blood and the air in these spaces.

▲
Snow and ice-covered peak in the Cordillera Huayhuash, Peru. Equilibrium considerations help explain the relationship between water vapour in the clouds and precipitations in the form of liquid (rain) and solid (snow) at different temperatures and pressures.

7.1 Equilibrium

Understandings:
- A state of equilibrium is reached in a closed system when the rates of the forward and reverse reactions are equal.

  Guidance
  Physical and chemical systems should be covered.
- The equilibrium law describes how the equilibrium constant (K_c) can be determined for a particular chemical equation.
- The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.
- The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. Q is the equilibrium expression with non-equilibrium concentrations. The position of the equilibrium changes with changes in concentration, pressure, and temperature.
- A catalyst has no effect on the position of equilibrium or the equilibrium constant.

Applications and skills:

- The characteristics of chemical and physical systems in a state of equilibrium.
- Deduction of the equilibrium constant expression (K_c) from an equation for a homogeneous reaction.
- Determination of the relationship between different equilibrium constants (K_c) for the same reaction at the same temperature.

  Guidance
  Relationship between K_c values for reactions that are multiples or inverses of one another should be covered.

- Application of Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure, and concentration on the position of equilibrium and on the value of the equilibrium constant.
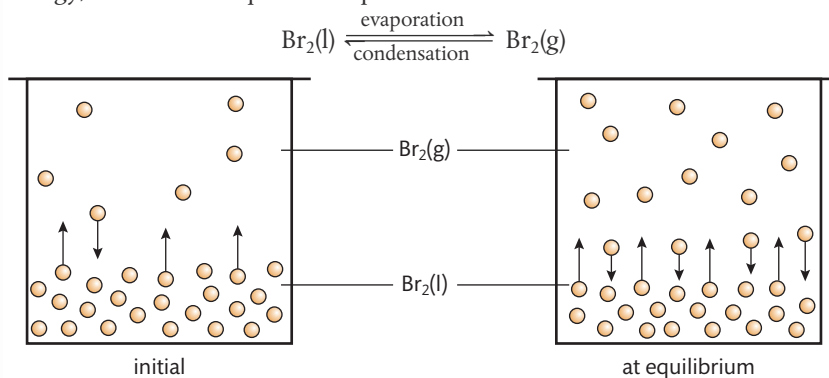
  Guidance
  Specific details of any industrial process are not required.
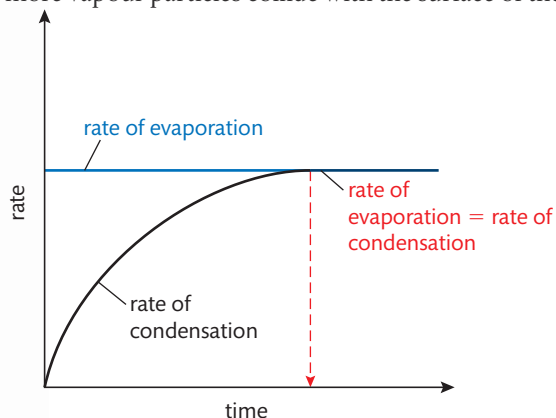
Physical systems

Consider what happens when some bromine, Br_2, is placed in a sealed container at room temperature.

As bromine is a **volatile** liquid, with a boiling point close to room temperature, a significant number of particles (molecules of Br_2) will have enough energy to escape from the liquid state and form vapour in the process known as **evaporation**. As the container is sealed, the bromine vapour cannot escape and so its concentration will increase. Some of these vapour molecules will collide with the surface of the liquid, lose energy, and become liquid in the process known as **condensation**.

$$Br_2(l) \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} Br_2(g)$$

Figure 7.1 Establishing dynamic equilibrium in the evaporation of bromine. Equilibrium is established when the rate of evaporation equals the rate of condensation.

The rate of condensation increases with the increase in concentration of vapour, as more vapour particles collide with the surface of the liquid. Eventually, the rate of condensation is *equal* to the rate of evaporation, and at this point there will be no net change in the amounts of liquid and gas present (Figure 7.2). We say that the system has reached **equilibrium**. This will only occur in a closed system, where the $Br_2(g)$ cannot escape as vapour but may condense back into the liquid.

Figure 7.2 The rates of evaporation and condensation as liquid–vapour equilibrium is established in a closed system. The rate of evaporation is constant, while the rate of condensation increases with increasing concentration of vapour. Equilibrium is established when the two rates are equal.

Chemical systems

Consider the reaction of dissociation between hydrogen iodide (HI) and its elements hydrogen (H_2) and iodine (I_2). Hydrogen and hydrogen iodide are both colourless, whereas iodine is released as a purple gas, so this helps us to see what is happening.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
colourless gas   colourless gas   purple gas
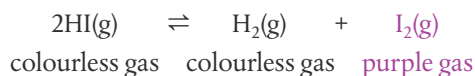
If we carry out this reaction starting with hydrogen iodide in a sealed container, there will at first be an increase in the purple colour owing to the production of iodine gas. But after a while this increase in colour will stop, and it may appear that the reaction too has stopped. In fact, what has happened is that the rate of the dissociation of HI is fastest at the start when the concentration of HI is greatest and falls as the reaction proceeds. Meanwhile, the reverse reaction, which initially has a zero rate because there is no H_2 and I_2 present, starts slowly and increases in rate as the concentrations of H_2 and I_2 increase. Eventually, the rate of dissociation of HI has become equal to the rate of the reverse reaction of association between H_2 and I_2, so the concentrations remain constant. This is why the colour in the flask remains the same. At this point, equilibrium has been reached. It is described as **dynamic** because both forward and backward reactions are still occurring.

If we were to analyse the contents of the flask at this point, we would find that HI, H_2, and I_2 would all be present and that if there were no change in conditions, their concentrations would remain constant over time. We refer to this as the **equilibrium mixture**.

If we reversed the experiment and started with H_2 and I_2 instead of HI, we would find that eventually an equilibrium mixture would again be achieved in which the concentrations of H_2, I_2, and HI would remain constant. These relationships are shown in Figure 7.3.
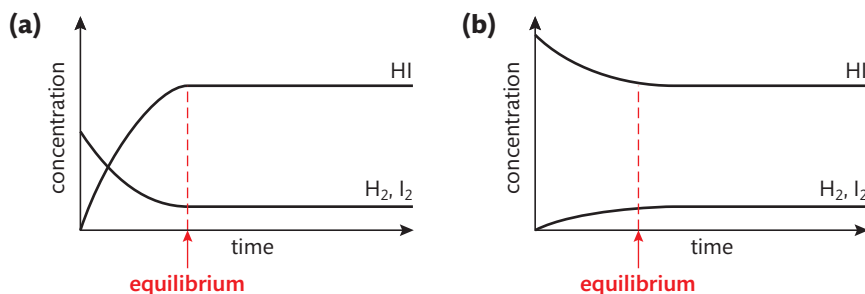
The equilibrium state has specific characteristics

In studies of equilibria we are dealing with reversible reactions – those that occur in both directions. The convention is to describe the reaction from left to right (reactants to products) as the **forward reaction**, and the reaction from right to left (products to reactants) as the **backward** or **reverse reaction**. The symbol $\rightleftharpoons$ is used to show that the reaction is an equilibrium reaction.

The examples of physical and chemical systems discussed have shown that:

> ❝ At equilibrium the rate of the forward reaction is equal to the rate of the backward reaction. ❞

Iodine gas in a stoppered flask. Iodine is a crystalline solid at room temperature, but sublimes on heating to form a purple gas.

TOK The study of chemical change often involves both the macroscopic and microscopic scales. Which ways of knowing do we use in moving from the macroscopic to the microscopic?

Figure 7.3 Equilibrium is reached when the concentrations of reactants and products become constant. Note the same equilibrium mixture is reached starting from (a) a mixture of H_2 and I_2 or (b) from pure HI.

forward
reaction
reactants $\rightleftharpoons$ products
backward
reaction

These reactions have also shown some of the main features of the equilibrium state, and these can now be summarized as they apply to *all* reactions at equilibrium.

	Feature of equilibrium state	Explanation
1	Equilibrium is dynamic	The reaction has not stopped but both forward and backward reactions are still occurring at the same rate.
2	Equilibrium is achieved in a closed system	A closed system has no exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
3	The concentrations of reactants and products remain constant at equilibrium	They are being produced and destroyed at an equal rate.
4	At equilibrium there is no change in macroscopic properties	Macroscopic properties are observable properties such as colour and density. These do not change as they depend on the concentrations of the components of the mixture.
5	Equilibrium can be reached from either direction	The same equilibrium mixture will result under the same conditions, no matter whether the reaction is started with all reactants, all products, or a mixture of both.

It is important to understand that even though the concentrations of reactant and product are *constant* at equilibrium, this in no way implies that they are *equal*. In fact, most commonly there will be a much higher concentration of either reactant or product in the equilibrium mixture, depending both on the reaction and on the conditions. We can see, for example, in Figure 7.3 that when the dissociation of HI reaches equilibrium, there is a higher concentration of HI than of H_2 and I_2.

Thinking back to the analogy in the introduction to this chapter, of you running in the opposite direction on a moving staircase where the top and bottom represent reactants and products respectively, it would be possible for you to be 'at equilibrium' near the top of the staircase, near the bottom, or anywhere in between. As long as you were moving at the same speed as the staircase you would still have no net change in position.

The proportion of reactant and product in the equilibrium mixture is referred to as its **equilibrium position**. Reactions where the mixture contains predominantly products are said to 'lie to the right' and reactions with predominantly reactants are said to 'lie to the left'. It is, however, often useful to be able to capture this information mathematically to compare the equilibrium mixtures of different reactions and the effect of different conditions. In the next section we will look at how this is done.

NATURE OF SCIENCE

At equilibrium no change is observed on the macroscopic level, although particles are reacting at the microscopic level. These changes can be deduced using techniques such as isotopic labelling, which allow the progress of a specific reactant to be followed. Our power of understanding is enhanced by contributions from instrumentation and sensors that may gather information beyond human sense perception.

1 Which statements are correct for a reaction at equilibrium?

I   The forward and reverse reactions both continue.
II The rates of the forward and reverse reactions are equal.
III The concentrations of reactants and products are equal.

A I and II only   **B** I and III only   **C** II and III only   **D** I, II, and III

2 Which statement is always true for a chemical reaction that has reached equilibrium at constant temperature?

A The yield of product(s) is greater than 50%.
B The rate of the reverse reaction is lower than that of the forward reaction.
C The amounts of reactants and products do not change.
D Both forward and reverse reactions have stopped.

3 Which statement is *not* true for a mixture of ice and water at equilibrium at constant temperature?

A The rates of melting and freezing are equal.
B The amounts of ice and water are equal.
C The same position of equilibrium can be reached by cooling water and by heating ice.
D There is no observable change in the system.

Sometimes you may see the equilibrium sign written with unequal arrows such as ⇌. This is used to represent the reaction that lies in favour of products. Likewise, ⇌ is used to represent a reaction that lies in favour of reactants.

CHALLENGE YOURSELF

1 A closed system is defined differently in different disciplines. In thermodynamics it means that no matter can be exchanged with the surroundings, but energy can flow. To what extent can the Earth can be considered a closed system?

The equilibrium constant K_c can be predicted from a reaction's stoichiometry

Consider now the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
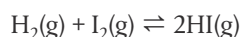
If we were to carry out a series of experiments on this reaction with different starting concentrations of H_2, I_2, and HI, we could wait until each reaction reached equilibrium and then measure the composition of each equilibrium mixture. Here are some typical results obtained at 440 °C.

Experiment I

	Initial concentration / mol dm⁻³	Equilibrium concentration / mol dm⁻³
H_2	0.100	0.0222
I_2	0.100	0.0222
HI	0.000	0.156

Experiment II

	Initial concentration / mol dm⁻³	Equilibrium concentration / mol dm⁻³
H_2	0.000	0.0350
I_2	0.0100	0.0450
HI	0.350	0.280

Experiment III

	Initial concentration / mol dm⁻³	Equilibrium concentration / mol dm⁻³
H_2	0.0150	0.0150
I_2	0.000	0.0135
HI	0.127	0.100

At a glance these data may not appear to show any pattern. However, there is a predictable relationship among the different compositions of these equilibrium mixtures, and the key to discovering it is in the stoichiometry of the reaction equation.

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

If we take the *equilibrium* concentrations and process them in the following way:

$$\frac{[HI]_{eqm}^2}{[H_2]_{eqm}^1 [I_2]_{eqm}^1}$$

2 = coefficient of HI in the reaction equation

1 = coefficient of H_2 in the reaction equation

1 = coefficient of I_2 in the reaction equation
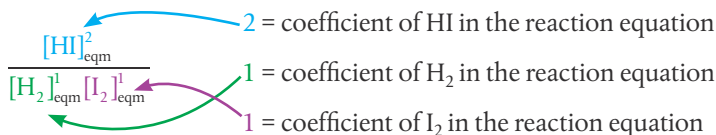
we find the following results:

Experiment I	Experiment II	Experiment III
$\dfrac{(0.156)^2}{0.0222 \times 0.0222} = 49.4$	$\dfrac{(0.280)^2}{0.035 \times 0.0450} = 49.8$	$\dfrac{(0.100)^2}{0.0150 \times 0.0135} = 49.4$

Clearly this way of processing the equilibrium data produces a constant value within the limits of experimental accuracy. This constant is known as the **equilibrium constant**, **K_c**. It has a fixed value for this reaction *at a specified temperature*.

In fact, every reaction has its own particular value of K_c which can be derived in a similar way. First we use the balanced reaction equation to write the **equilibrium constant expression**.

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$
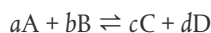
the equilibrium constant expression is

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

The value for K_c can then be determined by substituting the equilibrium concentrations of all reactants and products into this equation.

Note:

- The equilibrium constant expression has the concentrations of products in the numerator and the concentrations of reactants in the denominator.
- Each concentration is raised to the power of its coefficient in the balanced equation. (Where it is equal to one it does not have to be given.)
- Where there is more than one reactant or product the terms are multiplied together.

Worked example

Write the equilibrium expression for the following reactions.

(i) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

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

Solution

(i) $K_c = \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$

(ii) $K_c = \dfrac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

Exercises

4 Write the equilibrium constant expression for the following reactions:

   (a) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
   (b) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$
   (c) $CH_3Cl(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$

5 Write the equations for the reactions represented by the following equilibrium constant expressions

   (a) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$

   (b) $K_c = \dfrac{[CO][H_2]^3}{[CH_4][H_2O]}$

6 Write the equilibrium constant expressions for the following chemical reactions:

   (a) fluorine gas and chlorine gas combine to form $ClF_3(g)$
   (b) NO dissociates into its elements
   (c) methane, CH_4, and steam react to form carbon monoxide and hydrogen

> The equilibrium constant expressions described here apply to homogeneous reactions, that is reactions where reactants and products are in the same phase, as gases, liquids, or in solution. It is good practice always to include state symbols in your equations to ensure this is being applied correctly.

The magnitude of K_C gives information on the extent of reaction

Different reactions have different values of K_c. What does this value tell us about a particular reaction?
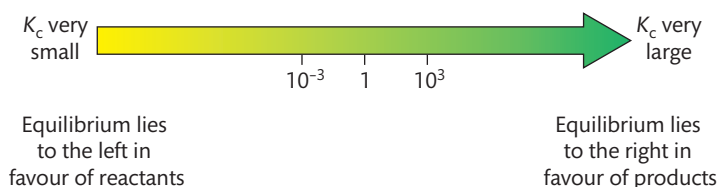
As the equilibrium constant expression puts products on the numerator and reactants on the denominator, a high value of K_c will mean that at equilibrium there are proportionally more products than reactants. In other words, such an equilibrium mixture lies to the right and the reaction goes almost to completion. By contrast, a low value of K_c must mean that there are proportionally less products with respect to reactants, so the equilibrium mixture lies to the left and the reaction has barely taken place.

Consider the following three reactions and their K_c values measured at 550 K.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\qquad K_c = 2$
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $\qquad K_c = 10^{10}$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ $\qquad K_c = 10^{18}$
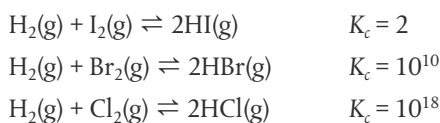
The large range in their K_c values tells us about the differing extents of these reactions. We can deduce that the reaction between H_2 and Cl_2 has taken place the most fully at this temperature, while H_2 and I_2 have reacted the least.

A good rule of thumb to apply to these situations is that if $K_c \gg 1$, the reaction is considered to go almost to completion (very high conversion of reactants into products), and if $K_c \ll 1$, the reaction hardly proceeds.

CHALLENGE YOURSELF

2 Why do you think the reactions of the three halogens Cl_2, Br_2, and I_2, with H_2 have such different values for their equilibrium constant at the same temperature? What can you conclude about the strength of bonding in the three hydrogen halides?

K_c very small — 10^{-3} — 1 — 10^3 — K_c very large

Equilibrium lies to the left in favour of reactants

Equilibrium lies to the right in favour of products

Figure 7.4 The larger the value of K_c, the further the equilibrium mixture lies to the right.

Note that the magnitude of K_c does not give us any information on the *rate* of the reaction. It informs us of the nature of the equilibrium mixture, but not on how quickly the equilibrium state will be achieved.

> **The magnitude of the equilibrium constant K_c gives information about how far a reaction goes at a particular temperature, but not about how fast it will achieve the equilibrium state.**

The reaction quotient, Q, enables us to predict the direction of reaction

Remember that the value of K_c is calculated from substituting the *equilibrium* concentrations of all reactants and products into the equilibrium constant expression. Any other values used will not give the equilibrium value K_c for that reaction at that temperature.

This in itself can be useful. If we take the concentrations of the reactants and products at one moment in time when the reaction is not at equilibrium, and substitute these into the equilibrium constant expression, we obtain a value known as the **reaction quotient**, **Q**. As time passes and the reaction continues, the concentrations of all reaction components change and eventually reach the equilibrium concentrations. In other words, the value of Q changes in the direction of K_c. This enables us to predict the direction in which the reaction will proceed.

For example, if we again consider the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
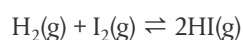
for which $K_c = 49.5$ at 440 °C, as we saw on page 316.

The table below shows experimental data for the concentrations of the reaction components from experiments I and II at a time when the reaction mixture was not at equilibrium.

	Experiment I: concentration at time t / mol dm^{-3}	Experiment II: concentration at time t / mol dm^{-3}
H_2	0.0500	0.0250
I_2	0.0500	0.0350
HI	0.100	0.300

The equilibrium constant expression $= \dfrac{[HI]^2}{[H_2][I_2]}$

Experiment I, time t $\qquad Q = \dfrac{(0.100)^2}{(0.0500)(0.0500)} = 4.00$

Experiment II, time t $\qquad Q = \dfrac{(0.300)^2}{(0.0250)(0.0350)} = 103$

In experiment I, $Q < K_c$ and so Q must increase as the reaction moves towards equilibrium. This means that the net reaction must be to the right, in favour of products.

In experiment II, $Q > K_c$ and so Q must decrease as the reaction moves towards equilibrium. This means that the net reaction must be to the left, in favour of reactants.

We can summarize the use of the reaction quotient, Q, in determining the direction of reaction as follows:

• if $Q = K_c$, reaction is at equilibrium, no net reaction occurs;
• if $Q < K_c$, reaction proceeds to the right in favour of products;
• if $Q > K_c$, reaction proceeds to the left in favour of reactants.

The reaction quotient, Q, is a measure of the relative amounts of reactants and products present in a reaction at a particular time. Its value is determined from substituting concentrations of reaction components, all measured at the same time, into the equilibrium expression.

Note that the value of Q for a reaction does not have a fixed value as it can be measured at any point in time, whereas the value of K_c for a reaction is a constant at a specified temperature.

The equilibrium constant K_c for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
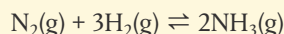
is 1.7×10^2 at 500 K.

Determine whether the reaction mixture is at equilibrium when the concentrations of the components at this temperature are as follows:

$[N_2] = 1.50$

$[H_2] = 1.00$

$[NH_3] = 8.00$.

If it is not at equilibrium, state and explain in which direction the reaction will proceed.

Solution

First write the equilibrium constant expression.

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

Calculate the value of Q at these conditions by substituting the given concentration values into the equilibrium expression.

$$Q = \frac{(8.00)^2}{(1.50)(1.00)^3} = 42.7$$

Compare the value of Q at the given conditions with K_c.

$$42.7 < 1.7 \times 10^2$$

Therefore the reaction is not at equilibrium. It will proceed to the right in favour of products, as the value of Q must increase to be equal to K_c at equilibrium.

The reaction quotient Q is used in the calculation of the electrode potential of a half-cell operating under non-standard conditions in the Nernst equation. This is discussed in topic C.6 in Chapter 14, Energy.

Relationships between K_c for different equations of a reaction

As K_c is defined with products on the numerator and reactants on the denominator, each raised to the power of their stoichiometric coefficients in the balanced equation, we can manipulate its value according to changes made to these terms. For this discussion we will consider the generic reaction:
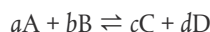
$$aA + bB \rightleftharpoons cC + dD$$

for which the equilibrium constant is:

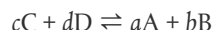$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Comparison of the value of the reaction quotient, Q, at a specific time in a reaction with the value of K_c for the reaction, enables us to predict the direction of change.

1 K_c for the inverse reaction

The inverse reaction

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

defines the products as reactants and vice versa. We will denote its equilibrium constant as $K_c{}'$.
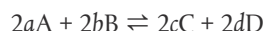
$$K_c = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

We can see that $K_c = \dfrac{1}{K_c}$ or $K_c{}' = K_c^{-1}$.

In other words the equilibrium constant for a reaction is the reciprocal of the equilibrium constant for its inverse reaction.

2 K_c for a multiple of a reaction

Consider now the reaction

$$2aA + 2bB \rightleftharpoons 2cC + 2dD$$

We will denote its equilibrium constant as K_c^{x}.

$$K_c^{x} = \frac{[C]^{2c} [D]^{2d}}{[A]^{2a} [B]^{2b}}$$

We can see that each term has been squared in K_c^{x} relative to its value in K_c.

So $K_c^{x} = K_c^{2}$.

By similar thinking, we can conclude that tripling of the stoichiometric coefficients would lead to a cubing of the value of K_c, halving of the stoichiometric coefficients would lead to a square rooting of the value of K_c, and so on.

These manipulations of the value of K_c are summarized below.

	Effect on equilibrium expression	Effect on K_c
inversing the reaction	inverts the expression	$\dfrac{1}{K_c}$ or K_c^{-1}
doubling the reaction coefficients	squares the expression	K_c^{2}
tripling the reaction coefficients	cubes the expression	K_c^{3}
halving the reaction coefficients	square roots the expression	$\sqrt{K_c}$
adding together two reactions	multiplies the two expressions	$K_c^{i} \times K_c^{ii}$

The equilibrium constant for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
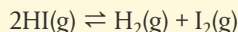
is 0.04 at a certain temperature. What would be the value of the equilibrium constant, K_c', for the following reaction at the same temperature?

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}I_2(g) \rightleftharpoons HI(g)$$
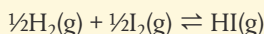
Solution

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

Note that the reaction is reversed and the coefficients in the equation are halved. Overall, the value of K_c' is the square root of the value of the reciprocal of K_c.

So $K_c' = \dfrac{1}{\sqrt{K_c}}$ or $\sqrt{(K_c)^{-1}}$.

$\therefore K_c' = \sqrt{\dfrac{1}{0.04}} = 5.0$

Exercises

7 When the following reactions reach equilibrium, does the equilibrium mixture contain mostly reactants or mostly products at the specified temperature? Assume that the value for K_c given corresponds to the temperature of the reaction mixture.

(a) $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ $K_c = 7.4 \times 10^{-26}$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 2.7 \times 10^{-18}$
(c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $K_c = 6.0 \times 10^{13}$

8 The equilibrium constant for the reaction:
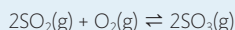
$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$
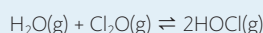
is 0.0900 at 298 K.

Determine whether the following sets of conditions represent an equilibrium mixture for the reaction at this temperature. For those not at equilibrium, determine in which direction the reaction will proceed.

	$[H_2O]$	$[Cl_2O]$	$[HOCl]$
(a)	0.100	0.100	1.00
(b)	0.49	0.040	0.042
(c)	0.19	0.00033	0.083

9 At a given temperature, the reaction

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

has a value of $K_c = 278$. Determine values of K_c for the following reactions at this temperature.

(a) $4SO_2(g) + 2O_2(g) \rightleftharpoons 4SO_3(g)$
(b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$
(c) $SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$

When equilibrium is disrupted

A system remains at equilibrium so long as the rate of the forward reaction equals the rate of the backward reaction. But as soon as this balance is disrupted by any change

Henri-Louis Le Chatelier was a French chemist who published his equilibria principle in 1884. Amongst other research, he also investigated the possibility of ammonia synthesis, but abandoned his efforts after suffering a devastating explosion in his laboratory. After Haber's later elucidation of the conditions required in the reaction, Le Chatelier realized that he had been very close to the discovery himself. Late in his life he wrote 'I let the discovery of the ammonia synthesis slip through my hands. It was the greatest blunder of my career.' We can only speculate on how history might have been re-written if this discovery had in fact been made in France rather than in Germany before World War I.
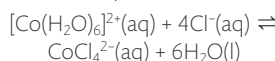
> When a system at equilibrium is subjected to a change, it will respond in such a way as to minimize the effect of the change.

Experiment to show the effect of changing the concentration of chloride ions on the cobalt chloride equilibrium reaction:

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

The flask on the left has a low concentration of chloride ions, giving the pink colour of the complex ion with water. As the concentration of chloride ions is increased, the equilibrium shifts to the right, changing the colour from pink to blue. Adding water would shift the equilibrium in the opposite direction. Cobalt chloride is often used to test for the presence of water because of this colour change.

Figure 7.5 Effects of the addition of reactant and removal of product on the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. When H_2 is added some N_2 reacts and more NH_3 is formed as the equilibrium shifts to the right. When NH_3 is removed, more N_2 reacts with H_2 as the equilibrium again shifts to the right. After each change a new equilibrium mixture is achieved.

in conditions that unequally affects the rates of these reactions, the equilibrium condition will no longer be met. It has been shown, however, that equilibria respond in a predictable way to such a situation, based on a principle known as **Le Chatelier's principle**. This states that *a system at equilibrium when subjected to a change will respond in such a way as to minimize the effect of the change.* Simply put, this means that whatever we do to a system at equilibrium, the system will respond in the opposite way. Add something and the system will react to remove it, remove something and the system will react to replace it. After a while, a new equilibrium will be established and this will have a different composition from the earlier equilibrium mixture. Applying the principle therefore enables us to predict the qualitative effect of typical changes that occur to systems at equilibrium.

Changes in concentration

Suppose an equilibrium is disrupted by an increase in the concentration of one of the reactants. This will cause the rate of the forward reaction to increase while the backward reaction will not be affected, so the reaction rates will no longer be equal. When equilibrium re-establishes itself, the mixture will have new concentrations of all reactants and products, and the equilibrium will have shifted in favour of products. The value of K_c will be unchanged. This is in keeping with the prediction from Le Chatelier's principle: addition of reactant causes the system to respond by removing reactant – this favours the forward reaction and so shifts the equilibrium to the right.

Similarly, the equilibrium could be disrupted by a decrease in the concentration of product by removing it from the equilibrium mixture. As the rate of the backward reaction is now decreased, there will be a shift in the equilibrium in favour of the products. A different equilibrium position will be achieved, but the value of K_c will be unchanged. Again this confirms the prediction from Le Chatelier's principle: removal of product causes the system to respond by making more product – this favours the forward reaction and so shifts the equilibrium to the right.

The graph in Figure 7.5 illustrates these disruptions to equilibrium for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
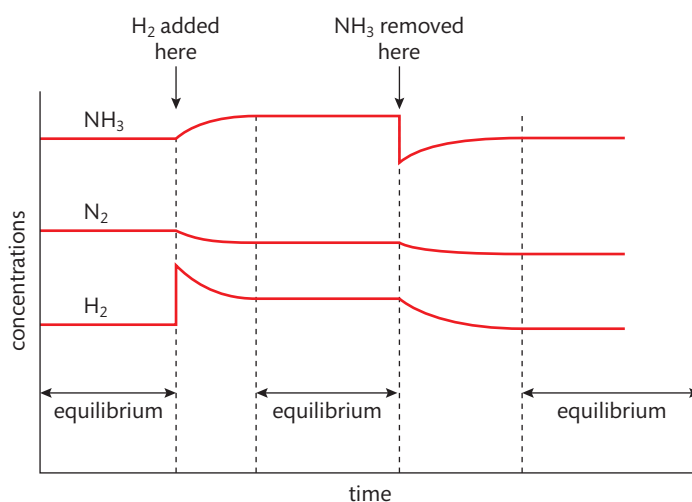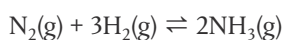
After H_2 is added, the concentrations of N_2 and H_2 decrease (in a 1 : 3 ratio in keeping with their reaction stoichiometry), while the concentration of NH_3 rises (in a 2 : 1 ratio relative to N_2) as the rate of the forward reaction increases and the equilibrium shifts

to the right. The new equilibrium mixture has a higher proportion of products. In the second part of the graph, removal of NH_3 from the equilibrium mixture causes a decrease in the concentrations of N_2 and H_2 as they react to form more NH_3.

Often in an industrial process the product will be removed as it forms. This ensures that the equilibrium is continuously pulled to the right, so increasing the yield of product.

Applying Le Chatelier's principle, can you think what concentration changes would cause an equilibrium to shift to the left? The answer is either an increase in concentration of product or a decrease in concentration of reactant.
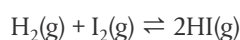
Changes in pressure

Equilibria involving gases will be affected by a change in pressure if the reaction involves a change in the number of molecules. This is because there is a direct relationship between the number of gas molecules and the pressure exerted by a gas in a fixed volume. So if such a reaction at equilibrium is subject to an increase in pressure, the system responds to decrease this pressure by favouring the side with the smaller number of molecules. Conversely, a decrease in pressure will cause a shift in the equilibrium position to the side with the larger number of molecules of gas. A different equilibrium position will be achieved but the value of K_c will be unchanged, so long as the temperature remains the same.

For example, consider the reaction used in the production of methanol:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
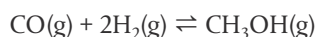
In total there are three molecules of gas on the left side and one molecule of gas on the right side. So here high pressure will shift the equilibrium to the right, in favour of the smaller number of gas molecules, which increases the yield of CH_3OH.

Note that many common equilibrium reactions do not involve a change in the number of gas molecules and so are not affected by changes in pressure. For example, the reaction

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

has two molecules of gas on both sides of the equation. Changing pressure for this reaction will affect the rate of the reaction but not the position of equilibrium or the value of K_c.

Changes in temperature

We have noted that K_c is temperature dependent, so changing the temperature will change K_c. However, in order to predict *how* it will change we must examine the enthalpy changes (see Chapter 5) of the forward and backward reactions. Remember that an exothermic reaction releases energy (ΔH negative), whereas an endothermic reaction absorbs energy (ΔH positive). The enthalpy changes of the forward and backward reactions are equal and opposite to each other.

So if we apply Le Chatelier's principle, including the energy change in the chemical reaction, we can predict how the reaction will respond to a change in temperature.

Consider the reaction:

$$\begin{array}{ccc} 2NO_2(g) & \rightleftharpoons & N_2O_4(g) \\ \text{brown} & & \text{colourless} \end{array} \qquad \Delta H = -57 \text{ kJ mol}^{-1}$$

Changes in the concentration of reactants or products alter the equilibrium position and so change the composition of the equilibrium mixture. But the value of K_c stays the same.

Changes in pressure or volume will affect the position of equilibrium of a reaction if it involves a change in the number of gas molecules. The value of K_c remains unchanged.

When describing the effects of volume or pressure on equilibrium reactions, you must state it depends on the relative number of *gas* molecules on both sides of the equation. Solids and liquids are hardly affected by changes in pressure.

An increase in pressure favours the side of an equilibrium reaction that has the smaller number of gas molecules.

When ΔH is given for an equilibrium reaction, by convention its sign refers to the forward reaction. So a negative sign for ΔH means that the forward reaction is exothermic, and the backward reaction is endothermic.

CHALLENGE YOURSELF

4 Use information from this section to explain why there is very little NO in the atmosphere under ordinary conditions, and why severe air pollution is often characterized by a brownish haze.

The negative sign of ΔH tells us that the forward reaction is exothermic and so releases heat. If this reaction at equilibrium is subjected to a decrease in temperature, the system will respond by producing heat and it does this by favouring the forward exothermic reaction. This means that the equilibrium will shift to the right, in favour of the product N_2O_4. A new equilibrium mixture will be achieved and the value of K_c will increase. So here we can see that the reaction will give a higher yield of products at a *lower temperature*.

Conversely, increasing the temperature favours the backward endothermic reaction, and so shifts the equilibrium to the left, decreasing the value of K_c. The reaction mixture becomes a darker colour as the concentration of NO_2 increases.

The table below illustrates the effect of temperature on the value of K_c for this reaction.

Temperature / K	K_c for $2NO_2(g) \rightleftharpoons N_2O_4(g)$
273	1300
298	170

Experiment to show the effect of temperature on the reaction that converts NO_2 (brown) to N_2O_4 (colourless). As the temperature is increased, more NO_2 is produced and the gas becomes darker, as seen in the tube on the left.

Even though in this case a lower temperature will produce an equilibrium mixture with a higher proportion of products, remember from Chapter 6 that low temperature also causes a lower rate of reaction. And so, although a higher yield will be produced eventually, it may simply take too long to achieve this from practical and economic considerations if this was an industrial-scale reaction. We will come back to this point later in this chapter.

Now consider the following reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +181 \text{ kJ mol}^{-1}$$

In this case we can see that the forward reaction is endothermic and so absorbs heat. So here the effect of a decreased temperature will be to favour the backward exothermic reaction. Therefore the equilibrium will shift to the left, in favour of reactants, and K_c will decrease. At higher temperatures, the forward endothermic reaction is favoured, so the equilibrium shifts to the right and K_c will increase.

TOK

Combustion reactions are generally described as exothermic, but the reaction

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

is endothermic. When is it appropriate to refer to an 'exception to a rule', and when does the rule need to be reconsidered?

The table below illustrates the effect of temperature on the value of K_c for this reaction.

Temperature / K	K_c for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
298	4.5×10^{-31}
900	6.7×10^{-10}
2300	1.7×10^{-3}

The reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
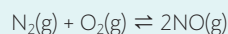
takes place in motor vehicles where the heat released by the combustion of the fuel is sufficient to cause the nitrogen and oxygen gases from the air to combine together in this way. Unfortunately, the product NO is toxic, and, worse still, quickly becomes converted into other toxins that form the components of acid rain and smog. It is therefore of great interest to vehicle manufacturers to find ways of lowering the temperature during combustion in order to reduce the production of NO in the reaction above.

Increasing the temperature causes an increase in the value of K_c for an endothermic reaction and a decrease in the value of K_c for an exothermic reaction.

These examples illustrate that, unlike changes in concentration and pressure, changes in temperature *do* cause the value of K_c to change. An increase in temperature increases the value of K_c for an endothermic reaction and decreases the value of K_c for an exothermic reaction. This is because changes in temperature have a different effect

on the rates of the forward and backward reactions, due to their different activation energies, as discussed in Chapter 6. In the next chapter, we will use this fact to explain why the pH of pure water is temperature dependent.

Addition of a catalyst

As we learned in Chapter 6, a catalyst speeds up the rate of a reaction by providing an alternate reaction pathway that has a transition state with a lower activation energy, E_a. This increases the number of particles that have sufficient energy to react without raising the temperature.
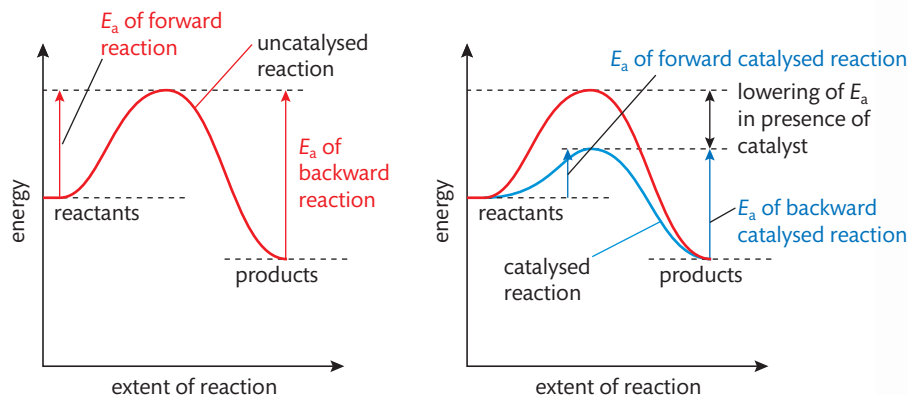
Because the forward and backward reactions pass through the same transition state, a catalyst lowers the activation energy by the same amount for the forward and backward reactions. So the rate of both these reactions will be increased by the same factor, as shown in Figure 7.6. The catalyst will therefore have no effect on the position of equilibrium, or on the value of K_c. In other words the catalyst will not increase the equilibrium yield of product in a reaction. It will, however, speed up the attainment of the equilibrium state and so cause products to form more quickly. Catalysts are generally not shown in the reaction equation or in the equilibrium constant expression as they are not chemically changed at the end of the reaction, and have no effect on the equilibrium concentrations.

Catalysts are widely used in industrial processes to increase the rate of product formation, and are involved in every single biochemical reaction. One of the key principles of Green Chemistry is that catalytic reagents, chosen to be as selective as possible, are superior to stoichiometric reagents as they are not consumed in the reaction. Catalysts, including the differences between homogeneous and heterogeneous catalysts, are discussed in more detail in Option A Materials, topic A.3.

Summary

We can now summarize the effects of concentration, pressure, temperature, and catalyst on the position of equilibrium and on the value of K_c.

	Effect of …	Change in position of equilibrium	Change in value of K_c
1	concentration	changes	no change
2	pressure	changes if reaction involves a change in the number of gas molecules	no change
3	temperature	changes	changes
4	catalyst	no change	no change

Observations of shifts in the position of chemical equilibria
Full details of how to carry out this experiment with a worksheet are available online.

Catalysts do not change the position of equilibrium or the yield of a single reaction, but they enable the equilibrium mixture to be achieved more quickly. Catalysts do not change the value of K_c.

A particular reaction at a specified temperature can have many different possible equilibrium positions, but only one value for the equilibrium constant K_c.

NATURE OF SCIENCE

Knowledge of how systems at equilibrium respond to change has many applications, as we will see in the next section. Le Chatelier's principle is a useful predictive tool for this purpose, and has the advantage of being relatively simple to apply and effective. But it has some disadvantages too. Firstly, it leads only to qualitative predictions of the system's response. In some cases, such as investigations of when a precipitate will form in aqueous solution, this is insufficient. Secondly, Le Chatelier's principle offers no *explanation* for the response – it predicts what will happen, but not why. It can even be misleading in that it can suggest a false sense of purpose to systems' responses if the language used is such as 'the system tries to...'.

On the other hand, use of the reaction quotient, Q, to predict the consequence of change can often provide an effective explanation. As disturbances in concentration or pressure change the value of Q, the system responds as Q progresses towards K_c. But changes in temperature are different because they change the value of K_c – in this case the system responds as Q progresses towards the new value of K_c. The response of K_c to temperature can be explained through thermodynamics and the fact that the forward and backward reactions respond differently to temperature changes due to their different activation energies. Increased temperature favours the endothermic reaction as it has the higher activation energy. Scientific explanations often draw on different approaches and theories in this way. So long as the approaches do not contradict each other, together they can clarify and strengthen the understanding.

Note that you are not expected to learn specific conditions for any reaction, so there is no need to focus on the names of catalysts, specific temperature used, etc. But you should be able to apply an understanding of equilibria to any given example, and predict the conditions likely to be effective.
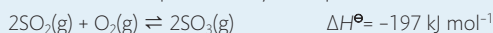
Fritz Haber 1868–1934

▼

Exercises

10 The manufacture of sulfur trioxide can be represented by the equation below:

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

What happens when a catalyst is added to an equilibrium mixture from this reaction?

A The rate of the forward reaction increases and that of the reverse reaction decreases.
B The rates of both forward and reverse reactions increase.
C The value of $\Delta H^\ominus$ increases.
D The yield of sulfur trioxide increases.

11 What will happen to the position of equilibrium and the value of the equilibrium constant when the temperature is increased in the following reaction?

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g) \qquad \Delta H^\ominus = +14 \text{ kJ}$$
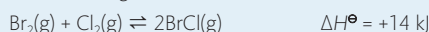
	Position of equilibrium	Value of equilibrium constant
A	shifts towards the reactants	decreases
B	shifts towards the reactants	increases
C	shifts towards the products	decreases
D	shifts towards the products	increases

12 Which changes will shift the position of equilibrium to the right in the following reaction?

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

I adding a catalyst
II decreasing the oxygen concentration
III increasing the volume of the container

A I and II only   **B** I and III only   **C** II and III only   **D** I, II, and III

13 For each of the following reactions, predict in which direction the equilibrium will shift in response to an increase in pressure:

(a) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$
(b) $CO(g) + 2H_2 \rightleftharpoons CH_3OH(g)$
(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

14 How will the equilibrium:

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H = +ve$$
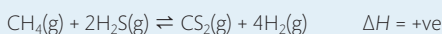
respond to the following changes?

(a) addition of $H_2(g)$
(b) addition of $CH_4(g)$
(c) a decrease in the volume of the container
(d) removal of $CS_2(g)$
(e) increase in temperature

15 The reaction

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H = -566 \text{ kJ mol}^{-1}$$
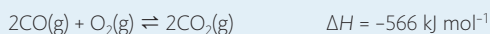
takes place in catalytic converters in cars. If this reaction is at equilibrium, will the amount of CO increase, decrease, or stay the same when:

(a) the pressure is increased by decreasing the volume?
(b) the pressure is increased by adding $O_2(g)$?
(c) the temperature is increased?
(d) a platinum catalyst is added?

# Equilibrium theory is applied in many industrial processes

In reactions involving the manufacture of a chemical it is obviously a goal to obtain as high a conversion of reactant to product as possible. Application of Le Chatelier's principle enables chemists to choose conditions that will cause the equilibrium to lie to the right, and so help to achieve this. But the *yield* of a reaction is only part of the consideration. The *rate* is also clearly of great significance as it would be of limited value if a process were able to claim a high equilibrium yield of product, but took several years to achieve this. The economics of the process will depend on considerations of both the equilibrium and the kinetics of the reaction – in other words on how far and how fast the reaction will proceed. Sometimes these two criteria work against each other, and so the best compromise must be reached. A few case studies of industrial processes are discussed here.

The Haber process: the production of ammonia, NH_3

Fritz Haber was born in what is now Poland but moved to Germany early in his career. Together with Carl Bosch, also of Germany, he developed the process for the industrial synthesis of ammonia from its elements, and the first factory for ammonia production opened in Germany in 1913, just before World War I. This development had enormous significance for the country at war: it enabled the continued production of explosives despite the fact that imports of nitrate from Chile, used for producing nitric acid and explosives such as TNT, were barred through the blockaded ports. This effectively enabled Germany to continue its war efforts for another 4 years. Haber was awarded the Nobel Prize in Chemistry in 1918. In many ways history has recorded this as a controversial choice – not only had Haber's work helped to prolong the war, he had also been responsible for the development and use of chlorine as the first poison gas. Ironically, despite his evident patriotism towards Germany, he was expelled from the country in 1933 when the rising tide of anti-Semitism conflicted with his Jewish ancestry.

The book *The alchemy of air: a Jewish genius, a doomed tycoon, and the scientific discovery that fed the world but fueled the rise of Hitler* is written by Thomas Hager. It is a fascinating account of the historic discovery of the process to synthesize ammonia, and its continuing mixed consequences – these include the revolution in global food production, the death of millions through wars, and growing concerns of nitrate pollution and obesity.

The Haber process is based on the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -93 \text{ kJ mol}^{-1}$$
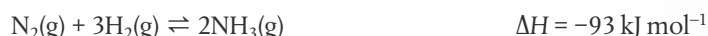
The following information can be derived from this equation:

- all reactants and products are gases;
- there is a change in the number of gas molecules as the reaction proceeds: four gas molecules on the left and two on the right;

It is estimated that as much as 130 million tonnes of ammonia, NH_3, are produced worldwide every year. China is responsible for nearly one-third of this, and India, Russia, and the USA also produce significant amounts. Approximately 80% of the ammonia is used to make fertilizers, notably ammonium nitrate, NH_4NO_3. Other uses include synthesis of textiles such as nylon and powerful explosives. In April 2013, a major explosion occurred in a fertilizer factory in Texas, USA, killing and injuring hundreds of people. It was caused by a fire in a stock of 250 000 kilograms of ammonium nitrate. Accidents such as this in industrial plants raise many questions regarding health and safety, storage, and handling of chemicals and the balance of responsibility between companies, governments, and individuals.

▲
Tractor applying a chemical solution of fertilizer to the soil. Ammonium salts such as ammonium nitrate and sulfate are particularly effective fertilizers as they supply nitrogen needed by plants and are readily soluble. It is estimated that without the use of ammonium fertilizers, two billion people would starve.
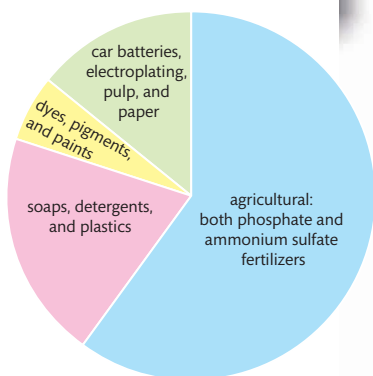
• the forward reaction is exothermic so releases heat; the backward reaction is endothermic so absorbs heat.

Application of Le Chatelier's principle to this reaction enables us to consider the optimum conditions.

• Concentration: the reactants nitrogen and hydrogen are supplied in the molar ratio 1 : 3 in accordance with their stoichiometry in the equation. The product ammonia is removed as it forms, thus helping to pull the equilibrium to the right and increasing the yield.
• Pressure: as the forward reaction involves a decrease in the number of gas molecules, it will be favoured by a *high pressure*. The usual pressure used in the Haber process is about 2×10^7 Pa.
• Temperature: as the forward reaction is exothermic, it will be favoured by a lower temperature. However, too low a temperature would cause the reaction to be uneconomically slow, and so a *moderate temperature* of about 450 °C is used.
• Catalyst: a catalyst will speed up the rate of production and so help to compensate for the moderate temperature used. A catalyst of finely divided iron is used, with small amounts of aluminium and magnesium oxides added to improve its activity. More recently, ruthenium has become the catalyst of choice, and this has helped reduce the energy requirement.

In fact, the Haber process achieves a conversion of H_2 and N_2 into NH_3 of only about 10–20% per pass through the reactor. After separation of the NH_3 product, the unconverted reactants are recycled to the reactor to obtain an overall yield of about 95%. This recycling of unconverted reactants is commonly used in industrial processes, and allows processes with low equilibrium yield to be made commercially viable.

The Contact process: the production of sulfuric acid H_2SO_4

The Contact process involves a series of three simple reactions:

(i) the combustion of sulfur to form sulfur dioxide;
(ii) the oxidation of sulfur dioxide to sulfur trioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1}$$
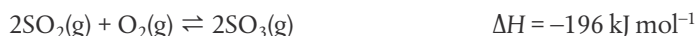
(iii) The combination of sulfur trioxide with water to produce sulfuric acid.

It has been shown that the overall rate of the process depends on step (ii), the oxidation of sulfur dioxide. So applying Le Chatelier's principle to this step, we can predict the conditions that will most favour the formation of product. These are summarized in the table below.

	Influence on reaction	Condition used
pressure	forward reaction involves reduction in the number of molecules of gas from three molecules reactant to two molecules product: high pressure will favour product	2×10^5 Pa (this gives a very high equilibrium yield, so still higher pressure is not needed)
temperature	forward reaction is exothermic: low temperature will increase the equilibrium yield, but decrease the rate	450 °C
catalyst	increases the rate of reaction	vanadium(V) oxide

Figure 7.7 The uses of sulfuric acid.

More sulfuric acid by mass is produced worldwide than any other chemical. It has been found that the production of sulfuric acid closely mirrors historical events such as major wars that affect a country's economy. For this reason some economists use sulfuric acid production as a measure of a country's industrial strength. Sulfuric acid is used directly or indirectly in nearly all industrial processes, including the production of fertilizers, detergents, and paints and in ore processing, steel production, and water treatment. Approximately 250 million tonnes are produced annually across all continents.

The process gets its name the *Contact process* from the fact that molecules of the gases O_2 and SO_2 react in *contact* with the surface of the solid catalyst V_2O_5.

The production of methanol

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90 \text{ kJ mol}^{-1}$$

Again, Le Chatelier's principle can be used to consider the conditions that will optimize the production.

	Influence on reaction	Condition used
pressure	forward reaction involves reduction in the number of molecules of gas from three molecules reactant to one molecule product: high pressure will favour product	$5-10 \times 10^6$ Pa
temperature	forward reaction is exothermic: low temperature will increase the equilibrium yield, but decrease the rate	250 °C
catalyst	increases the rate of reaction	$Cu-ZnO-Al_2O_3$

NATURE OF SCIENCE

Scientific research is largely influenced by the social context, which helps to determine funding and set priorities. A good example is Haber's work on ammonia synthesis, which became pressing in Germany in the early years of the 20th century. Scientific discoveries often have significant economic, ethical, and political implications. Some of these may be unintended consequences of the discovery, such as the environmental degradation caused by the excess use of nitrate fertilizers as an outcome of the Haber process. This raises the question of who must take moral responsibility for the applications of scientific discoveries. The process of science includes risk benefit analyses, risk assessment, and ethical considerations, but sometimes the full consequences cannot be predicted and do not become known until much later.

Exercises

16 In the Haber process for the synthesis of ammonia, what effects does the catalyst have?

	Rate of formation of $NH_3(g)$	Amount of $NH_3(g)$ formed
A	increases	increases
B	increases	decreases
C	increases	no change
D	no change	increases

17 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^\ominus = -200$ kJ

According to the above information, what temperature and pressure conditions produce the greatest amount of SO_3?

	Temperature	Pressure
A	low	low
B	low	high
C	high	high
D	high	low

18 Predict how you would expect the value for K_c for the Haber process to change as the temperature is increased. Explain the significance of this in terms of the reaction yield.

CHALLENGE YOURSELF

5 Consider the atom economy of the reactions described here using the formula

$$\text{atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100$$

Explain how this is different from the reaction yield.

▲ Land contaminated by waste impurities from an old sulfuric acid plant close to a residential area in Bilbao, Spain. The waste largely derives from smelting and combustion processes. The full consideration of any industrial process must include an assessment of its impact on the environment, both locally and globally.

Methanol is used as a **chemical feedstock**, that is used to make other chemicals. A high proportion is converted into methanal, HCHO, which is then converted into plastics, paints, explosives, and plywood. Methanol is used as a laboratory solvent, as an antifreeze agent, and in the process of producing biodiesel fuel from fats. Interest has also focused on the potential of methanol as an energy storage molecule in the so-called 'methanol economy'. In on-going efforts to reduce dependence on imported fossil fuels, China has greatly increased production capacity and consumption of methanol for its transportation sector, and plans to produce five million alternative-energy vehicles a year by 2020.

17.1 The equilibrium law

Understandings:
- Le Chatelier's principle for changes in concentration can be explained by the equilibrium law.
- The position of equilibrium corresponds to a maximum value of entropy and a minimum in the value of the Gibb's free energy.
- The Gibbs free energy change of a reaction and the equilibrium constant can both be used to measure the position of an equilibrium reaction and are related by the equation, $\Delta G = -RT \ln K$.

  Guidance
  - *The expression $\Delta G = -RT \ln K$ is given in the data booklet in section 1.*
  - *Students will not be expected to derive the expression $\Delta G = -RT \ln K$.*

Applications and skills:
- Solution of homogeneous equilibrium problems using the expression for K_c.

  Guidance
  The use of quadratic equations will not be assessed.
- Relationship between ΔG and the equilibrium constant.
- Calculations using the equation $\Delta G^\circ = RT \ln K$.

So far we have learned how to derive the equilibrium constant K_c from the equation for a reaction, and have considered in qualitative terms what its value tells us about the composition of an equilibrium mixture. We now want to take this further by quantifying these values.

There are two processes involved here, which we will consider in turn:

- calculation of the equilibrium constant, K_c
- calculation of the concentrations of reactants and products present at equilibrium.

As we will see, the equilibrium constant expression is the key to all these calculations.

In the examples here we will consider only **homogeneous equilibria**, that is those where reactants and products are all in the same phase, as gases or solutions.

Calculating the equilibrium constant from initial and equilibrium concentrations

If we know the equilibrium concentrations of all reactants and products in a reaction, we can simply substitute these into the equilibrium expression to calculate K_c – as we did on page 316. The first step in such a calculation is always to write the equilibrium expression from the chemical equation.

TOK

The study of systems at equilibrium uses mathematics. Does this indicate that the systems are inherently mathematical, or have we constructed the mathematics to fit the system?

Worked example

Hydrogen can be prepared by the combination of carbon monoxide and water at 500 °C. At equilibrium the concentrations in the reaction mixture were found to be:

CO	0.150 mol dm^{-3}	H$_2$O	0.0145 mol dm^{-3}
H$_2$	0.200 mol dm^{-3}	CO$_2$	0.0200 mol dm^{-3}

Calculate the equilibrium constant for the reaction at this temperature.

Solution

First write the equation for the reaction, making sure it is correctly balanced:

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$
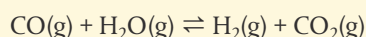
Next write the equilibrium expression:

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

Now substitute the given values for each component:

$$K_c = \frac{(0.200)(0.0200)}{(0.150)(0.0145)} = 1.84$$

Remember to check that the precision of your answer is consistent with the data given in the question – the answer here must be given to three significant figures.

More commonly, we may first have to work out the value for the equilibrium concentration for one or more reactants or products from data on initial concentrations and equilibrium concentrations of other components. The important thing here is to be sure that only *equilibrium* concentrations are substituted into the equilibrium expression. The steps given below will help you to do this. These steps will be a useful guide through many calculations in this chapter and the work on acids and bases that follows.

1   Write the balanced equation.
2   Under the equation, write in the values of the concentrations of each component using three rows: *initial, change,* and *equilibrium*.
   • *Initial* represents the concentration originally placed in the flask; unless stated otherwise, we assume the initial product concentration is zero.
   • *Change* represents the amount that reacts to reach equilibrium. A minus sign for reactants represents a decrease in concentration as they are used up, and a plus sign for products represents an increase in concentration as they form. The changes that occur must be in the same ratio as the coefficients in the balanced equation, so if we know one of the change values we can deduce the others.
   • *Equilibrium* is the concentration present in the equilibrium mixture. This can be calculated by applying the amount of change to the initial concentration for each component.
        equilibrium concentration = initial concentration ± change in concentration
3   Write the expression for K_c from the balanced equation. Substitute the values for equilibrium concentration and calculate K_c.

Worked example

A student placed 0.20 mol of $PCl_3(g)$ and 0.10 mol of $Cl_2(g)$ into a 1.0 dm³ flask at 350 °C. The reaction, which produced PCl_5, was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of PCl_3. What is the value of K_c for this reaction?

Solution

1   Write the equation for the reaction.
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$
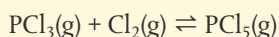
The example above involved a 1 dm³ reaction volume, so we could use the given amounts in mol directly as concentration in mol dm⁻³. Sometimes though we will need to calculate concentrations from given amounts and volumes. For example, if the data were given for a 3 dm³ volume, we would need to divide the amounts in mol by 3 to express this as mol dm⁻³. The volume must also be taken into account in this way when the reaction involves a change in the number of molecules of gas.

2 Insert the data under the equation in the three rows for initial, change, and equilibrium. In this example, the numbers in black are data that were given in the question and numbers in blue have been derived as explained below.

	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
initial (mol dm⁻³)	0.20		0.10		0.00
change (mol dm⁻³)	−0.08		−0.08		+0.08
equilibrium (mol dm⁻³)	0.12		0.02		0.08

The change in concentration of PCl_3, the amount that reacted to reach equilibrium, is $0.20 - 0.12 = 0.08$. It is given a minus sign to show that the concentration decreases by this amount. As PCl_3 and Cl_2 react in a $1:1$ ratio and form a $1:1$ ratio of PCl_5, the same change in concentration must apply to Cl_2 and PCl_5. The equilibrium concentrations are calculated by applying the change amount to the initial values.

3 $K_c = \dfrac{[PCl_5]}{[PCl_3][Cl_2]} = \dfrac{0.08}{0.12 \times 0.02} = 33$

Worked example

The oxidation of NO to form NO_2 occurs during the formation of smog. When 0.60 mol of NO was reacted with 0.60 mol of O_2 in a 2.0 dm³ container at 500 °C, the equilibrium mixture was found to contain 0.20 mol of NO_2. Calculate the equilibrium constant for the reaction at this temperature.

Solution

1 $2NO + O_2 \rightleftharpoons 2NO_2$

2 Insert the data from the question under the equation. Note that because the volume is 2 dm³ the amounts must be divided by two to give concentration as mol dm⁻³. As before, derived data are shown in blue, with explanations for these below.

	$2NO$	+	O_2	$\rightleftharpoons$	$2NO_2$
initial (mol dm⁻³)	0.30		0.30		0.00
change (mol dm⁻³)	−0.10		−0.05		+0.10
equilibrium (mol dm⁻³)	0.20		0.25		0.10

The change in concentration of NO_2, the amount that had formed at equilibrium, is +0.10. From the stoichiometry of the reaction, for every two moles of NO_2 that form, two moles of NO and one mole of O_2 are used. Therefore we can deduce the corresponding changes in concentration for NO and O_2 and use these values to calculate the equilibrium concentrations of all components.

**3** $K_c = \dfrac{[NO_2]^2}{[NO]^2[O_2]} = \dfrac{(0.10)^2}{(0.20)^2 \times 0.25} = 1.0$

Aerial view over Los Angeles showing a thick smog. The formation of smog involves several chemical equilibria including those involving nitrogen and sulfur oxides.

Don't miss out the step showing the equilibrium constant expression. It will help to ensure you substitute the values correctly, and even if you make a mistake with the numbers, you can still get credit for this part of your answer.

Calculating equilibrium concentrations from the equilibrium constant

If we know the value of K_c and the equilibrium concentrations of all but one of the components, we can calculate the remaining equilibrium concentration simply by substituting the values into the equilibrium expression.

Worked example

The reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$
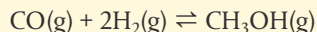
has $K_c = 0.500$ at 350 K. If the concentrations at equilibrium are:

CO   0.200 mol dm^{-3}

H$_2$ 0.155 mol dm^{-3}

what is the equilibrium concentration of CH$_3$OH?

Solution

Write the equilibrium expression:

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

Substitute the data from the question and solve the equation to give the unknown concentration.

$$0.500 = \frac{[CH_3OH]}{(0.200)(0.155)^2}$$

Therefore [CH$_3$OH] = 0.00240 mol dm^{-3} or 2.40×10^{-3} mol dm^{-3}

A more complex situation arises when we need to calculate equilibrium concentrations given K_c and initial concentrations. Here we use algebra to deduce the concentrations that have reacted to reach equilibrium and so calculate the equilibrium concentrations. The process developed in the previous section will also help to set the data out clearly here.

Worked example

The equilibrium constant K_c for the reaction

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$
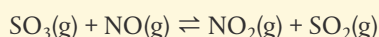
was found to be 6.78 at a specified temperature. If the initial concentrations of NO and SO$_3$ were both 0.0300 mol dm^{-3}, what would be the equilibrium concentration of each component?

Solution

To calculate the equilibrium concentrations of the reactants and products, we need to know how much has reacted, in other words the change in concentration:

let the change in concentration of NO = $-x$

therefore change in concentration of SO$_3$ = $-x$

and change in concentration of both NO$_2$ and SO$_2$ = $+x$ (due to the 1:1 stoichiometry)

Insert the relevant data from the question under the equation:

	SO$_3$(g) +	NO(g) $\rightleftharpoons$	NO$_2$(g) +	SO$_2$(g)
initial (mol dm^{-3})	0.0300	0.0300	0.00	0.00
change (mol dm^{-3})	$-x$	$-x$	$+x$	$+x$
equilibrium (mol dm^{-3})	$0.0300 - x$	$0.0300 - x$	x	x

Always look for a way to simplify calculations of this type, for example, by taking the square root of both sides of the equation. If you think you need to use the quadratic equation to solve equilibria calculations at this level, you have almost certainly made a mistake or have missed a simplifying step – so go back and look again.

Write the equilibrium expression and substitute the equilibrium concentrations.

$$K_c = \frac{[NO_2][SO_2]}{[SO_3][NO]} = \frac{x^2}{(0.0300-x)^2} = 6.78$$

This can be solved by taking the square root of both sides of the equation and collecting the terms in x.

$$\frac{x}{0.0300-x} = \sqrt{6.78} = 2.60$$

$$x(1 + 2.60) = 2.60 \times 0.0300 = 0.0780$$

$$x = \frac{0.0780}{3.60} = 0.0217$$

The equilibrium concentration of each component can now be calculated.

$[SO_3]$ = 0.0300 − 0.0217 = 0.00830 mol dm^{-3}

$[NO]$ = 0.0300 − 0.0217 = 0.00830 mol dm^{-3}

$[NO_2]$ = 0.0217 mol dm^{-3}

$[SO_2]$ = 0.0217 mol dm^{-3}

Do not make the mistake of stopping when you have calculated x. The question asks for the equilibrium concentrations so you must substitute the value for x in the expressions you derived for the equilibrium concentrations to give the answer.

TOK What ways of knowing do we use when we make an assumption in a calculation to simplify the mathematics? What is the difference between intuition and reason in this context?

The approximation made in this calculation that [reactant]$_{initial}$ ≈ [reactant]$_{equilibrium}$ assumes that the value of x is extremely small, so that subtracting x (or in this case $2x$) from the initial concentration will not make a difference to the result within the precision used. You can check this assumption against your answer: subtracting 5.3×10^{-7} from 0.10 will still give 0.10 when rounded to this precision. Note though that multiplying or dividing by x, however small its value, will make a significant difference to the answer, so the values of x on the numerator in the K_c expression must be retained through the calculation.

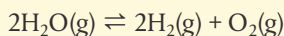## Calculating equilibrium concentrations when K_c is very small

In some reactions the value of K_c is very small, less than 10^{-3}. As we learned in section 7.1, this represents a reaction in which the forward reaction has hardly proceeded and the equilibrium mixture consists almost entirely of reactants. In other words, the change in reactant concentrations is close to zero, as the equilibrium concentrations of reactants are approximately equal to their initial concentrations:

$$[reactant]_{initial} \approx [reactant]_{equilibrium}$$

This situation is common in the study of weak acids and bases as they dissociate only slightly, and so this approximation will help you in these calculations in Chapter 8.

Worked example

The thermal decomposition of water has a very small value of K_c. At 1000 °C, $K_c = 7.3 \times 10^{-18}$ for the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

A reaction is set up at this temperature with an initial H_2O concentration of 0.10 mol dm^{-3}. Calculate the H_2 concentration at equilibrium.

Solution

We need to know the change in concentration of H_2, so we could assign this as x. But from the stoichiometry of the reaction, this would make change in $[O_2] = ½x$. So it will make the calculation easier if we proceed as follows:

    let change in concentration of $H_2 = 2x$

    therefore change in concentration of $O_2 = x$

    so change in concentration of $H_2O = -2x$ (due to the 2 : 2 : 1 stoichiometry)

Insert the relevant data from the question under the equation.

	$2H_2O(g)$	$\rightleftharpoons$	$2H_2(g)$	$+$	$O_2(g)$
initial (mol dm⁻³)	0.10		0.00		0.00
change (mol dm⁻³)	$-2x$		$+2x$		$+x$
equilibrium (mol dm⁻³)	$0.10 - 2x$		$2x$		x
	≈ 0.10				

The approximation $[H_2O]_{initial} \approx [H_2O]_{equilibrium}$ follows from the very small value of K_c.

Write the equilibrium expression and substitute the equilibrium concentrations.

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = \frac{(2x)^2 x}{(0.10)^2} = 7.3 \times 10^{-18}$$

This can now be solved for x.

$4x^3 = (7.3 \times 10^{-18})(0.010) = 7.3 \times 10^{-20}$

$x = 2.632 \times 10^{-7}$

The equilibrium concentration of H_2 can now be calculated.

$[H_2]_{equilibrium} = 2x = 5.3 \times 10^{-7}$ mol dm⁻³

As a rule of thumb, when $K_c < 10^{-3}$, approximations of this type are justified.

Exercises

19 The dissociation of hydrogen iodide into its elements takes place in a 1.0 dm³ container at 440 °C. When 1.0 mole of hydrogen iodide is used, it is found to have decreased to 0.78 moles at equilibrium.

   (a) Calculate the equilibrium constant for this reaction at this temperature.
   (b) Deduce whether the dissociation reaction is endothermic or exothermic, given that at 600 °C the value of K_c is 0.04.

20 The reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is carried out in a closed container with initial concentrations of both reactants of 1.6 mol dm⁻³. K_c for the reaction is 1.7×10^{-3}.

   Calculate the concentration of NO(g) at equilibrium.

21 (a) The reaction $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$ was studied at 550 °C. When 4.0 moles of CO and 6.4 moles of H_2O were introduced into a 1 dm³ vessel, the equilibrium mixture was found to contain 3.2 moles of both H_2 and CO_2.

   Calculate the concentrations of CO and H_2O at equilibrium and the value of K_c.

   (b) At the same temperature and pressure a different experiment was found to have 4.0 moles of both CO and H_2O, and 3.0 moles of both H_2 and CO_2 present in the mixture after a period of reaction. Show mathematically that this mixture had not reached equilibrium, and in which direction it will react.

Free energy and equilibrium

Different reactions have widely differing values of their equilibrium constant K_c, reflecting the range in the direction and extent of the chemical reaction. In some cases, such as the ionization of water, the reaction barely takes place, while other reactions, such as the combustion of methane, go almost to completion. What determines this fundamental difference between reactions?

To answer this, we will visit again some of the thermodynamic concepts we learned in Chapter 5. Remember that the Gibbs free energy change, ΔG, is a measure of the work that is available from a system. Its sign is used to predict the spontaneity of a reaction.

$\Delta G^{\ominus} = $ **negative** $\Rightarrow$ **reaction proceeds in the forward direction**

$\Delta G^{\ominus} = $ **positive** $\Rightarrow$ **reaction proceeds in the backward direction**

$\Delta G^{\ominus} = 0 \Rightarrow$ **reaction is at equilibrium**

Equilibrium occurs when a reaction mixture is at the minimum value of Gibbs free energy.

Figure 7.8 The total free energy of a reaction mixture as the reaction progresses. Starting with either pure reactants or pure products, the free energy decreases as the reaction moves towards equilibrium. In (a) $G^\ominus_{reactants} > G^\ominus_{products}$ so $\Delta G^\ominus$ is negative for the reaction and it progresses forward towards equilibrium. The equilibrium mixture consists largely of products. In(b) $G^\ominus_{reactants} < G^\ominus_{products}$ so $\Delta G^\ominus$ is positive for the reaction and very little reaction occurs before equilibrium. The equilibrium mixture consists largely of reactants.

The free energy change $\Delta G^\ominus$ can be calculated for a reaction from the equation:

$$\Delta G^\ominus = G^\ominus_{products} - G^\ominus_{reactants}$$

so at equilibrium:

$$G^\ominus_{products} = G^\ominus_{reactants}$$

Consider what happens to the total free energy during a reaction, such as when a fully charged battery is used until it is fully discharged (dead).

- At the start of the reaction, the total free energy of the reactants is greater than that of the products so a lot of work is available. $\Delta G^\ominus$ is negative and the reaction proceeds in the forward direction.
- As the battery discharges, the reaction continues converting reactants to products. So the total free energy of the reactants decreases while the free energy of the products increases. $\Delta G^\ominus$ becomes less negative and less work is available.
- The system reaches equilibrium when the total free energies of the reactants and products are equal and no work can be extracted from the system. The battery is dead.
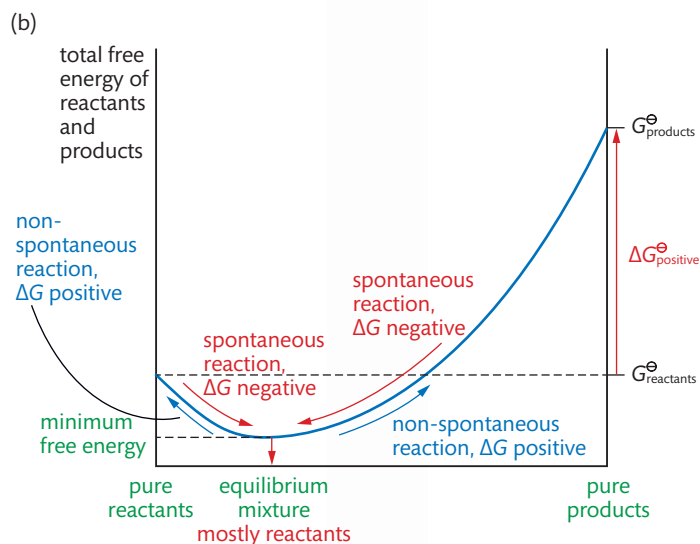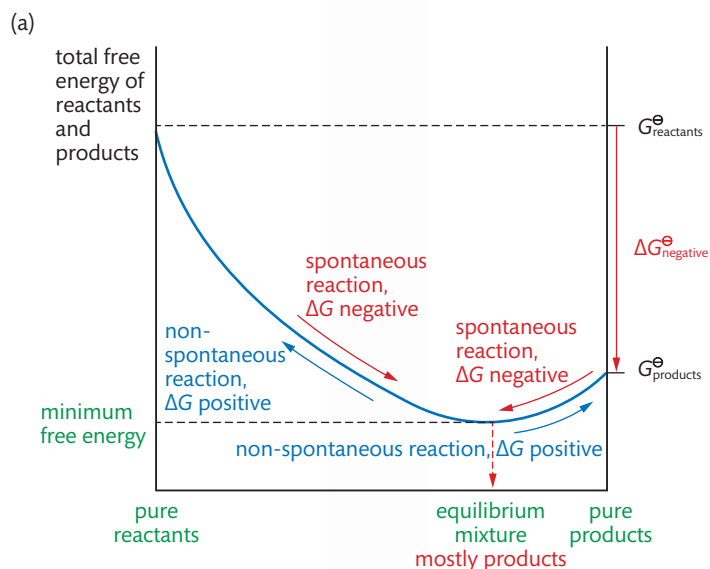
As the reaction progresses, there is a decrease in the total free energy as work is done by the system. Figure 7.8 shows that this occurs whether the reaction starts with pure reactants or with pure products. Because the free energy decreases in both directions, the reaction must go through a composition which corresponds to the minimum value of free energy. This is the equilibrium state where the net reaction stops. The relative amounts of reactants and products at equilibrium, the composition of this equilibrium mixture, is determined by the difference in free energy between the reactants and products.

The decrease in free energy during the reaction appears as work done by the system or as an increase in the entropy. Therefore the system has the highest possible value of entropy when free energy is at a minimum – in other words at equilibrium.

So $\Delta G^\ominus$ can be used to predict the spontaneity of a reaction and the position of equilibrium as follows.

- A reaction with a value of $\Delta G^\ominus$ that is both large and negative, appears to occur spontaneously and has an equilibrium mixture with a high proportion of products.
- A reaction with a value of $\Delta G^\ominus$ that is large and positive, appears to be non-spontaneous as only minute amounts of product form. It has an equilibrium mixture that is predominantly reactants.

(a)

(b)

K_c can be calculated from thermodynamic data

We have now identified two terms which relate to the position of equilibrium:

- K_c, the equilibrium constant;
- $\Delta G^{\ominus}$, the change in free energy.

Clearly these terms must be related to each other. The equation which shows this relationship is derived from the principles of thermodynamics.

$$\Delta G^{\ominus} = -RT \ln K$$

This equation is given in section 1 of the IB data booklet. In this equation:

$\Delta G^{\ominus}$ = standard free energy change of the reaction

R = the gas constant $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

T = the absolute temperature, in kelvin

$\ln K$ = the natural logarithm of the equilibrium constant, K_c.

From this equation we can deduce relationships between $\Delta G^{\ominus}$ and K_c for a reaction. These are summarized below.

$\Delta G^{\ominus}$	ln K	K	Equilibrium mixture
$\Delta G^{\ominus}$ negative	ln K positive	$K > 1$	mainly products
$\Delta G^{\ominus}$ positive	ln K negative	$K < 1$	mainly reactants
$\Delta G^{\ominus} = 0$	ln $K = 0$	$K = 1$	appreciable amounts of both reactants and products

The equation can also be used to calculate the equilibrium constant from the standard free energy change of a reaction and vice versa. This can be useful in situations where the equilibrium constant is difficult to measure directly, for example because a reaction may be too slow to reach equilibrium, or where the amounts of some of the components are too small to measure.

Worked example

The esterification reaction that produces ethyl ethanoate has a free energy change $\Delta G^{\ominus} = -4.38 \text{ kJ mol}^{-1}$.

$$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(aq)$$
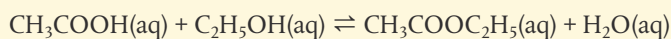
Calculate the value of the equilibrium constant of this reaction at 298 K.

Solution

$$\Delta G^{\ominus} = -RT \ln K_c$$

$\therefore -4.38 \times 1000 \text{ J mol}^{-1} = -(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln K_c$

$\ln K_c = \dfrac{-4380 \text{ J mol}^{-1}}{2478 \text{ J mol}^{-1}} = 1.77$

$\therefore K_c = e^{1.77} = 5.9$

We have now answered the question about what determines the fact that different reactions have such different values of equilibrium constant. The answer is the value of $\Delta G^{\ominus}$. Remember from Chapter 5 that this in turn depends on the values of enthalpy change (ΔH) and entropy change (ΔS) for the reaction.

The position of equilibrium corresponds to a maximum value of entropy for the system.

The equilibrium constant for a reaction is determined by the sign and value of its free energy change, $\Delta G^{\ominus}$, through the equation $\Delta G^{\ominus} = -RT \ln K_c$.
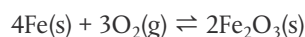
Kinetics and equilibrium

Rusting of iron is a complex process, but it can be represented by the equation:

$$4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$$

This is a heterogeneous equilibrium as its reaction components are in different phases, so we will not derive the equilibrium expression here. We can, however, calculate the value of the equilibrium constant from $\Delta G^\ominus = 1490 \times 10^6$ J, using the equation $\Delta G^\ominus = -RT \ln K_c$. This gives a value of $K_c = 10^{261}$. This very large value indicates that this is a thermodynamically favourable reaction, which will proceed towards completion. Clearly $\Delta G^\ominus$ is large and negative. But we know that rusting is a slow process, which can take years to complete.

This is an example of what has been mentioned earlier in this chapter – the magnitude of the equilibrium constant gives no information on the rate of reaction. Nonetheless, a study of the relative values of the rate constants for the forward and backward steps can help to explain some aspects of equilibria and Le Chatelier's principle.

We will consider a reaction which we will assume occurs in a single step. In other words, the overall reaction is an elementary bimolecular reaction (see Chapter 6).

$$A + B \rightleftharpoons C + D$$
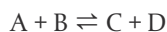
In this case (and only in this case), we can write the rate laws for the forward and backward reactions from the stoichiometry of the reaction.

$$\text{rate of forward reaction} = k\,[A]\,[B]$$

$$\text{rate of backward reaction} = k'\,[C]\,[D]$$

where k = rate constant for the forward reaction and k' = rate constant for the backward reaction.

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[C][D]}{[A][B]}$$

At equilibrium, the rate of the forward reaction = rate of backward reaction, so

$$k\,[A]\,[B] = k'\,[C]\,[D]$$

Rearranging this gives

$$\frac{k}{k'} = \frac{[C][D]}{[A][B]} \quad \text{or} \quad K_c = \frac{k}{k'}$$

In other words, the equilibrium constant is the ratio of the rate constants of the forward and backward reactions. This equation provides a fundamental link between chemical equilibrium and chemical kinetics.

Rusting of iron is a slow reaction which proceeds in the forward direction. In other words, it has a high equilibrium constant but a small rate constant.

The position of equilibrium is determined by the relative values of the rate constants of the forward and backward reactions.

- If $k \gg k' \Rightarrow K_c$ is large and the reaction progresses towards completion.
- If $k \ll k' \Rightarrow K_c$ is small and the reaction barely takes place.

We can finish this study by using the relationship between equilibrium constant and rate constants for a reaction to add to our interpretation of how equilibrium responds to changing conditions.

- Concentration: Increasing the concentration of reactant increases the rate of the forward reaction and so shifts the equilibrium to the right. Increasing the concentration of product increases the rate of the backward reaction and so shifts the equilibrium to the left. The value of the equilibrium constant stays constant because concentration changes do not affect the values of the rate constants.
- Catalyst: Adding a catalyst increases the values of k and k' by the same factor so the ratio of their values, the equilibrium constant, is not affected.
- Temperature dependence of K_c: From the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$, we know that the rate constant increases with increasing temperature. But because the activation energies of the forward and backward reactions are different, their rate constants k and k' are differently affected by temperature. So the ratio k/k', the equilibrium constant, is temperature dependent. For an endothermic reaction, in which E_a(forward reaction) > E_a(backward reaction), the increase in temperature has a greater effect on increasing k than k', so K_c increases as temperature increases.

NATURE OF SCIENCE

Le Chatelier's principle enables qualitative predictions about changes to systems at equilibrium to be made, but we rely on thermodynamics for an explanation of these changes. Several seemingly different approaches can be used, but because they are applications of the same thermodynamic and kinetic concepts they support the same conclusions. Quantitative measurements provide evidence for equilibrium theory and enable us to make calculations of related variables.

Exercises

22 Which of the following correctly describes the entropy and free energy of a system at equilibrium?

	Entropy S	Free energy G
A	maximum value	maximum value
B	minimum value	maximum value
C	maximum value	minimum value
D	minimum value	minimum value

23 What is the sign of $\Delta G^{\ominus}$ for a reaction when:

(a) $K_c = 1$
(b) $K > 1$
(c) $K < 1$

24 (a) The ionization of water has an equilibrium constant 1.00×10^{-14} at 298 K.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
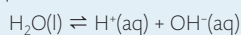
Calculate $\Delta G^{\ominus}$ for this reaction at this temperature.

(b) At 313 K the equilibrium constant has a value of 2.92×10^{-14}. What can you conclude about the enthalpy change ΔH of the reaction?

Practice questions

1 Which statement about chemical equilibria implies they are dynamic?

    A The position of equilibrium constantly changes.
    B The rates of forward and backward reactions change.
    C The reactants and products continue to react.
    D The concentrations of the reactants and products continue to change.

2 The reaction below represents the Haber process for the industrial production of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad\qquad \Delta H^{\ominus} = -92 \text{ kJ}$$
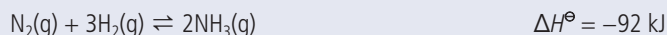
The optimum conditions of temperature and pressure are chosen as a compromise between those that favour a high yield of ammonia and those that favour a fast rate of production. Economic considerations are also important. Which statement is correct?

    A A higher temperature would ensure a higher yield and a faster rate.
    B A lower pressure would ensure a higher yield at a lower cost.
    C A lower temperature would ensure a higher yield and a faster rate.
    D A higher pressure would ensure a higher yield at a higher cost.

3 What is the effect of an increase of temperature on the yield and the equilibrium constant for the following reaction?

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(l) \qquad\qquad \Delta H^{\ominus} = -128 \text{ kJ}$$
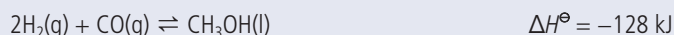
	Yield	Equilibrium constant
A	increases	increases
B	increases	decreases
C	decreases	increases
D	decreases	decreases

4 Consider the equilibrium between methanol, $CH_3OH(l)$, and methanol vapour, $CH_3OH(g)$.

$$CH_3OH(l) \rightleftharpoons CH_3OH(g)$$
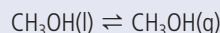
What happens to the position of equilibrium and the value of K_c as the temperature decreases?

	Position of equilibrium	Value of K_c
A	shifts to the left	decreases
B	shifts to the left	increases
C	shifts to the right	decreases
D	shifts to the right	increases

5 0.50 mol of $I_2(g)$ and 0.50 mol of $Br_2(g)$ are placed in a closed flask. The following equilibrium is established.

$$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$$
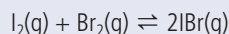
The equilibrium mixture contains 0.80 mol of $IBr(g)$. What is the value of K_c?

    A 0.64   **B** 1.3   **C** 2.6   **D** 64

6 An increase in temperature increases the amount of chlorine present in the following equilibrium.

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

What is the best explanation for this?

    A The higher temperature increases the rate of the forward reaction only.
    B The higher temperature increases the rate of the reverse reaction only.

C The higher temperature increases the rate of both reactions but the forward reaction is affected more than the reverse.

D The higher temperature increases the rate of both reactions but the reverse reaction is affected more than the forward.

7 Consider the following reversible reaction.

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$
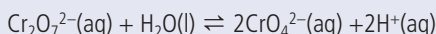
What will happen to the position of equilibrium and the value of K_c when more H^+ ions are added at constant temperature?

|	Position of equilibrium	Value of K_c
A	shifts to the left	decreases
B	shifts to the right	increases
C	shifts to the right	does not change
D	shifts to the left	does not change

8 Consider this equilibrium reaction in a sealed container:

$$H_2O(g) \rightleftharpoons H_2O(l)$$
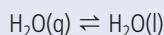
What will be the effect on the equilibrium of increasing the temperature from 20 °C to 30 °C?

A More of the water will be in the gaseous state at equilibrium.

B More of the water will be in the liquid state at equilibrium.

C At equilibrium the rate of condensation will be greater than the rate of evaporation.

D At equilibrium the rate of evaporation will be greater than the rate of condensation.

9 Which statement is correct for the equilibrium:

$$H_2O(l) \rightleftharpoons H_2O(g)$$
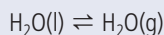
in a closed system at 100 °C?

A All the $H_2O(l)$ molecules have been converted to $H_2O(g)$.

B The rate of the forward reaction is greater than the rate of the reverse reaction.

C The rate of the forward reaction is less than the rate of the reverse reaction.

D The pressure remains constant.

10 (a) Consider the following equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad\qquad \Delta H^\ominus = -198 \text{ kJ mol}^{-1}$$
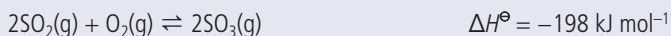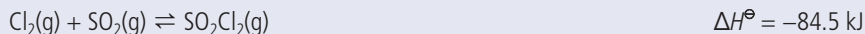
  (i) Deduce the equilibrium constant expression, K_c, for the reaction. (1)

  (ii) State and explain the effect of increasing the pressure on the yield of sulfur trioxide. (2)

  (iii) State and explain the effect of increasing the temperature on the yield of sulfur trioxide. (2)

  (iv) State the effects of a catalyst on the forward and reverse reactions, on the position of equilibrium, and on the value of K_c. (3)

(b) When a mixture of 0.100 mol NO, 0.051 mol H_2, and 0.100 mol H_2O were placed in a 1.0 dm³ flask at 300 K, the following equilibrium was established.

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$
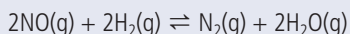
At equilibrium, the concentration of NO was found to be 0.062 mol dm⁻³. Determine the equilibrium constant, K_c, of the reaction at this temperature. (4)

(Total 12 marks)

11 Consider the following equilibrium reaction.

$$Cl_2(g) + SO_2(g) \rightleftharpoons SO_2Cl_2(g) \qquad \Delta H^\ominus = -84.5 \text{ kJ}$$

In a 1.00 dm³ closed container, at 375 °C, 8.60×10^{-3} mol of SO_2 and 8.60×10^{-3} mol of Cl_2 were introduced. At equilibrium, 7.65×10^{-4} mol of SO_2Cl_2 was formed.

(a) Deduce the equilibrium constant expression, K_c, for the reaction. (1)

(b) Determine the value of the equilibrium constant, K_c. (3)

(c) If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO_2Cl_2 and the value of K_c will increase or decrease. (3)

(d) If the volume of the container is changed to 1.50 dm³, predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K_c. (3)

(e) Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2. (2)
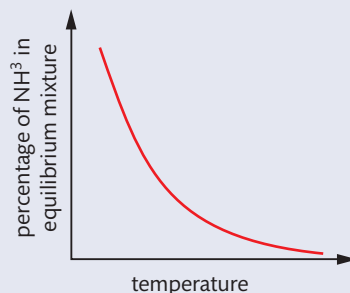
(Total 12 marks)

12 The Haber process enables the large-scale production of ammonia needed to make fertilizers. The equation for the Haber process is given below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
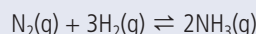
The percentage of ammonia in the equilibrium mixture varies with temperature.

(a) Use the graph to deduce whether the forward reaction is exothermic or endothermic and explain your choice. (2)

(b) State and explain the effect of increasing the pressure on the yield of ammonia. (2)

(c) Deduce the equilibrium constant expression, K_c, for the reaction. (1)

(d) A mixture of 1.00 mol N_2 and 3.00 mol H_2 was placed in a 1.0 dm³ flask at 400 °C. When the system was allowed to reach equilibrium, the concentration of NH_3 was found to be 0.062 mol dm⁻³. Determine the equilibrium constant, K_c, of the reaction at this temperature. (3)

(e) Iron is used as a catalyst in the Haber process. State the effect of a catalyst on the value of K_c. (1)

(Total 9 marks)

13 An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
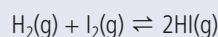
(a) Outline the characteristics of a homogeneous chemical system that is in a state of equilibrium. (2)

(b) Deduce the expression for the equilibrium constant, K_c. (1)

(c) Predict what would happen to the position of equilibrium if the pressure is increased from 1 atm to 2 atm. (1)

(d) The value of K_c at 500 K is 160 and the value of K_c at 700 K is 54. Deduce what this information tells us about the enthalpy change of the forward reaction. (1)

(e) At a temperature just above 700 K it is found that when 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a 4.00 dm^3 flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature. (4)

(f) The reaction can be catalysed by adding platinum metal. State and explain what effect the addition of platinum would have on the value of the equilibrium constant. (2)
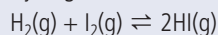
(*Total 11 marks*)

14 (a) What is the value of $\Delta G^\ominus$ for a reaction in which $K = 1$? (1)

(b) Nitrogen oxide, NO, is oxidized in the air to NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
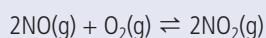
At 298 K, the value of K_c for this reaction is 1.7×10^{12}. Calculate the value of $\Delta G^\ominus$ for the reaction. (3)

(*Total 4 marks*)

15 Hydrogen and iodine react together as follows:

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

(a) 6.0 moles of $H_2(g)$ and 3.0 moles of $I_2(g)$ are placed in a 1.0 dm^3 flask. At the temperature of the reaction, $K_c = 4.00$. Calculate the equilibrium concentrations of $H_2(g)$, $I_2(g)$ and HI. (3)

(b) At a different temperature, the value of K_c for the reaction is 51.50. A sample of HI was placed into a 1.0 dm^3 flask at this temperature. At equilibrium, 0.218 mol $H_2(g)$ was present.

  (i) How much HI was originally placed into the flask? (1)

  (ii) How much I_2 and HI were present at equilibrium? (2)

(*Total 6 marks*)