

7 Equilibrium

Learning objectives

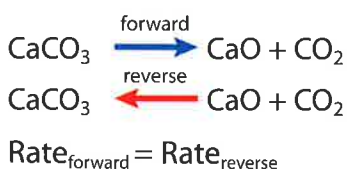
- Understand that a reversible reaction can come to a state of equilibrium
- Explain what is meant by dynamic equilibrium

Extension

At the microscopic level all reactions are reversible – if two particles come together with the formation of a bond, that bond could also break as the two components move apart. This is often likened to the idea of running a film backwards, so that, at the molecular level, the ‘film of a reaction’ can always be run backwards.

Calcium oxide is also known as quicklime or lime. When heated strongly it glows bright white. This was used as theatre lighting, which gave rise to the phrase *in the limelight*.

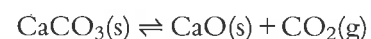
A system has reached equilibrium when no further change appears to occur – all concentrations remain constant.



7.1 Equilibrium

7.1.1 Reversible reactions

As the name suggests, reversible reactions are reactions that can go either way. In a common reversible reaction, calcium carbonate, when heated strongly, decomposes to form calcium oxide and carbon dioxide. But calcium oxide also reacts with carbon dioxide to form calcium carbonate:



The double arrow (\rightleftharpoons) shows that the reaction is reversible.

Equilibrium

The decomposition of CaCO_3 is reversible, but what happens if we put solid calcium carbonate in an open container and keep it at a constant high temperature for an extended period of time (Figure 7.1)?

All the calcium carbonate is converted to calcium oxide because the carbon dioxide escapes and is not available to react with the calcium oxide to re-form calcium carbonate.

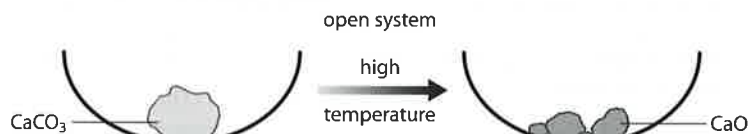


Figure 7.1 In an open container, all the calcium carbonate is converted to calcium oxide.

If we do exactly the same experiment, at the same temperature, but with the calcium carbonate in a sealed container (Figure 7.2), we find that after the same amount of time we still have some calcium carbonate present. No matter how long we continue the experiment (keeping it at a constant temperature), the amounts of calcium carbonate, calcium oxide and carbon dioxide stay the same. The reaction appears to have stopped, and we say that the system has reached a state of **equilibrium**.

The reaction has not actually stopped but is proceeding in both directions at equal rates. In other words, the calcium carbonate is

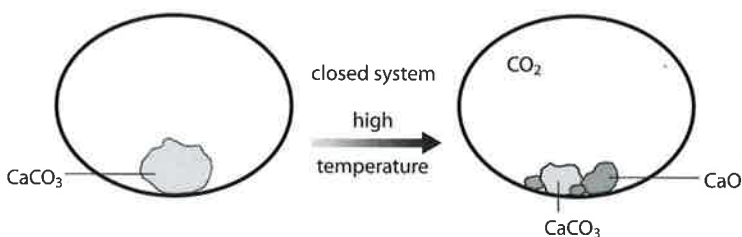


Figure 7.2 In a closed system, a state of equilibrium is attained.

decomposing to give calcium oxide and carbon dioxide at exactly the same rate as the calcium oxide and carbon dioxide are recombining to form calcium carbonate. This type of equilibrium is called a **dynamic equilibrium**. All equilibria in chemistry are dynamic.

In **dynamic equilibrium**, macroscopic properties are constant (concentrations of all reactants and products remains constant) and the rate of the forward reaction is equal to the rate of the reverse reaction.

Nature of science

Radioisotopes can be used to provide evidence for the dynamic nature of equilibrium. If, for instance a small amount of calcium carbonate labelled with radioactive ^{14}C is introduced into the equilibrium system shown in Figure 7.2, there will be no overall change in the amount of CO_2 present but the radioactive ^{14}C will be distributed between the CaCO_3 and the CO_2 , indicating that reactions are still going on.

Equilibrium and rate of reaction

Consider the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. If we start with just hydrogen and iodine vapour in a closed container at a certain temperature and follow how the concentration of hydrogen and hydrogen iodide change with time, we obtain a graph of the form shown in Figure 7.3.

The concentration of H_2 decreases at first, until it levels off when equilibrium is reached. The concentration of HI is initially zero, but it increases until it flattens off and does not change any more after equilibrium has been reached. If we plot a graph of rate against time for the forward and reverse reactions we get a graph of the form shown in Figure 7.4.

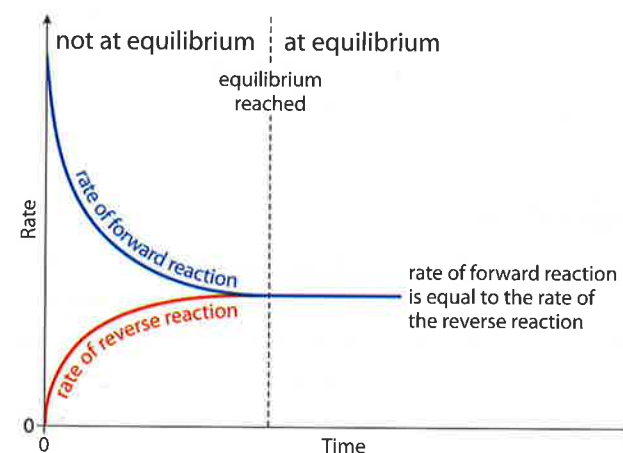


Figure 7.4 Graph showing how the rates of the forward and reverse reactions change as a reversible reaction comes to equilibrium.

Exam tip

When asked to define dynamic equilibrium you must address both the ‘dynamic’ part and the ‘equilibrium’ part.

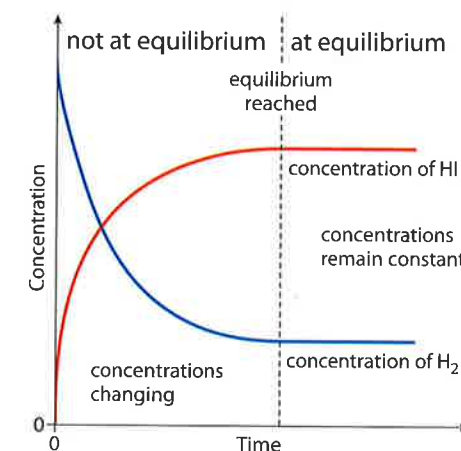
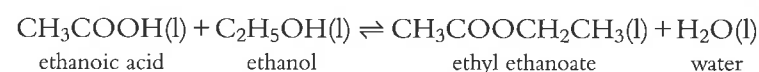


Figure 7.3 Graph showing how the concentrations of hydrogen and hydrogen iodide change with time.

The characteristics of the equilibrium state

Some of these have been discussed above.

- 1 **Macroscopic properties are constant at equilibrium** – at equilibrium the concentrations of all reactants and products remain constant.
- 2 **At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction.**
- 3 **Equilibrium can be attained only in a closed system** – as we saw above, if calcium carbonate is heated in an open container, equilibrium is never reached because the carbon dioxide escapes and has no opportunity to recombine with the calcium oxide. In effect, a reaction going on in solution, but not involving the production of a gas, represents a closed system.
- 4 **All species in the chemical equation are present in the equilibrium reaction mixture** – for example, if nitrogen and hydrogen are allowed to come to equilibrium according to the equation $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, the reaction mixture at equilibrium contains nitrogen, hydrogen and ammonia.
- 5 **Equilibrium can be attained from either direction** – consider the equilibrium:



If we mix together ethanoic acid and ethanol in the presence of an acid catalyst and incubate them at 60 °C, they come to equilibrium. If we do the same starting with ethyl ethanoate and water, they also come to equilibrium. A state of equilibrium, in which all four species are present, can be reached by mixing:

- ethanoic acid and ethanol
- ethyl ethanoate and water
- all four substances
- any three substances.

In each case, equilibrium is reached but the actual concentrations present at equilibrium depend on how much of each substance we started with.

Physical equilibria

All the above reactions involved **chemical equilibria** – equilibria established as a result of chemical reactions. There are also **physical equilibria** (equilibria involving a change in state), for example, the equilibrium between a liquid and its vapour.

Evaporation

When a liquid is in an open container it evaporates. At the molecular level, the particles must overcome the forces holding them in the liquid (intermolecular forces) in order to escape into the gas phase – evaporation is an endothermic process.

The spread of molecular kinetic energies in a liquid is shown in Figure 7.5. Molecules in the shaded region have sufficient energy to escape and evaporate. The faster moving molecules (higher kinetic energy) are able to overcome the intermolecular forces, so they escape first and the average kinetic energy of the particles in the liquid phase drops. Average kinetic energy is an indication of the temperature and, therefore, the temperature of the liquid falls. Heat is drawn from the surroundings to allow further molecules to evaporate. If the container is open then all the liquid will eventually evaporate.

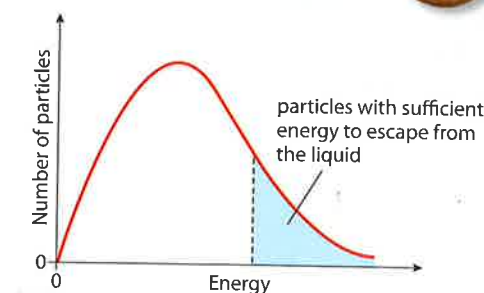


Figure 7.5 The spread of molecular energies in a liquid.

Liquid–vapour equilibrium

Consider a volatile liquid, such as bromine, in a closed container (Figure 7.6). At the beginning there are no molecules of vapour above the liquid – molecules escape from the liquid (evaporation) but there is no condensation (Figure 7.6a). As molecules of vapour appear, these strike the surface of the liquid and some re-enter it – this process is condensation. At first the rate of condensation is low, but as the number of molecules in the vapour phase increases the rate of condensation increases (Figure 7.6b). Eventually the rate of condensation becomes equal to the rate of evaporation and nothing more appears to change (Figure 7.6c).

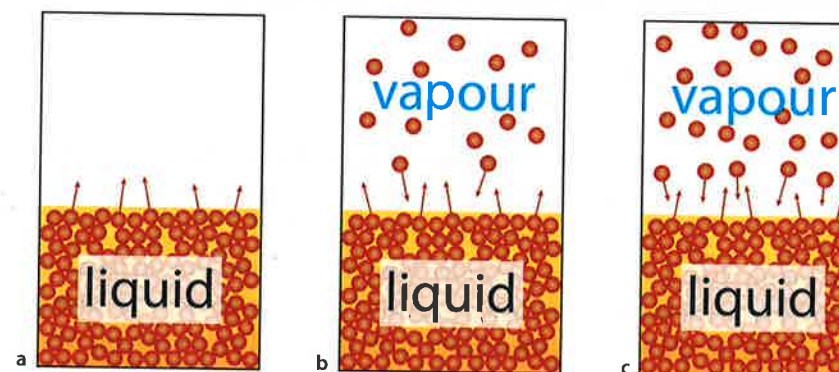


Figure 7.6 Equilibrium is attained when the rate of evaporation is equal to the rate of condensation.

Because the rate of evaporation and the rate of condensation are equal, this is a dynamic equilibrium.

When the rate of evaporation (vaporisation) is equal to the rate of condensation, the colour of the vapour remains constant (it does not get any darker or lighter) and a state of equilibrium has been reached. This is known as a **phase equilibrium** because it involves a change of phase (state).

7.1.2 Position of equilibrium

The 'position of equilibrium' refers to the relative amounts of reactants and products present at equilibrium. Some reactions go almost to completion, for example:

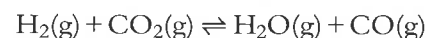


Learning objectives

- Understand what is meant by the position of equilibrium
- Apply Le Chatelier's principle to predict the effect of changes in conditions on the position of equilibrium

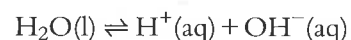
Equilibrium does not imply 50% reactants and 50% products.

At 700 K, the position of equilibrium lies a long way to the **right**. There is a large amount of N_2 and O_2 and not very much NO at equilibrium – roughly one and a half million times as many N_2 and O_2 molecules as NO molecules. However, for:



at 1100 K, the total number of H_2 and CO_2 molecules at equilibrium is roughly equal to the total number of H_2O and CO molecules – the equilibrium is evenly balanced.

Water dissociates according to the equation:



At 298 K the number of water molecules present at equilibrium is over 250 million times greater than the total number of H^+ and OH^- ions. The position of this equilibrium lies a long way to the **left** – not many H^+ and OH^- ions are present at equilibrium.

The effect of changing conditions on the position of equilibrium – Le Chatelier's principle

Le Chatelier's principle

If a system at equilibrium is subjected to a change, the position of equilibrium will shift in order to minimise the effect of the change.

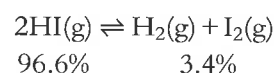
This means that, if we take a particular system at equilibrium under a certain set of conditions and change one of those conditions, such as the temperature or the pressure, the system will move to a new position of equilibrium. **Le Chatelier's principle** allows us to predict in which direction the position of equilibrium will shift.

The effect of temperature

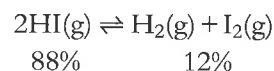
Consider the equilibrium:



At room temperature (298 K), the number of molecules of HI is roughly 28 times the total number of molecules of H_2 and I_2 :



However, when the system reaches equilibrium at 700 K, the number of HI molecules is only approximately seven times the total number of H_2 and I_2 molecules:



This means that there are relatively more H_2 and I_2 molecules present at equilibrium at 700 K than at 298 K. In this case, as the temperature increases, the position of equilibrium shifts to the right (there is more H_2 and I_2 present).

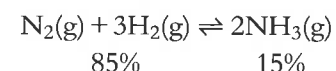
The effect of a temperature change on the position of an equilibrium can be considered in terms of Le Chatelier's principle. The value of ΔH given above refers to the forward direction – so in this case the forward reaction is endothermic and the reverse reaction is exothermic.

As the temperature is increased, the position of equilibrium shifts in the direction that will minimise the effect of the change. So to minimise the effect of the increase in temperature in this reaction, the position of equilibrium shifts in the endothermic direction to take in the heat that is added (heat energy is converted to chemical energy). The endothermic direction is to the right and, therefore, as the temperature is increased the position of equilibrium shifts to the right to produce relatively more H_2 and I_2 .

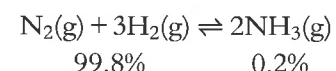
Consider another reaction:



This time, at 300 K and 10 atmosphere pressure, we have:



At 700 K and the same pressure:



In this case, increasing the temperature causes the position of equilibrium to be shifted to the left, i.e. there is less ammonia present at equilibrium at the higher temperature.

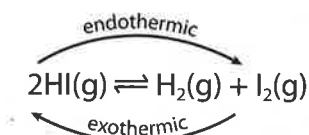
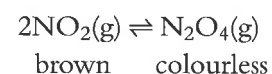
As the temperature is increased, the position of equilibrium shifts in the endothermic direction to take in heat and minimise the effect of the change. This time, the endothermic direction is to the left and, therefore, as the temperature is increased the position of equilibrium shifts to the left:

HEAT reaction mixture: position of equilibrium is shifted in the endothermic direction.

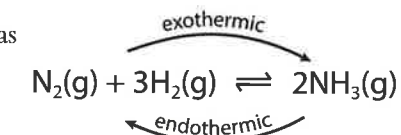
COOL reaction mixture: position of equilibrium is shifted in the exothermic direction.

The effect of pressure

Consider this equilibrium:



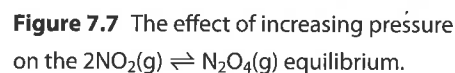
This is analogous to the idea that, if the heating is turned up you might take off your jumper in order to minimise the change and keep your temperature roughly the same as it was before.



Henri Louis Le Chatelier (1850–1936) was a French chemist.

His original statement on his principle is:

Every system in stable equilibrium submitted to the influence of an exterior force which tends to cause variation, either in its temperature or its condensation (pressure, concentration, number of molecules in the unit of volume) in its totality or only in some one of its parts can undergo only those interior modifications which, if they occur alone, could produce a change of temperature, or of condensation, of a sign contrary to that resulting from the exterior force.



$PV = nRT$, so the number of moles of gas is proportional to the volume and pressure of the gas. If we imagine this reaction going to completion and two moles of $\text{NO}_2(\text{g})$ being completely converted to one mole of $\text{N}_2\text{O}_4(\text{g})$, the volume of gas at the end would be half what we started with. If this reaction were carried out in a vessel of constant volume, the conversion of two moles of $\text{NO}_2(\text{g})$ to one mole of $\text{N}_2\text{O}_4(\text{g})$ would involve the pressure decreasing to half its original value.

Exam tip

You must remember the word 'gas' – solids and liquids are affected very little by changes in pressure.

Some NO_2 (brown) is put into a sealed gas syringe (Figure 7.7). As the pressure is increased, the colour initially gets slightly darker because the same number of molecules are squeezed into a smaller space. The mixture then becomes less brown as a new position of equilibrium is established. At higher pressure there is less NO_2 (brown) and more N_2O_4 (colourless) present in the equilibrium mixture, and therefore it is a paler brown than at lower pressure. So it can be seen that, in this case, as the pressure increases, the position of equilibrium shifts to the right (more N_2O_4 is present at equilibrium).

This reaction involves a decrease in the number of gaseous molecules, from two on the left-hand side to one on the right-hand side. Two moles of gas take up more space than one mole of gas, so as the pressure is increased the position of equilibrium shifts in order to minimise the effect of this pressure change. This is achieved by the position of equilibrium shifting to the side with fewer gaseous molecules and therefore lower volume – that is, the right-hand side.

Consider the following reaction:



This reaction involves the conversion of two molecules of **gas** (on the left-hand side) to three molecules of **gas** (on the right-hand side). As the pressure is increased, the position of equilibrium shifts to the left-hand side – i.e. the side with **fewer gas molecules** – to minimise the effect of the change.

Now consider this equilibrium:



Because there is the same number of molecules of **gas** on both sides, changing the pressure has **no effect** on the position of equilibrium.

In these three examples, it has been stressed that we have to consider the number of molecules of **gas** when predicting the effect of a change in pressure on the position of equilibrium.

Consider once again the decomposition of calcium carbonate:

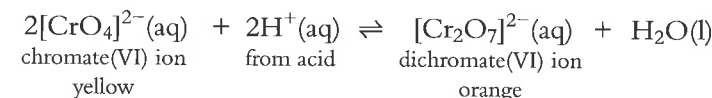


There is one molecule of gas on the right-hand side but none on the left-hand side – therefore increasing the pressure causes the position of equilibrium to shift to the left.

If a reaction involves a change in the number of gas molecules, an increase in pressure results in the position of equilibrium shifting in the direction that gives a decrease in the number of gas molecules.

The effect of concentration

Consider this system at equilibrium:



The fact that the colour of the solution on the left of Figure 7.8 is yellow indicates that the position of equilibrium lies to **left**, so there is significantly more of the yellow ion present than the orange ion.

When some acid (H^+) is added to the mixture in the flask, the colour of the solution changes to orange. There is now much more of the orange dichromate(VI) ion present, which means that the position of equilibrium has shifted to the right. This can be explained in terms of Le Chatelier's principle – as more acid is added, the position of equilibrium shifts to the right to use up the excess acid and so minimise the effect of the change.

If we now add an alkali (OH^-) to the solution, the colour changes back to yellow. The OH^- ions react with the H^+ ions to form water. So adding alkali reduces the concentration of H^+ ions in the solution and the position of equilibrium must shift to the left in order to minimise the effect of the change by replacing the H^+ ions.

Test yourself

- 1** Predict the effect of increasing pressure on the position of equilibrium in the following systems:
 - a** $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$
 - b** $\text{N}_2\text{O}_5(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons 3\text{NO}_2(\text{g})$
 - c** $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_3(\text{g})$
- 2** Predict the effect of increasing temperature on the position of equilibrium in the following systems:
 - a** $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_3(\text{g})$
 $\Delta H = -40 \text{ kJ mol}^{-1}$
 - b** $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 $\Delta H = +206 \text{ kJ mol}^{-1}$
 - c** $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
 $\Delta H = -90 \text{ kJ mol}^{-1}$
- 3** Predict the effect of the following changes on the position of equilibrium:
 - a** Removing the CO_2 from the equilibrium:
 $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - b** Adding acid (H^+) to the system:
 $\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$
 - c** Adding sodium hydroxide to the system:
 $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$
 - d** Adding sodium hydroxide to the system:
 $3\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons 5\text{HI}(\text{aq}) + \text{HIO}_3(\text{aq})$

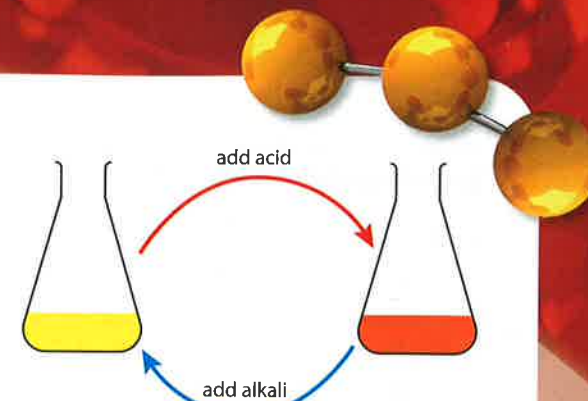


Figure 7.8 The chromate(VI) / dichromate(VI) equilibrium.



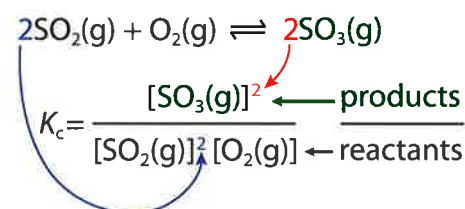
In general, if the concentration of one of the species in an equilibrium mixture is increased, the position of equilibrium shifts to the opposite side to reduce the concentration of this species.

Learning objectives

- Write the expression for the equilibrium constant for a given reversible reaction
- Understand what is meant by reaction quotient
- Understand the connection between the size of the equilibrium constant and the extent of reaction
- Understand that it is possible to write more than one equilibrium constant for a particular reaction
- Understand how changing conditions affect the value of the equilibrium constant and the position of equilibrium

All concentrations are measured at equilibrium.

[A] represents the concentration of A at equilibrium.

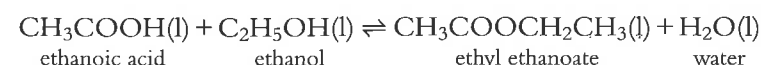


Extension

The equilibrium constant K_p is often calculated. This is the equilibrium constant expressed in terms of partial pressures. The partial pressure of a gas in a mixture of gases is the pressure that the gas would exert if it were present in the container by itself.

7.1.3 Equilibrium constants

A series of experiments is carried out on the reaction:



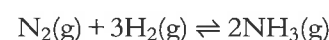
Various known amounts of ethanol and ethanoic acid are reacted together and allowed to come to equilibrium at the same temperature. The **equilibrium concentrations** of each component of the reaction mixture are determined and it is found that the ratio:

$$\frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{C}_2\text{H}_5\text{OH}(\text{l})]}$$

is constant for all the experiments

where $[\text{CH}_3\text{COOH}(\text{l})]$ represents the concentration of CH_3COOH at equilibrium.

If the same procedure is repeated for the reaction:



it is found that the following ratio is constant at a particular temperature:

$$\frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

This leads us to the general **equilibrium law**. For the reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ (where all reactants are in the same phase), the value of the following ratio is constant at a particular temperature:

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

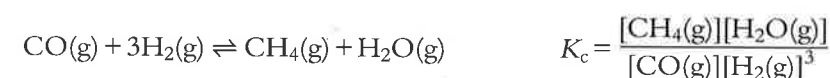
Because this ratio is constant at a particular temperature we can write:

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

where K_c is the **equilibrium constant**. The 'c' indicates that this equilibrium constant is expressed in terms of concentrations.

K_c is constant for a particular reaction at a particular temperature.

The expressions for the equilibrium constant for some reactions are given below:



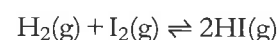
What use is an equilibrium constant?

An equilibrium constant provides information about how far a reaction proceeds at a particular temperature.

The values of the equilibrium constants for a series of reactions at 298 K are given in Table 7.1. These equilibrium constants are all very much greater than one. These reactions proceed almost totally towards the products, so that there is virtually no hydrogen and halogen in the equilibrium mixture. However, for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ the value of the equilibrium constant is 10^{-31} at 298 K. This value is very much less than one, indicating that the reaction hardly proceeds at all towards the products – that is, the position of equilibrium lies a long way to the left.

The reaction quotient

The reaction quotient, Q , is the ratio of the concentrations of the reactants and products (raised to the appropriate powers) at any point in time. An expression for Q is exactly the same as that for the equilibrium constant – except that the concentrations are **not** equilibrium concentrations. So, for the reaction:



$$Q = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

When the system is at equilibrium, the concentrations are all equilibrium concentrations and the value of Q is equal to the value of K_c at that temperature.

The value K_c for the above reaction is 54 at 700 K. If we mix together 2 mol HI, 1 mol H_2 and 1 mol I_2 in a 1 dm^3 vessel then the concentrations of the species present in the reaction mixture are $[\text{HI}] = 2 \text{ mol dm}^{-3}$, $[\text{H}_2] = 1 \text{ mol dm}^{-3}$ and $[\text{I}_2] = 1 \text{ mol dm}^{-3}$.

$$\text{So the value of } Q \text{ is } \frac{2^2}{1 \times 1} = 4$$

Extension

You only need to write equilibrium constants for homogeneous equilibria (all reactants and products in the same physical state). Reactions involving solids and gases, for example, are more complicated and the concentrations of pure solids do not appear in the equilibrium constant expression. The equilibrium constant for the decomposition of CaCO_3 (page 278) is $K_c = [\text{CO}_2]$.

$K_c \gg 1$ – the reaction proceeds almost totally towards the products.

$K_c \ll 1$ – the reaction hardly proceeds at all towards the products.

Reaction	K_c
$\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g})$	10^{95}
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$	10^{33}
$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2\text{HBr}(\text{g})$	10^{19}

Table 7.1 Equilibrium constants for reactions at 298 K.

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}}$$

Because the value of Q is not equal to the value of the equilibrium constant, we can see immediately that the system is not at equilibrium. We can also see that, because the value of Q is less than that of K_c , the reaction must proceed to the right (to produce more HI) to reach equilibrium. If the reaction proceeds to the right, there will be more HI and less H_2 and I_2 in the reaction mixture and the value of Q will increase.

If 0.5 mol of the H_2 reacts with 0.5 mol I_2 to produce an extra 1 mol HI then the new concentrations are:

$$[HI] = 3 \text{ mol dm}^{-3}, [H_2] = 0.5 \text{ mol dm}^{-3} \text{ and } [I_2] = 0.5 \text{ mol dm}^{-3}$$

So the new value of Q is $\frac{3^2}{0.5 \times 0.5} = 36$

The system is still not at equilibrium because Q is not equal to K_c , but it is closer to equilibrium. Because the value of Q is still smaller than K_c , more H_2 and I_2 must react together to form HI.

In general:

- If $Q < K_c$ then the reaction must proceed towards the products (to the right) to reach equilibrium.
- If $Q > K_c$ then the reaction must proceed towards the reactants (to the left) to reach equilibrium.

Two different values of the equilibrium constant for the same reaction under the same conditions.

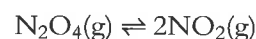
There can be different values of K_c for the same reaction under the same conditions.

Consider the equilibrium $2NO_2(g) \rightleftharpoons N_2O_4(g)$. The expression for its equilibrium constant is:

$$K_c = \frac{[N_2O_4(g)]}{[NO_2(g)]^2}$$

and the equilibrium constant is 0.69 at 400 K.

However, the reaction could also have been written the other way round:



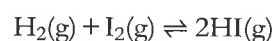
The expression for the equilibrium constant in this case is:

$$K_c' = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

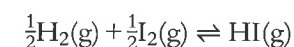
The value of the equilibrium constant at 400 K for this reaction is $\frac{1}{0.69}$ or 1.45.

It can be seen then that the value of the equilibrium constant depends on how the reaction is written, and therefore these constants are only useful when quoted in conjunction with their equilibrium reactions.

Consider the equilibrium:



which can also be written:



Both expressions are completely valid and accurate representations of the reaction.

The equilibrium constant expression for the first of these is:

$$K_c' = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

whereas for the second reaction it is:

$$K_c'' = \frac{[HI(g)]}{[H_2(g)]^{\frac{1}{2}}[I_2(g)]^{\frac{1}{2}}}$$

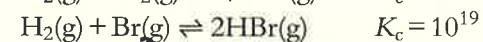
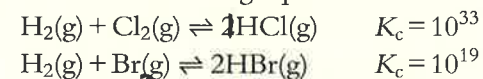
At 700 K, $K_c' = 54$, whereas for the second reaction at the same temperature $K_c'' = \sqrt{54}$ or 7.3. The relationship between the two equilibrium constants is $K_c'' = \sqrt{K_c'}$.

? Test yourself

4 Write expressions for the equilibrium constants for the following reactions:

- $NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$
- $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
- $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
- $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
- $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

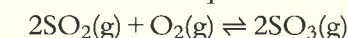
5 Given the following equilibrium constants:



work out the values for the equilibrium constants for these reactions:

- $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$
- $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$
- $HBr(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g)$

6 a Consider the equilibrium:



The value of the equilibrium constant at 500 K is 1.03×10^{12} . What is the value of the equilibrium constant for the reaction: $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ at 500 K?

b The value of the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 K is 59.8. What is the value of the equilibrium constant for the reaction: $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ at the same temperature?

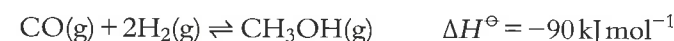
The principal use of HI is to make hydriodic acid, which is used to make iodides and as a reducing agent. Hydriodic acid is a controlled chemical in the USA because it can be used in the production of methamphetamine (crystal meth).

How changing the conditions affects the value of the equilibrium constant

The value of the equilibrium constant for a particular reaction is **only** affected by a change in **temperature**.

The effect of temperature

Exothermic reactions



The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\text{CH}_3\text{OH(g)}]}{[\text{CO(g)}][\text{H}_2\text{(g)}]^2}$$

We use Le Chatelier's principle to explain the effect of temperature changes on the equilibrium. The reaction is exothermic in the forward direction and so, according to Le Chatelier's principle, an increase in temperature causes the position of equilibrium to shift in the endothermic direction – that is, the position of equilibrium shifts to the left. The concentration on the top of the expression for K_c decreases and the concentrations on the bottom increase. Therefore, the overall value of K_c decreases (Table 7.2).

For an exothermic reaction, the value of the equilibrium constant decreases as the temperature is increased.

Endothermic reactions



$$K_c = \frac{[\text{NO(g)}]^2}{[\text{N}_2\text{(g)}][\text{O}_2\text{(g)}]}$$

As the temperature increases, the value of the equilibrium constant increases (Table 7.3). This is an endothermic reaction and so, according to Le Chatelier's principle, as the temperature increases the position of equilibrium shifts in the endothermic direction in order to take in heat and reduce the effect of the change. The position of equilibrium is shifted to the right so that more NO and less N_2 and O_2 are present at equilibrium. This results in the value of the equilibrium constant increasing.

Catalysts and the equilibrium constant

Catalysts are substances that increase the rate of a chemical reaction without being permanently changed in the process. Because they are the same at the beginning as at the end of the reaction, catalysts do not appear in the chemical equation.

A potential energy profile for a reversible reaction is shown in Figure 7.9. Catalysts work by providing an alternative pathway of lower activation energy (E_a) for the reaction (Figure 7.10). In a reversible reaction, a catalyst not only reduces the activation energy for the forward reaction but also that for the reverse reaction. The lowering of the activation energy is the same for both forward and reverse reactions. This means that a catalyst speeds up forward and reverse reactions **equally** and reduces the time taken to reach equilibrium. This is the only change that results from the introduction of a catalyst and therefore a catalyst has no effect on the position of equilibrium or on the value of the equilibrium constant.

A catalyst increases the rate of forward and reverse reactions equally.

The presence of a catalyst does not affect the position of equilibrium or the value of the equilibrium constant; it only reduces the time taken to reach equilibrium.

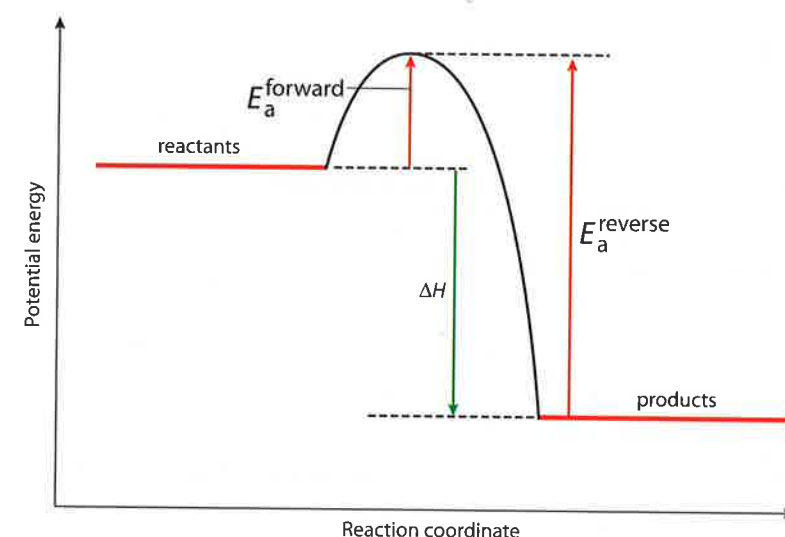


Figure 7.9 A potential energy profile for a reversible reaction.

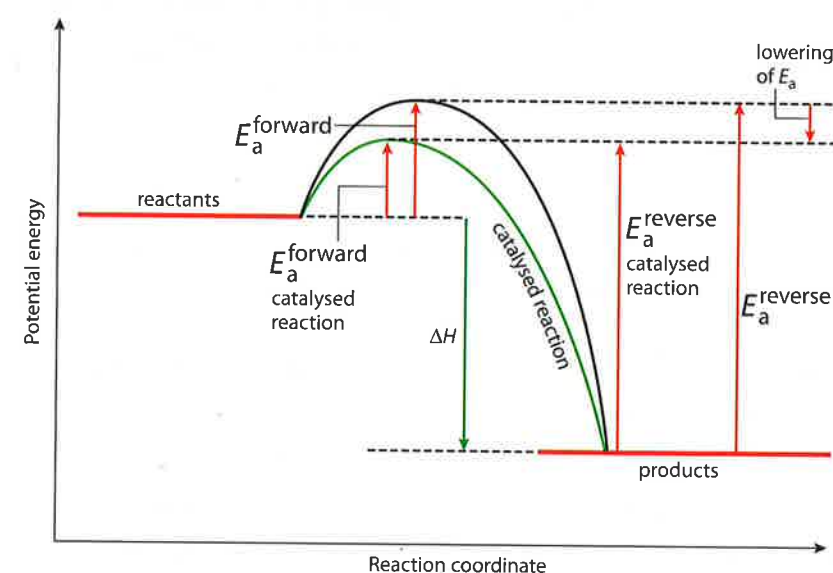


Figure 7.10 A potential energy profile for catalysed and uncatalysed reactions.

Temperature / K	K_c
298	1.7×10^{17}
500	1.1×10^{11}
1000	2.1×10^6

Table 7.2 K_c for an exothermic reaction.

$[\text{CH}_3\text{OH(g)}]$	↓ concentration decreases
$[\text{CO(g)}][\text{H}_2\text{(g)}]^2$	↑ concentration increases

Temperature / K	K_c
298	4.3×10^{-31}
500	2.7×10^{-18}
1000	7.5×10^{-9}
2000	4.0×10^{-4}
3000	0.015

Table 7.3 K_c for an endothermic reaction.

For an endothermic reaction, the value of the equilibrium constant increases as the temperature is raised.

The equilibrium constant and rate

The equilibrium constant gives us information about how far a reaction goes towards completion (that is, about the extent of the reaction). It gives us absolutely no information about how quickly the reaction occurs. Kinetic data, such as the rate constant, indicate how quickly equilibrium is attained but provide no information whatsoever about the position of equilibrium and how far the reaction proceeds.

Summary

A summary of the effect of changes in conditions on the position of equilibrium and the value of the equilibrium constant is given in Table 7.4.

Condition	Effect on position of equilibrium	Effect on value of K_c
Pressure	If a reaction involves a change in the number of gas molecules, an increase in pressure results in the position of equilibrium shifting in the direction that gives a decrease in the number of gas molecules.	no change
Concentration	The position of equilibrium will shift in order to use up any substance that has been added or replace any substance that has been removed from the equilibrium mixture.	no change
Catalyst	no effect	No effect because both forward and reverse reaction rates increase equally.
Temperature	If the temperature is increased, the position of equilibrium shifts in the endothermic direction. If the temperature is decreased, the position of equilibrium shifts in the exothermic direction.	For an exothermic reaction, K_c decreases as the temperature is increased. For an endothermic reaction, K_c increases as the temperature is increased.

Table 7.4 The effect of changes in conditions on the position of equilibrium and the value of the equilibrium constant.

? Test yourself

- 7 Explain the effect of the stated changes in conditions on the position of equilibrium and the value of the equilibrium constant. In each case state whether the value of the equilibrium constant increases, decreases or stays the same.
- a Increasing pressure in: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$ $\Delta H = +206 \text{ kJ mol}^{-1}$
 - b Increasing temperature in: $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$ $\Delta H = +206 \text{ kJ mol}^{-1}$
 - c Decreasing temperature in: $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$ $\Delta H = -40 \text{ kJ mol}^{-1}$
 - d Increasing concentration of H_2 in: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $\Delta H = -92 \text{ kJ mol}^{-1}$
 - e Increasing pressure in: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ $\Delta H = -92 \text{ kJ mol}^{-1}$
 - f Introducing a catalyst into the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ $\Delta H = -197 \text{ kJ mol}^{-1}$

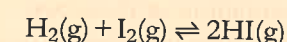
7.2 The equilibrium law (HL)

7.2.1 Calculation of equilibrium constants

If the concentrations of all reaction components at equilibrium are given, calculating a value for the equilibrium constant simply involves putting these values into the equilibrium constant expression.

Worked example

7.1 Use the data given to calculate the value of the equilibrium constant at 700 K for the reaction:



Substance	$\text{H}_2(\text{g})$	$\text{I}_2(\text{g})$	$\text{HI}(\text{g})$
Equilibrium concentration / mol dm^{-3}	0.18	0.39	1.95

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

Substituting in the equilibrium concentrations we get:

$$K_c = \frac{1.95^2}{0.18 \times 0.39} = 54.$$

If we are given a value for the equilibrium constant, we can work out the concentration of any one of the species at equilibrium.

Worked examples

7.2 Given that the equilibrium constant for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ at 700 K is 54 and that the concentrations of H_2 and I_2 at equilibrium are 0.25 mol dm^{-3} and 0.50 mol dm^{-3} , respectively, what is the equilibrium concentration of HI?

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

Substituting the equilibrium concentrations we get $54 = \frac{[\text{HI}(\text{g})]^2}{0.25 \times 0.50}$

Rearranging this $[\text{HI}(\text{g})]^2 = 54 \times 0.25 \times 0.50$

$$[\text{HI}(\text{g})]^2 = 6.75$$

Therefore, the equilibrium concentration of hydrogen iodide is 2.6 mol dm^{-3} .

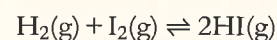
A variation on this calculation is given in the next example.

Learning objectives

- Solve problems involving equilibrium constants
- Understand the relationship between the equilibrium constant and the Gibbs free energy

Equilibrium constants are normally worked out in terms of **activities** (effective concentrations). These are calculated relative to a standard concentration of 1 mol dm^{-3} . This results in equilibrium constants having no units. Equilibrium concentrations do have units (mol dm^{-3}), but in expressions for K_c what we are using is concentration / mol dm^{-3} , which does not have any units and therefore overall equilibrium constants have no units.

7.3 Equal concentrations of hydrogen and iodine are mixed together in a closed container at 700 K and allowed to come to equilibrium. If the concentration of HI at equilibrium is 0.85 mol dm^{-3} , what are the equilibrium concentrations of H_2 and I_2 ? $K_c = 54$ at this temperature.



$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$$

We can substitute the values we know: $54 = \frac{0.85^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$

From the chemical equation 1 mol H_2 reacts with 1 mol I_2 , and since the initial concentrations of these two species were equal, their concentrations must stay equal as they react together. This means that the equilibrium concentration of H_2 is the same as that of I_2 and we can write:

$$54 = \frac{0.85^2}{[\text{H}_2(\text{g})]^2}$$

Rearranging this $[\text{H}_2(\text{g})]^2 = \frac{0.85^2}{54}$

$$[\text{H}_2(\text{g})] = 0.12 \text{ mol dm}^{-3}$$

Therefore the equilibrium concentrations of H_2 and I_2 are both 0.12 mol dm^{-3} .

Note: if we had the equation $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ and started off with equal concentrations of SO_2 and O_2 , the concentrations would not be equal at equilibrium because 2 mol SO_2 react with 1 mol O_2 and therefore, as the reaction proceeds to equilibrium, the concentration of SO_2 drops by twice as much as the concentration of O_2 .

Next we will look at questions in which we need to find the value of the equilibrium constant but have not been given all the equilibrium concentrations.

Worked examples

7.4 5.00 mol H_2 and 3.00 mol I_2 are mixed together in a vessel of volume 10.0 dm^3 and allowed to come to equilibrium at 1100 K. At equilibrium there were 0.43 mol I_2 present in the reaction mixture. Calculate the value of the equilibrium constant.

We need to consider the initial situation and see how the concentrations change as the system reaches equilibrium.

	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$		
Initial number of moles / mol	5.00	3.00	0.00
Equilibrium number of moles / mol	?	0.43	?

The numbers of moles at equilibrium can be worked out as follows. 3.00 mol I_2 were originally present, and this became 0.43 mol I_2 at equilibrium. This means that $3.00 - 0.43$, i.e. 2.57, mol I_2 reacted. From the chemical equation we can see that 1 mol I_2 reacts with 1 mol H_2 , so 2.57 mol I_2 reacts with 2.57 mol H_2 . If there were 5.00 mol H_2 originally present and 2.57 mol H_2 react, this leaves $5.00 - 2.57$, i.e. 2.43 mol H_2 present at equilibrium. From the chemical equation, 1 mol I_2 reacts to form 2 mol HI. Therefore, 2.57 mol I_2 will react to form 2×2.57 , i.e. 5.14 mol HI.

This can be summarised:

initial number of moles / mol	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
	5.00		3.00		0.00
	2.57 mol H_2 react		2.57 mol I_2 react		2×2.57 mol HI formed
equilibrium number of moles / mol	2.43		0.43		5.14

Now that we have the equilibrium number of moles, we must work out the equilibrium concentration of each species. To do this we use the equation:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}}$$

In this case, because there is the same number of molecules on both sides of the equation, all the concentrations will cancel, and so this step makes no difference to the overall answer.

Because the volume of the reaction vessel is 10.0 dm^3 , we must divide each number of moles by 10.0, and therefore the equilibrium concentrations are:

	$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$		
equilibrium number of moles / mol	2.43	0.43	5.14
equilibrium concentration / mol dm^{-3}	0.243	0.043	0.514

The expression for the required constant is: $K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$

The equilibrium concentrations are substituted into this equation:

$$K_c = \frac{0.514^2}{0.243 \times 0.043} = 25.3$$

The equilibrium constant for this reaction at 1100 K is 25.3.

7.5 3.00 mol NO_2 and 1.00 mol N_2O_4 are mixed together in a vessel of volume 1.00 dm^3 and allowed to come to equilibrium at 398 K. At equilibrium there were 1.74 mol N_2O_4 present in the reaction mixture. Calculate the value of the equilibrium constant. The equation for the reaction is: $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$.

	$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$	
Initial number of moles / mol	3.00	1.00
Equilibrium number of moles / mol	?	1.74

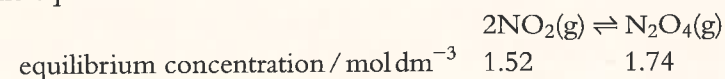
The equilibrium numbers of moles can be worked out as follows. 1.00 mol N_2O_4 was originally present, and this became 1.74 mol N_2O_4 at equilibrium. This means that $1.74 - 1.00$, i.e. 0.74, mol N_2O_4 were formed by NO_2 reacting. From the chemical equation we can see that 2 mol NO_2 reacts to form 1 mol N_2O_4 . This means that 2×0.74 , i.e. 1.48, mol NO_2 must have reacted to form 0.74 mol N_2O_4 . There were 3.00 mol NO_2 originally present and 1.48 mol NO_2 reacted, so this leaves $3.00 - 1.48$, i.e. 1.52, mol NO_2 present at equilibrium.

	$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$	
Initial number of moles / mol	3.00	1.00
Equilibrium number of moles / mol	1.52	1.74

Equilibrium concentrations are worked out using the equation:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}}$$

The volume of the reaction vessel is 1.00 dm^3 , so we must simply divide the numbers of moles by 1 and therefore the equilibrium concentrations are:



The expression for K_c is:

$$K_c = \frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2}$$

The equilibrium concentrations are substituted into this equation:

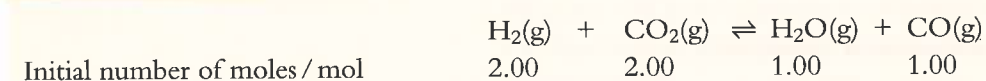
$$K_c = \frac{1.74}{1.52^2} = 0.753$$

So the equilibrium constant for this reaction at 398 K is 0.753.

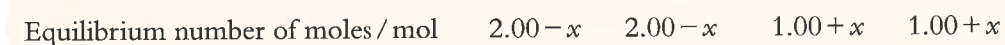
Given the initial number of moles and the equilibrium constant it is also possible to work out the number of moles at equilibrium.

Worked example

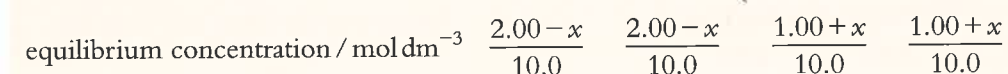
7.6 Consider the reaction $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$. In this reaction, 2.00 mol H_2 and 2.00 mol CO_2 are put into a container of volume 10.0 dm^3 together with 1.00 mol H_2O and 1.00 mol CO . They are allowed to come to equilibrium at 1200 K. Given that the value of the equilibrium constant at 1200 K is 2.10, work out the composition of the equilibrium mixture in terms of concentrations.



We will assume that x mol H_2 react with x mol CO_2 to form x mol H_2O and x mol CO .



We must divide each of these values by 10.0 to get equilibrium concentrations:



The equilibrium concentrations and the value of K_c are substituted into the expression for K_c :

$$K_c = \frac{[\text{H}_2\text{O}(\text{g})][\text{CO}(\text{g})]}{[\text{H}_2(\text{g})][\text{CO}_2(\text{g})]}$$

$$2.10 = \frac{\frac{1.00 + x}{10.0} \times \frac{1.00 + x}{10.0}}{\frac{2.00 - x}{10.0} \times \frac{2.00 - x}{10.0}}$$

$$2.10 = \frac{(1.00 + x)(1.00 + x)}{(2.00 - x)(2.00 - x)}$$

$$2.10 = \frac{(1.00 + x)^2}{(2.00 - x)^2}$$

The number of species on both sides of the equation is the same so the volumes cancel.

The right-hand side is a perfect square, and so the square root of each side can be taken:

$$\sqrt{2.10} = \frac{(1.00 + x)}{(2.00 - x)}$$

$$1.45 = \frac{(1.00 + x)}{(2.00 - x)}$$

This can be rearranged to give:

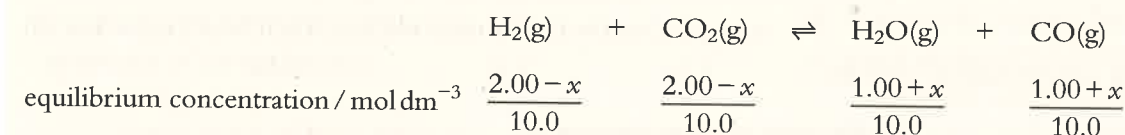
$$1.45(2.00 - x) = 1.00 + x$$

$$2.90 - 1.45x = 1.00 + x$$

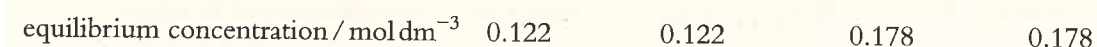
$$1.90 = 2.45x$$

Therefore, $x = 0.776 \text{ mol}$.

The equilibrium concentrations are worked out from:



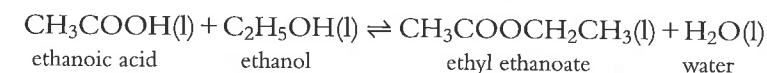
Substituting in the value of x we get:



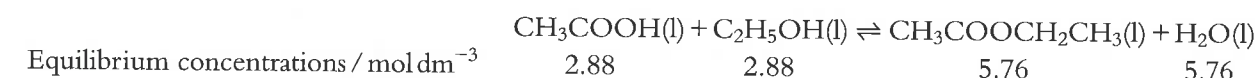
Explaining the effect of changes in concentration on the position of equilibrium

The value of the equilibrium constant is not affected by a change in concentration.

Let us consider the equilibrium:

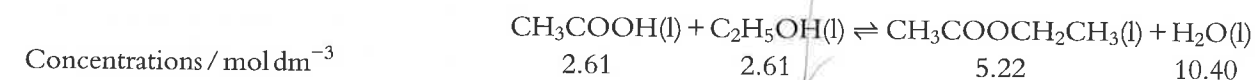


At 373 K, the equilibrium constant is 4.0. An equilibrium mixture at this temperature could be:



If some water is now added so that the concentration of water in the mixture changes to $10.40 \text{ mol dm}^{-3}$, the concentrations of the other species in the mixture will drop slightly because the total volume of the reaction mixture has increased.

The new values for the concentrations are:



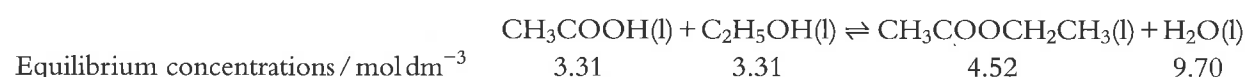
Working out the reaction quotient:

$$Q = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3(\text{l})][\text{H}_2\text{O}(\text{l})]}{[\text{CH}_3\text{COOH}(\text{l})][\text{C}_2\text{H}_5\text{OH}(\text{l})]}$$

$$= \frac{5.22 \times 10.40}{2.61 \times 2.61}$$

$$= 8.0$$

This value of Q is higher than the equilibrium constant (4.0) at this temperature and so the system is not at equilibrium. The value of Q must decrease to bring the value back to 4.0 – so ethyl ethanoate must react with water (these are on the top of the reaction quotient expression). The reverse reaction is favoured over the forward reaction until a new equilibrium is established:



The new reaction quotient is:

$$Q = \frac{4.52 \times 9.70}{3.31 \times 3.31}$$

$$= 4.0$$

Q is now equal to K_c at this temperature and so the system is at equilibrium. The concentrations of ethanoic acid and ethanol are higher than in the original equilibrium mixture. So the position of equilibrium has shifted to the left to use up the added water, which is what we would have predicted using Le Chatelier's principle.

Similar arguments can be used to explain the effect of changes in pressure on the position of equilibrium.

We can see from the above discussion that, if a system at equilibrium is subjected to a change in concentration (or pressure), the system will no longer be at equilibrium ($Q \neq K_c$). The reaction will then proceed in one direction or the other until the value of $Q = K_c$ and a new position of equilibrium is reached.

This means that we can re-state Le Chatelier's principle for changes in concentration (or pressure) as 'if a system at equilibrium is subjected to a change in concentration (or pressure), the position of equilibrium will shift so that the value of the reaction quotient, Q , is restored to the value of K_c again'.

Nature of science

Scientists often employ quantitative reasoning. For a simple reaction such as $A \rightleftharpoons B$ the rate of the forward and reverse reactions could be determined as $\text{Rate}_{\text{forward}} = k_f[A]$ and $\text{Rate}_{\text{reverse}} = k_r[B]$. At equilibrium we get $k_f[A] = k_r[B]$. If some B is added to the equilibrium mixture then the rate of the reverse reaction is increased and some of the B is used up, which is in accordance with Le Chatelier's principle.

? Test yourself

- 8 Given the equilibrium concentrations, calculate the value of the equilibrium constant for each reaction:
 - a $2A(g) \rightleftharpoons Z(g)$
equilibrium concentrations are:

$[A] \ 0.150 \text{ mol dm}^{-3}$
 $[Z] \ 0.500 \text{ mol dm}^{-3}$
 - b $2Q(g) + 3X(g) \rightleftharpoons 2Z(g) + 4E(g)$
equilibrium concentrations are:

$[Q] \ 1.50 \times 10^{-3} \text{ mol dm}^{-3}$
 $[X] \ 2.75 \times 10^{-3} \text{ mol dm}^{-3}$
 $[Z] \ 7.86 \times 10^{-4} \text{ mol dm}^{-3}$
 $[E] \ 9.37 \times 10^{-5} \text{ mol dm}^{-3}$
- 9 In each of the following reactions use the given data to calculate the equilibrium number of moles of each substance.
 - a $2A(g) \rightleftharpoons Z(g)$
initial moles of $A = 0.100 \text{ mol}$
initial moles of $Z = 0.500 \text{ mol}$
moles of A at equilibrium = 0.0600 mol
 - b $2A(g) + X(g) \rightleftharpoons 2Z(g)$
initial moles of $A = 1.00 \text{ mol}$
initial moles of $X = 2.00 \text{ mol}$
initial moles of $Z = 0.00 \text{ mol}$
moles of Z at equilibrium = 0.400 mol
- 10 Consider the reversible reaction:
 $A(g) + X(g) \rightleftharpoons Q(g)$
 - a Write the expression for K_c for this reaction.
 - b In each of the following situations calculate a value for the equilibrium constant from the data given:
 - i initial moles of $A = 0.200 \text{ mol}$
initial moles of $X = 0.400 \text{ mol}$
initial moles of $Q = 0.000 \text{ mol}$
moles of A at equilibrium = 0.100 mol
volume of container = 1.00 dm^3
temperature = 300 K
 - ii initial moles of $A = 0.200 \text{ mol}$
initial moles of $X = 0.100 \text{ mol}$
initial moles of $Q = 0.100 \text{ mol}$
moles of A at equilibrium = 0.150 mol
volume of container = 10.0 dm^3
temperature = 400 K
 - c Use the values of K_c that you have calculated to work out whether the forward reaction is exothermic or endothermic.
- 11 Consider the reversible reaction:
 $2A(g) + X(g) \rightleftharpoons 4Q(g) + Z(g)$
 - a Write the expression for K_c for this reaction.
 - b In each of the following situations calculate a value for the equilibrium constant from the data given:
 - i initial moles of $A = 0.800 \text{ mol}$
initial moles of $X = 0.400 \text{ mol}$
initial moles of $Q = 0.000 \text{ mol}$
initial moles of $Z = 0.000 \text{ mol}$
moles of Z at equilibrium = 0.100 mol
volume of container = 10.0 dm^3
temperature = 800 K
 - ii initial moles of $A = 0.000 \text{ mol}$
initial moles of $X = 0.000 \text{ mol}$
initial moles of $Q = 1.000 \text{ mol}$
initial moles of $Z = 2.000 \text{ mol}$
moles of A at equilibrium = 0.200 mol
volume of container = 20.0 dm^3
temperature = 500 K
 - c Use the values of K_c that you have calculated to work out whether the forward reaction is exothermic or endothermic.
- 12 Consider the equilibrium:
 $A(g) + Z(g) \rightleftharpoons X(g) + Q(g)$
 - a At a certain temperature, the value of the equilibrium constant for this reaction is 9.00. At this temperature $0.100 \text{ mol } A$ and $0.100 \text{ mol } Z$ are placed in a container of volume 1.00 dm^3 and allowed to come to equilibrium. Calculate the number of moles of X present at equilibrium.
 - b At a different temperature, the value of the equilibrium constant for this reaction is 16.0. At this temperature $0.200 \text{ mol } A$, $0.200 \text{ mol } Z$, $0.200 \text{ mol } X$ and $0.200 \text{ mol } Q$ are placed in a container of volume 2.00 dm^3 and allowed to come to equilibrium. Calculate the concentration of A at equilibrium.

Ans is wrong divide
answer
by 2

The position of equilibrium corresponds to the mixture of reactants and products that produces the minimum value of the Gibbs free energy and the maximum value of entropy.

When $K < 1$ the value of $\ln K$ is negative and so ΔG is positive. When $K > 1$ the value of $\ln K$ is positive and so ΔG is negative.

The relationship between ΔG and the position of equilibrium is discussed on pages 232–233.

7.2.2 The relationship between equilibrium constants and Gibbs free energy

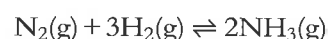
An equilibrium constant is related to the change in Gibbs free energy by the equation:

$$\Delta G = -RT \ln K$$

where R is the gas constant and T is the temperature in kelvin. The equilibrium constant in this equation has no subscript because there is more than one type of equilibrium constant and which one is obtained depends on the reaction involved. If this equation is used to determine the value for an equilibrium constant for a reaction in solution then the equilibrium constant obtained will be K_c , which we are familiar with from work above. However, for reactions involving gases, the equilibrium constant obtained is K_p , which is the equilibrium constant in terms of partial pressures.

Partial pressure refers to the pressure exerted by a particular gas in a mixture of gases. If the gases behave ideally the partial pressure is the same as the pressure that the same amount of a particular gas would exert if it were in the container by itself. If the pressure exerted by a mixture of 80% nitrogen and 20% hydrogen is 100 kPa, the partial pressure of nitrogen is 80 kPa and that of hydrogen is 20 kPa.

The expression for K_p is the same as that for K_c except concentrations are replaced by partial pressures. For the reaction



the expression for K_p is

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$

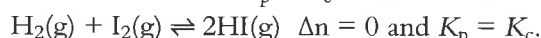
where P_{N_2} represents the partial pressure of nitrogen at equilibrium.

The relationship between a partial pressure and a concentration can be worked out using $PV = nRT$. Concentration is number of moles per unit volume (n/V), therefore

$$P = \frac{n}{V} \times RT$$

or, partial pressure of a gas = [concentration] $\times RT$

It can then be worked out that $K_p = K_c \times (RT)^{\Delta n}$ where Δn is the number of molecules of gas on the right hand side of an equation – the number of molecules of gas on the left hand side. For the reaction given above $\Delta n = -2$ and $K_p \neq K_c$ but for



Worked example

7.7 Consider the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Given that the value of ΔG^\ominus at 298 K for this reaction is $+1.3 \text{ kJ mol}^{-1}$, calculate the value of the equilibrium constant.

$$\Delta G = -RT \ln K$$

Because R has units of $\text{J K}^{-1} \text{ mol}^{-1}$ the value of ΔG must be converted into J mol^{-1} .

$$\Delta G = 1300 \text{ J mol}^{-1}$$

Substituting in values we get:

$$1300 = -8.31 \times 298 \times \ln K$$

Rearranging:

$$\begin{aligned} \ln K &= \frac{-1300}{8.31 \times 298} \\ &= -0.525 \end{aligned}$$

The inverse function for $\ln x$ is e^x , therefore both sides need to be raised as powers of e

$$K = e^{-0.525}$$

$$K = 0.59$$

The equilibrium constant has a value of 0.59, which is less than 1, which implies that the position of equilibrium lies closer to reactants than products. This is also consistent with the value of ΔG being positive.

The relationship between ΔG and the value of K is summarised in Table 7.5.

ΔG	K	Position of equilibrium
negative	>1	closer to products than reactants
positive	<1	closer to reactants than products

Table 7.5 The relationship between ΔG and K_c .

? Test yourself

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

13 Calculate the value of ΔG (in kJ mol^{-1}) given the following values:

- a $K = 2.78$ $T = 298 \text{ K}$
b $K = 3.58 \times 10^5$ $T = 333 \text{ K}$
c $K = 7.56 \times 10^{-4}$ $T = 455^\circ \text{C}$

14 Calculate the value of K given the following values:

- a $\Delta G = 50.0 \text{ kJ mol}^{-1}$ $T = 298 \text{ K}$
b $\Delta G = -25.2 \text{ kJ mol}^{-1}$ $T = 350 \text{ K}$
c $\Delta G = -154 \text{ kJ mol}^{-1}$ $T = 27^\circ \text{C}$

Exam tip

When doing this calculation the other way round, that is working out ΔG given a value for K , the units of ΔG will come out as J mol^{-1} .

Use the key combination shift/2nd function + \ln on your calculator.



Figure 7.11 Fritz Haber

Nature of science

There are ethical and political sides to science and the story of Fritz Haber (Figure 7.11) illustrates some aspects of this.

One of the most important industrial processes in the world is the **Haber (Haber–Bosch) process** for the production of ammonia. Fritz Haber was born in 1868 in Silesia, which was then part of Germany but is now part of Poland. His parents were Jewish, but Haber later renounced his religion in favour of Christianity because the opportunities available to Jews in Germany in the late 19th century were limited. He is most famous for developing a process for ‘fixing’ nitrogen – converting nitrogen in the air into a much more reactive chemical – ammonia.

Nitrogen is an important element for plant growth and, because most plants are unable to ‘fix’ nitrogen from the air, they rely on absorbing it in some soluble form from the soil. At the beginning of the 20th century, scientists were struggling to come up with a method of producing ammonia and Germany, along with other countries, were reliant on imported guano as a fertiliser.

It was Haber and his co-workers who came up with a solution. Their process was scaled up to industrial level by Carl Bosch of BASF and the first industrial ammonia production plant opened in Germany in 1913. Ammonia can be further converted into fertilisers such as ammonium nitrate. Without artificial fertilisers it is likely that, in the last hundred years, millions of people around the world would have died of starvation. For his work on this process, which was regarded as benefiting the ‘whole of humanity’, Haber was awarded the Nobel Prize for Chemistry in 1918.

There is, however, another side to Fritz Haber and ammonia. As well as being the basis of artificial fertilisers, ammonia can be used to make explosives. Without Haber’s process, Germany would have very quickly run out of explosives in World War I, the war would almost certainly have been shorter and millions of lives might have been saved. To what extent is Haber personally responsible for lengthening the war? How far does the responsibility of a scientist stretch? Can he or she be expected to foresee all possible uses of their discoveries?

Haber also developed and supervised the use of chemical weapons, such as chlorine gas, in World War I and could perhaps be regarded as the founder of chemical warfare. He was a staunch patriot who fully supported the German war effort, but he did not make the ultimate decision to use these weapons. How far was Haber responsible for the deaths of people through the use of poison gas? Is he more responsible for this than for the deaths that arose due to the lengthening of the war through the use of ammonia to make explosives?

After World War I, Germany had to pay huge sums of money in war reparations and Haber yet again tried to use chemistry to save his country. He investigated processes for extracting gold from sea water, but eventually had to abandon the project when it became apparent that the concentration of gold in sea water was substantially lower than had been originally estimated.

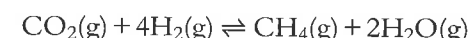
When the Nazis took control of Germany in 1933, laws were passed to prevent Jews from holding positions in universities. Although Haber could have remained in his position as head of the Kaiser Wilhelm Institute, he resigned his post. Shortly afterwards he left Germany and died a few months later in Switzerland. It is a sad postscript to the life of a talented chemist that Zyklon B, which was developed as an insecticide at Haber’s institute, was used in the gas chambers of the Nazi concentration camps in World War II. Could Haber be held in any way responsible for this?

Exam-style questions

1 Which of the following is a property of a system at equilibrium?

- A The concentrations of reactants and products are equal.
- B The rate of the forward reaction is zero.
- C The rate of the forward reaction is equal to the rate of the reverse reaction.
- D The rate of the reverse reaction is a maximum.

2 Consider the reaction:



What is the expression for the equilibrium constant?

- A $K_c = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CH}_4][\text{H}_2\text{O}]}$
- B $K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]^2}{[\text{CO}_2][\text{H}_2]^4}$
- C $K_c = \frac{[\text{CH}_4][2\text{H}_2\text{O}]}{[\text{CO}_2][4\text{H}_2]}$
- D $K_c = \frac{[\text{CH}_4] + [\text{H}_2\text{O}]^2}{[\text{CO}_2] + [\text{H}_2]^4}$

3 In which system will decreasing the pressure increase the equilibrium concentration of the species in bold?

- A $\text{CH}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{H}_2(\text{g})$
- B $\text{N}_2\text{O}_5(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons 3\text{NO}_2(\text{g})$
- C $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- D $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_3(\text{g})$

4 What is the effect of increasing the temperature on the position of equilibrium and the value of the equilibrium constant for the reaction:



- | | Position of equilibrium | Value of equilibrium constant |
|---|-------------------------|-------------------------------|
| A | shifts to left | decreases |
| B | shifts to right | decreases |
| C | shifts to right | increases |
| D | shifts to left | increases |

5 Consider the system: $A(g) \rightleftharpoons B(g)$

What is the effect of introducing a catalyst?

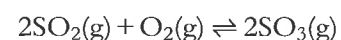
- A The rate of the forward reaction increases but the rate of the reverse reaction remains the same.
- B The position of equilibrium is shifted to the right.
- C The time taken to reach equilibrium is decreased.
- D The value of the equilibrium constant is reduced.

6 Which of the following changes will increase the equilibrium yield of ammonia according to the following equation?



- A decreasing the temperature from 200 °C to 100 °C
- B introducing a catalyst
- C decreasing the pressure from 200 atm to 100 atm
- D increasing the temperature from 100 °C to 200 °C

HL 7 The equilibrium concentrations at a certain temperature for the reaction

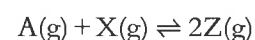


are 0.20 mol dm^{-3} for $[SO_2]$, 0.40 mol dm^{-3} for $[O_2]$, 0.80 mol dm^{-3} for $[SO_3]$.

The value of the equilibrium constant at this temperature is:

- A 0.025
- B 2
- C 10
- D 40

HL 8 Consider the equilibrium:



0.20 mol Z are placed in a sealed 10 dm^3 container and allowed to come to equilibrium at 500 K. At equilibrium, 0.040 mol X were present in the reaction vessel. The value of the equilibrium constant at this temperature is:

- A 5
- B 9
- C 16
- D 25

HL 9 Consider the reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

The value of the equilibrium constant at certain temperature, T , is 2.0.

Given the following concentrations in the reaction mixture:

Reactant	Concentration / mol dm^{-3}
$N_2(g)$	1.0
$H_2(g)$	2.0
$NH_3(g)$	4.0

which of the following is correct?

- A $Q = 0.50$ and the system is not at equilibrium
- B $Q = 1.3$ and the system is not at equilibrium
- C $Q = 2.0$ and the system is at equilibrium
- D $Q = 2.0$ and the system is not at equilibrium

10 Which of the following describes the relationship between the change in Gibbs free energy, ΔG , and the equilibrium constant, K ?

- A If $K > 1$ then $\Delta G > 0$.
- B If $K = 0$ then $\Delta G = 0$.
- C If $K < 0$ then $\Delta G < 0$.
- D If $K > 1$ then $\Delta G < 0$.

11 a Explain what is meant by 'dynamic equilibrium'. [2]

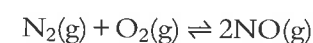
b Consider the following system at equilibrium:



State and explain the effect of the following changes on the position of equilibrium and the value of the equilibrium constant.

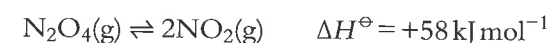
- i Increasing the temperature at constant pressure. [3]
- ii Increasing the pressure at constant temperature. [2]
- iii Introducing a catalyst at constant temperature and pressure. [2]

12 Consider the reaction:



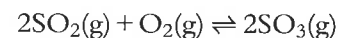
- a Write an expression for the equilibrium constant for this reaction. [1]
- b The value of the equilibrium constant for this reaction at 700 K is 5×10^{-13} , but the value at 1100 K is 4×10^{-8} . Use these values to state and explain whether this reaction is exothermic or endothermic in the forward direction as written. [3]

13 Consider the reversible reaction between colourless N_2O_4 and brown NO_2 :



- a Write an expression for the equilibrium constant for this reaction. [1]
- b State and explain how the colour of the mixture will change as the temperature is increased. [3]
- c State and explain the effect of increasing the pressure on the colour of the equilibrium mixture and the value of the equilibrium constant. [4]
- HL d 0.200 mol N_2O_4 is placed in a container of volume 4.00 dm^3 at a certain temperature and allowed to come to equilibrium. At equilibrium there were 0.140 mol N_2O_4 present. Calculate the equilibrium concentrations of N_2O_4 and NO_2 and hence the value of the equilibrium constant at this temperature. [4]

HL 14 The following reaction is an important stage in the Contact process for the production of sulfuric acid:



- a 0.120 mol SO_2 and 0.120 mol O_2 are introduced into a reaction vessel of volume 2.00 dm^3 and allowed to come to equilibrium at 1100 K. At equilibrium there were 0.060 mol SO_3 present.

i Write an expression for the equilibrium constant for this reaction.

ii Calculate the concentration of O_2 at equilibrium.

iii Calculate a value for the equilibrium constant for this reaction at 1100 K.

[1]

[2]

[3]

- b The standard enthalpy changes of formation of $\text{SO}_2(\text{g})$ and $\text{SO}_3(\text{g})$ are -297 kJ mol^{-1} and -395 kJ mol^{-1} , respectively.

i Calculate a value for the enthalpy change for the conversion of two moles of SO_2 to two moles of SO_3 .

[2]

ii State and explain whether the value of the equilibrium constant for this reaction at 1500 K will be higher or lower than the value you found in a iii.

[2]

15 Consider the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

- a Write an expression for the equilibrium constant for this reaction.

[1]

- b The value of the equilibrium constant for this reaction at 700 K is 54.0. What is the value of the equilibrium constant for the following reaction?



[1]

- c 2.00 mol of HI are introduced into a closed reaction vessel of volume 4.00 dm^3 and allowed to come to equilibrium at 700 K. Calculate the equilibrium concentration of H_2 .

[3]

Summary

EQUILIBRIUM

In chemistry, equilibria are always **dynamic**.

characteristics of chemical equilibria

rate of forward reaction = rate of reverse reaction

concentrations of reactants and products are constant

all species in equation present at equilibrium

can be attained from either direction

can only be attained in a closed system

in which there is no exchange of matter with the surroundings

A **phase equilibrium** involves a change of state rather than a chemical change. e.g. rate of vaporisation = rate of condensation

position of equilibrium – relative amount of reactants and products

not affected by catalyst – this increases rate of forward and reverse reactions equally

Le Chatelier's principle – if a system at equilibrium is subjected to change, it will shift in order to minimise the effect of that change.

factors that can be changed

If **temperature** is increased, position of equilibrium will shift in endothermic direction.

If **pressure** is increased, position of equilibrium will shift to side with fewer gas molecules.

If **concentration** of a species is increased, position of equilibrium will shift in the direction away from that species.

equilibrium constant (K_c) for $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

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

(concentrations at equilibrium)

provides information about how far a reaction proceeds at a given temperature

If $K_c \gg 1$, the reaction proceeds almost completely towards the products.

If $K_c \ll 1$, the reaction proceeds hardly at all towards the products.

value only affected by change in temperature

For an exothermic reaction, K_c decreases as the temperature increases.

Reaction quotient, $Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$
(concentration not equilibrium concentrations)

If $Q = K_c$ the system is at equilibrium.
If $Q \neq K_c$ the system is not at equilibrium.

If $Q < K_c$ the reaction must proceed towards the products (to the right) to reach equilibrium.

HL

$$\Delta G = -RT \ln K$$

The position of equilibrium corresponds to the mixture of reactants and products that produces the minimum value of the Gibbs free energy and the maximum value of entropy.