



Chapter 8: Equilibrium

Learning outcomes

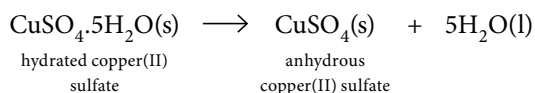
You should be able to:

- explain what is meant by a **reversible reaction** and **dynamic equilibrium**
- state Le Chatelier's principle and apply it to deduce qualitatively the effect of changes in temperature, concentration or pressure on a system at equilibrium
- state whether changes in temperature, concentration or pressure or the presence of a catalyst affect the value of the equilibrium constant for a reaction
- deduce expressions for equilibrium constants in terms of concentrations, K_c , and partial pressure, K_p
- calculate:
 - the value of equilibrium constants in terms of concentrations or partial pressures
 - the quantities of substances present at equilibrium
- describe and explain the conditions used in the Haber process and the Contact process
- show understanding of, and use, the Brønsted–Lowry theory of acids and bases
- explain qualitatively the differences in behaviour between strong and weak acids and bases and the pH values of their aqueous solutions in terms of the extent of dissociation.

Reversible reactions and equilibrium

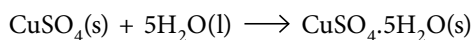
Reversible reactions

Some reactions can be reversed. For example, when blue, hydrated copper(II) sulfate is heated, it loses its water of crystallisation and changes to white, anhydrous copper(II) sulfate.



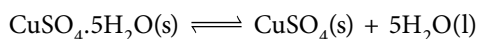
This is called the forward reaction.

When water is added to anhydrous copper(II) sulfate, the reaction is reversed.



This is called the backward (or reverse) reaction.

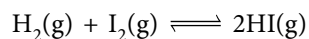
We can show these two reactions in the same equation by using two arrows.



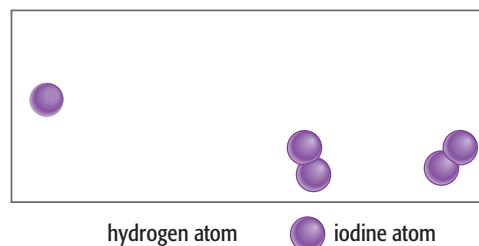
A reaction in which the products can react to re-form the original reactants is called a **reversible reaction**. In this case heating and adding water are not being carried out at the same time. However, there is a type of chemical reaction in which the forward reaction and the backward reaction take place at the same time.

In many chemical reactions the reactants are not used up completely. Some products are formed but the maximum theoretical yield is not obtained. A mixture of products and reactants is formed. The products react together to re-form reactants at the same time as the reactants are forming products. This type of reversible reaction is called an **equilibrium** reaction. We show that equilibrium reactions are reversible by the sign \rightleftharpoons .

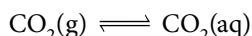
For example, consider the reaction between hydrogen and iodine carried out in a sealed glass tube at 400°C:



Molecules of hydrogen iodide are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules are reacting together to form hydrogen iodide.



When fizzy drinks are made, carbon dioxide gas is dissolved in the drink under pressure. When you take the lid off a bottle of fizzy drink, bubbles of carbon dioxide suddenly appear. When you put the lid back on, the bubbles stop. This is because of the equilibrium



The forward reaction happens during manufacture and the backward reaction happens on opening.

Characteristics of equilibrium

An equilibrium reaction has four particular features under constant conditions:

- it is dynamic
- the forward and reverse reactions occur at the same rate
- the concentrations of reactants and products remain constant at equilibrium
- it requires a closed system.

1 It is dynamic

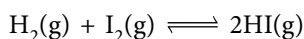
The phrase **dynamic equilibrium** means that the molecules or ions of reactants and products are continuously reacting. Reactants are continuously being changed to products and products are continuously being changed back to reactants.

2 The forward and backward reactions occur at the same rate

At equilibrium the rate of the forward reaction equals the rate of the backward reaction. Molecules or ions of reactants are becoming products, and those in the products are becoming reactants, at the same rate.

3 The concentrations of reactants and products remain constant at equilibrium

The concentrations remain constant because, at equilibrium, the rates of the forward and backward reactions are equal. The equilibrium can be approached from two directions. For example, in the reaction



We can start by either:

- using a mixture of colourless hydrogen gas and purple iodine vapour, or
- using only colourless hydrogen iodide gas.

Figure 8.4 shows what happens when 5.00 mol of hydrogen molecules and 5.00 mol of iodine molecules react at 500 K in a vessel of volume 1 dm³. As time passes, the purple colour of the iodine vapour fades until equilibrium is reached. At equilibrium the mixture contains 0.68 mol of iodine, 0.68 mol of hydrogen and 8.64 mol of hydrogen iodide.

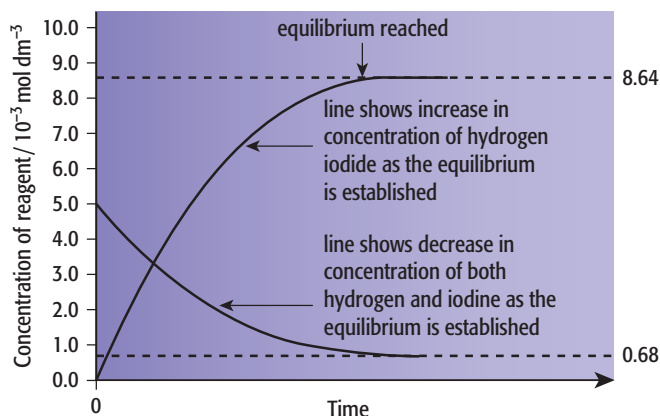


Figure 8.4 The changes in the concentrations of reagents as 5.00 mol of each of hydrogen and iodine react to form an equilibrium mixture with hydrogen iodide in a vessel of volume 1 dm³.

Figure 8.5 shows that the same equilibrium can be achieved when 10.00 mol of hydrogen iodide molecules decompose to iodine and hydrogen iodide. You can see that the same equilibrium concentrations of all three molecules are achieved.

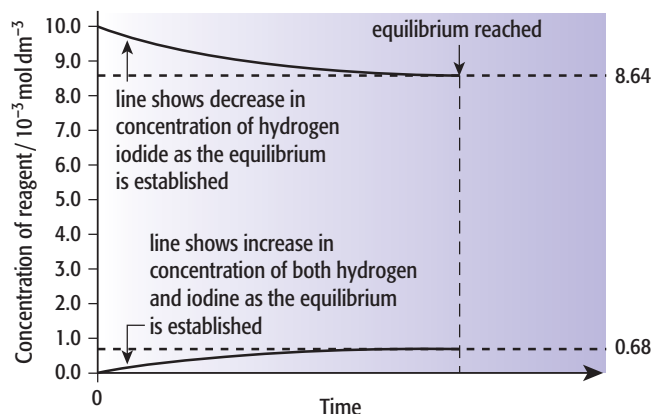


Figure 8.5 The changes in the concentrations of reagents as 10.00 mol of hydrogen iodide react to form an equilibrium mixture with hydrogen and iodine gases in a vessel of 1 m³.

QUESTION

- 1 These questions relate to the information in Figure 8.5.
- Why are the concentrations of iodine and hydrogen at equilibrium the same?
 - Describe how the depth of colour of the reaction mixture changes as time progresses.
 - Explain why there must be 8.64 mol of hydrogen iodide molecules in the equilibrium mixture if 0.68 mol of iodine are present.

4 Equilibrium requires a closed system

A **closed system** is one in which none of the reactants or products escapes from the reaction mixture. In an open system some matter is lost to the surroundings. Figure 8.6 shows the difference between a closed system and an **open system** when calcium carbonate is heated at a high temperature in a strong container.

Many chemical reactions can be studied without placing them in closed containers. They can reach equilibrium in open flasks if the reaction takes place entirely in solution and no gas is lost.

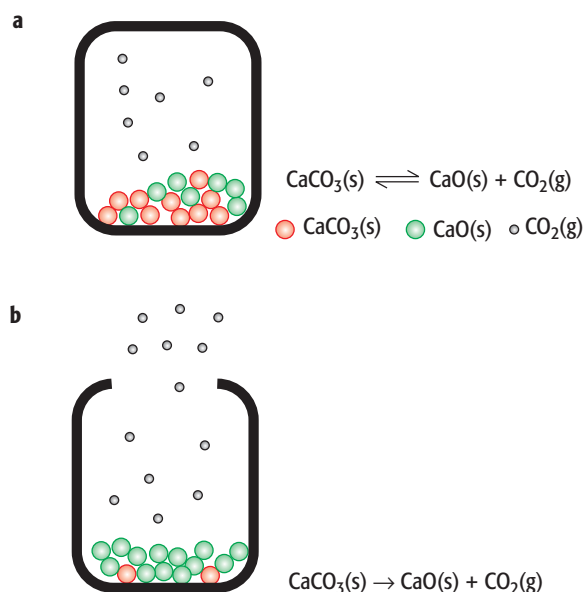


Figure 8.6 **a** A closed system. No carbon dioxide escapes. The calcium carbonate is in equilibrium with calcium oxide and carbon dioxide. **b** An open system. The calcium carbonate is continually decomposing as the carbon dioxide is lost. The reaction eventually goes to completion.

QUESTION

- 2 A beaker contains saturated aqueous sodium chloride solution in contact with undissolved solid sodium chloride. Sodium ions and chloride ions are constantly moving from solid to solution and from solution to solid.
- Explain why this is a closed system.
 - Explain why the concentration of the saturated sodium chloride solution does not change, even though ions are still moving into the solution from the solid.
 - Bromine is a reddish-brown liquid that vaporises at room temperature. Some liquid bromine is put in a closed jar. The colour of the bromine vapour above the liquid gets darker and darker until the depth of colour remains constant. Bromine liquid still remains in the jar. Explain what is happening in terms of changes in concentration of the bromine molecules in the vapour.

Changing the position of equilibrium

Position of equilibrium

The position of equilibrium refers to the relative amounts of products and reactants present in an equilibrium mixture.

- If a system in equilibrium is disturbed (e.g. by a change in temperature) and the concentration of products is increased relative to the reactants, we say that the position of equilibrium has shifted to the right.
- If the concentration of products is decreased relative to the reactants, we say that the position of equilibrium has shifted to the left.

Le Chatelier's principle

Changes in both concentration and temperature affect the position of equilibrium. When any of the reactants or products are gases, changes in pressure may also affect the position of equilibrium. French chemist Henri Le Chatelier (1850–1936) observed how these factors affect the position of equilibrium. He put forward a general rule, known as

Le Chatelier's principle:

If one or more factors that affect an equilibrium is changed, the position of equilibrium shifts in the direction that reduces (opposes) the change.

We can predict the effect of changing concentration and pressure by referring to the stoichiometric equation for the reaction. We can predict the effect of changing the temperature by referring to the enthalpy change of the reaction.

How does change in concentration affect the position of equilibrium?

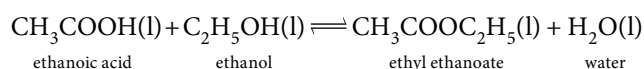
When the concentration of one or more of the reactants is increased:

- the system is no longer in equilibrium
- the position of equilibrium moves to the right to reduce the effect of the increase in concentration of reactant
- more products are formed until equilibrium is restored.

When the concentration of one or more of the products is increased:

- the system is no longer in equilibrium
- the position of equilibrium moves to the left to reduce the effect of the increase in concentration of product
- more reactants are formed until equilibrium is restored.

For example, look at the reaction:



What happens when we add more ethanol?

- The concentration of ethanol is increased.
- According to Le Chatelier's principle, some of the ethanol must be removed to reduce the concentration of the added ethanol.
- The position of equilibrium shifts to the right.
- More ethanol reacts with ethanoic acid and more ethyl ethanoate and water are formed.

What happens when we add more water?

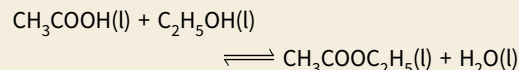
- The concentration of water is increased.
- According to Le Chatelier's principle, some of the water must be removed to reduce the concentration of the added water.
- The position of equilibrium shifts to the left.
- So more water reacts with ethyl ethanoate and more ethanoic acid and ethanol are formed.

What happens when we remove some water?

- The concentration of water is decreased.
- According to Le Chatelier's principle, some water must be added to increase its concentration.
- The position of equilibrium shifts to the right.
- So more ethanoic acid reacts with ethanol and more water and ethyl ethanoate are formed.

QUESTION

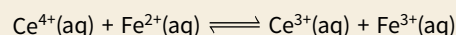
3 a Use this reaction:



Explain what happens to the position of equilibrium when:

- i more $\text{CH}_3\text{COOC}_2\text{H}_5\text{(l)}$ is added
- ii some $\text{C}_2\text{H}_5\text{OH(l)}$ is removed.

b Use this reaction:

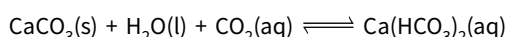


Explain what happens to the position of equilibrium when:

- i the concentration of $\text{Fe}^{2+}(\text{aq})$ ions is increased
- ii water is added to the equilibrium mixture.



Figure 8.7 Stalactites and stalagmites are formed as a result of water passing through rocks containing calcium carbonate. The solution running through these rocks contains water, dissolved carbon dioxide and calcium hydrogencarbonate:



When droplets of this mixture are formed on the roof of the cave, some of the carbon dioxide in the droplets escapes into the air. The position of equilibrium shifts to the left and calcium carbonate is deposited.

The effect of pressure on the position of equilibrium

Change in pressure only affects reactions where gases are reactants or products. The molecules or ions in solids and liquids are packed closely together and cannot be compressed very easily. In gases, the molecules are far apart (Figure 8.8).

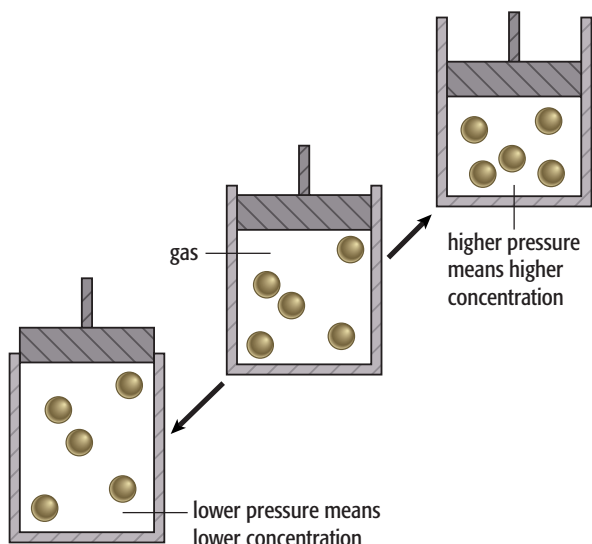
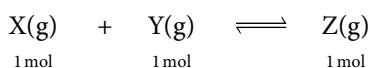


Figure 8.8 Pressure has a considerable effect on the concentration of gases.

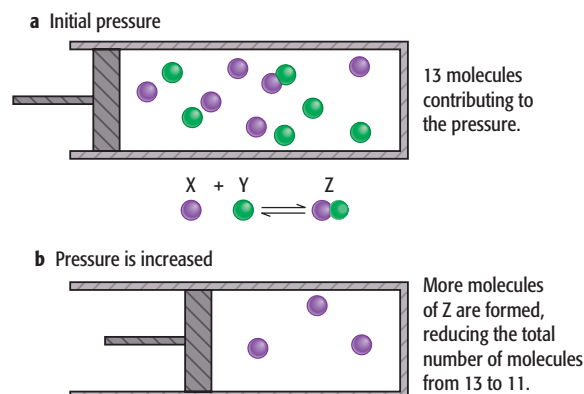
The pressure of a gas is caused by the molecules hitting the walls of the container. Each molecule in a mixture of gases contributes towards the total pressure. So, at constant temperature, the more gas molecules there are in a given volume, the higher the pressure.

Figure 8.9 shows what happens when we increase the pressure on the reaction represented by:

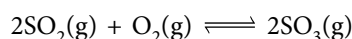


In this reaction there are two moles of gas on the left and one on the right. When the pressure is increased at constant temperature:

- the molecules are closer together, because the pressure has increased
- the position of equilibrium shifts to minimise this increase
- it shifts in the direction of fewer gas molecules (in the direction that opposes the increase in pressure)
- more product, Z, is formed from X and Y until equilibrium is re-established.



For example, consider the reaction:



There are three moles of gas molecules on the left of the equation and two on the right.

What happens when we increase the pressure?

- The molecules are closer together, because the pressure is higher.
- According to Le Chatelier's principle, the reaction must shift in the direction that reduces the number of molecules of gas.
- The position of equilibrium shifts to the right.
- So more SO_2 reacts with O_2 to form SO_3 .

What happens when we decrease the pressure?

- The molecules are further apart, because the pressure is lower.
- According to Le Chatelier's principle, the reaction must shift in the direction that increases the number of molecules of gas.
- The position of equilibrium shifts to the left.
- So more SO_2 and O_2 molecules are formed by the decomposition of SO_3 molecules.

Table 8.1 summarises the effect of changes in pressure on two other gas reactions.

Note that:

- if there are equal numbers of molecules of gas on each side of the equation, the position of equilibrium is not affected by a change in pressure
- in a reaction involving gases and solids (or liquids), it is only the molecules of gases that count when determining how pressure affects the position of equilibrium.

Change in pressure	Fewer molecules of gas on right $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	More molecules of gas on right $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
pressure increase	equilibrium position shifts towards products: more NH_3 forms	equilibrium position shifts towards reactants: more N_2O_4 forms
pressure decrease	equilibrium position shifts towards reactants: more N_2 and H_2 form	equilibrium position shifts towards products: more NO_2 forms

Table 8.1 The effect of changes in pressure on gas reactions.**QUESTION**

- 4 a** Predict the effect of increasing the pressure on the following reactions:
- $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
 - $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- b** Predict the effect of decreasing the pressure on the reaction:
- $$2\text{NO}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$$

The effect of temperature on the position of equilibrium

The decomposition of hydrogen iodide is an endothermic reaction.



The effect of temperature on the equilibrium concentration of hydrogen iodide and hydrogen at equilibrium for the forward reaction is shown in [Table 8.2](#).

Temperature / °C	Equilibrium concentration of HI / mol dm ⁻³	Equilibrium concentration of H ₂ (or I ₂) / mol dm ⁻³
25	0.934	0.033
230	0.864	0.068
430	0.786	0.107
490	0.773	0.114

Table 8.2 Effect of temperature on the decomposition of hydrogen iodide.

You can see from [Table 8.2](#) that, as the temperature increases, the concentration of product increases. The

position of equilibrium shifts to the right. We can explain this using Le Chatelier's principle:

- an increase in temperature increases the energy of the surroundings
- according to Le Chatelier's principle, the reaction will go in the direction that opposes the increase in energy
- so the reaction will go in the direction in which energy is absorbed, which is the endothermic reaction
- the position of equilibrium shifts to the right, producing more H_2 and I_2 .

If an endothermic reaction is favoured by an increase in temperature, an exothermic reaction must be favoured by a decrease in temperature:

- a decrease in temperature decreases the energy of the surroundings
- according to Le Chatelier's principle, the reaction will go in the direction that opposes the decrease in energy
- so the reaction will go in the direction in which energy is released, which is the exothermic reaction.

[Table 8.3](#) summarises the effect of temperature changes on the position of equilibrium for endothermic and exothermic reactions.

Temperature change	Endothermic reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$	Exothermic reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
Temperature increase	position of equilibrium shifts towards products: more H_2 and I_2 formed	position of equilibrium shifts towards reactants: more SO_2 and O_2 formed
Temperature decrease	position of equilibrium shifts towards reactant: more HI formed	position of equilibrium shifts towards product: more SO_3 formed

Table 8.3 Effect of temperature on endothermic and exothermic reactions.**QUESTION**

- 5 a** Predict the effect of increasing the temperature on the reaction:
- $$\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$$
- $$\Delta H_r = +41.2 \text{ kJ mol}^{-1}$$
- b** In the reaction
- $$\text{Ag}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{Ag}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$$
- increasing the temperature increases the amount of carbon dioxide formed at constant pressure. Is this reaction exothermic or endothermic? Explain your answer.

Do catalysts have any effect on the position of equilibrium?

A catalyst is a substance that increases the rate of a chemical reaction. Catalysts speed up the time taken to reach equilibrium, but they have no effect on the position of equilibrium once this is reached. This is because they increase the rate of the forward and reverse reactions equally.

Equilibrium expressions and the equilibrium constant, K_c

Equilibrium expressions

When hydrogen reacts with iodine in a closed tube at 500 K, the following equilibrium is set up:

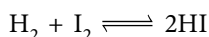


Table 8.4 shows the relationship between the equilibrium concentrations of H_2 , I_2 and HI . The square brackets in the last column refer to the concentration, in mol dm^{-3} , of the substance inside the brackets. The results are obtained as follows:

- several tubes are set up with different starting concentrations of hydrogen and iodine
- the contents of the tubes are allowed to reach equilibrium at 500 K
- the concentrations of hydrogen, iodine and hydrogen iodide at equilibrium are determined.

The last column in Table 8.4 shows the number we get by arranging the concentrations of H_2 , I_2 and HI in a particular way. We get this expression by taking the square of the concentration of hydrogen iodide and dividing it by the concentrations of hydrogen and iodine at equilibrium. So for the first line of data in Table 8.4:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(8.64 \times 10^{-3})^2}{(0.68 \times 10^{-3})(0.68 \times 10^{-3})} = 161$$

Concentration of H_2 at equilibrium / mol dm^{-3}	Concentration of I_2 at equilibrium / mol dm^{-3}	Concentration of HI at equilibrium / mol dm^{-3}	$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
0.68×10^{-3}	0.68×10^{-3}	8.64×10^{-3}	161
0.50×10^{-3}	0.50×10^{-3}	6.30×10^{-3}	159
1.10×10^{-3}	2.00×10^{-3}	18.8×10^{-3}	161
2.50×10^{-3}	0.65×10^{-3}	16.1×10^{-3}	160

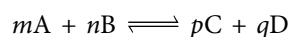
Table 8.4 The relationship between the equilibrium concentrations of H_2 , I_2 and HI in the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

You can see that this expression gives an approximately constant value close to about 160 whatever the starting concentrations of H_2 , I_2 and HI .

We call this constant the **equilibrium constant**, K_c . The subscript 'c' refers to the fact that concentrations have been used in the calculations.

There is a simple relationship that links K_c to the equilibrium concentrations of reactants and products and the stoichiometry of the equation. This is called an **equilibrium expression**.

For a general reaction:

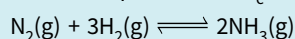


(where m , n , p and q are the number of moles in the equation)

$$K_c = \frac{\begin{array}{c} \text{concentration of product D} \\ \downarrow \\ [\text{C}]^p [\text{D}]^q \end{array}}{\begin{array}{c} \uparrow \\ [\text{A}]^m [\text{B}]^n \\ \text{concentration of reactant B} \end{array}} \begin{array}{l} \leftarrow \text{number of moles of product D} \\ \leftarrow \text{number of moles of reactant B} \end{array}$$

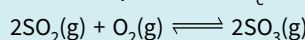
WORKED EXAMPLES

- 1** Write an expression for K_c :



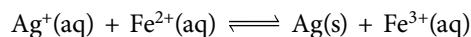
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

- 2** Write an expression for K_c :



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

In equilibrium expressions involving a solid, we ignore the solid. This is because its concentration remains constant, however much solid is present. For example:



The equilibrium expression for this reaction is:

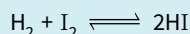
$$K_c = \frac{[\text{Fe}^{3+}(\text{aq})]}{[\text{Ag}^+(\text{aq})][\text{Fe}^{2+}(\text{aq})]}$$

What are the units of K_c ?

In the equilibrium expression each figure within a square bracket represents the concentration in mol dm^{-3} . The units of K_c therefore depend on the form of the equilibrium expression.

WORKED EXAMPLES

- 3** State the units of K_c for the reaction:

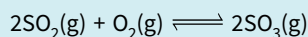


$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$\text{Units of } K_c = \frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

The units of mol dm^{-3} cancel, so K_c has no units.

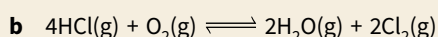
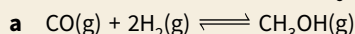
- 4** State the units of K_c for the reaction:



$$\begin{aligned} \text{Units of } K_c &= \frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})} \\ &= \frac{1}{(\text{mol dm}^{-3})} = \text{dm}^3 \text{ mol}^{-1} \end{aligned}$$

QUESTION

- 6** Write equilibrium expressions for the following reactions and state the units of K_c .

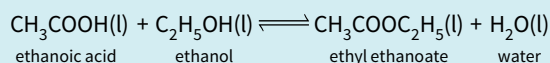


Some examples of equilibrium calculations

WORKED EXAMPLES

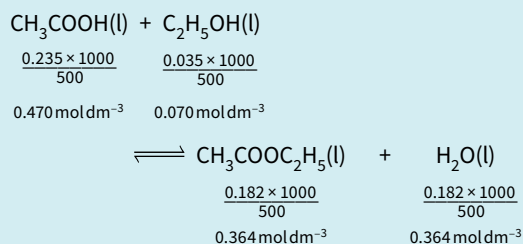
- 5** In this calculation we are given the number of moles of each of the reactants and products at equilibrium together with the volume of the reaction mixture.

Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.



500 cm^3 of the reaction mixture at equilibrium contained 0.235 mol of ethanoic acid and 0.0350 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of K_c for this reaction.

Step 1 Write out the balanced chemical equation with the concentrations beneath each substance.



Step 2 Write the equilibrium constant for this reaction in terms of concentrations.

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

Step 3 Substitute the equilibrium concentrations into the expression

$$K_c = \frac{(0.364) \times (0.364)}{(0.470) \times (0.070)} = 4.03$$

(to 3 significant figures)

Step 4 Add the correct units by referring back to the equilibrium expression:

$$\frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

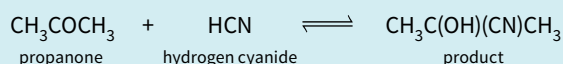
The units of mol dm^{-3} cancel, so K_c has no units. Therefore $K_c = 4.03$.

Note: if there are equal numbers of moles on the top and bottom of the equilibrium expression, you can use moles rather than concentration in mol dm^{-3} in the calculation. In all other cases, if volumes are given, the concentrations must be calculated before they are substituted into the equilibrium expression.

WORKED EXAMPLES (CONTINUED)

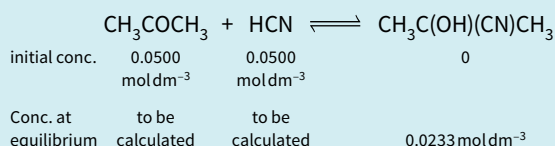
- 6** In this example we are only given the initial concentrations of the reactants and the equilibrium concentration of the product.

Propanone reacts with hydrogen cyanide as follows:



A mixture of $0.0500 \text{ mol dm}^{-3}$ propanone and $0.0500 \text{ mol dm}^{-3}$ hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is $0.0233 \text{ mol dm}^{-3}$. Calculate K_c for this reaction.

Step 1 Write out the balanced chemical equation with all the data underneath:



Step 2 Calculate the equilibrium concentrations of the reactants.

The chemical equation shows that for every mole of product formed, 1 mole of CH_3COCH_3 and 1 mole of HCN are consumed. So the equilibrium concentrations are as follows:

$$\text{CH}_3\text{COCH}_3; 0.0500 - 0.0233 = 0.0267 \text{ mol dm}^{-3}$$

$$\text{HCN}; 0.0500 - 0.0233 = 0.0267 \text{ mol dm}^{-3}$$

Step 3 Write the equilibrium constant for this reaction in terms of concentrations:

$$K_c = \frac{[\text{CH}_3\text{C(OH)(CN)CH}_3]}{[\text{CH}_3\text{COCH}_3][\text{HCN}]}$$

Step 4 Substitute the equilibrium concentrations into the expression

$$K_c = \frac{(0.0233)}{(0.0267) \times (0.0267)} = 32.7$$

(to 3 significant figures)

Step 5 Add the correct units by referring back to the equilibrium expression.

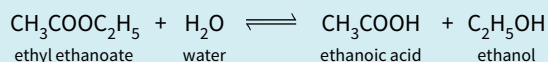
$$\frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \frac{1}{\text{mol dm}^{-3}} = \text{dm}^3 \text{ mol}^{-1}$$

$$\text{So } K_c = 32.7 \text{ dm}^3 \text{ mol}^{-1}$$

WORKED EXAMPLES (CONTINUED)

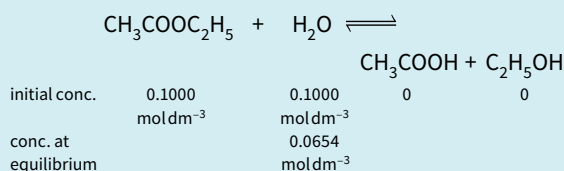
- 7** In this example we are given the initial and equilibrium concentrations of the reactants but not the products.

Ethyl ethanoate is hydrolysed by water:



0.1000 mol of ethyl ethanoate are added to 0.1000 mol of water. A little acid catalyst is added and the mixture made up to 1 dm^3 with an inert solvent. At equilibrium 0.0654 mol of water are present. Calculate K_c for this reaction.

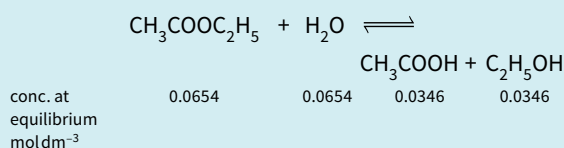
Step 1 Write out the balanced chemical equation with all the data underneath.



Step 2 Calculate the unknown concentrations:

- the chemical equation shows that 1 mole of $\text{CH}_3\text{COOC}_2\text{H}_5$ reacts with 1 mole water, so the equilibrium concentration of $\text{CH}_3\text{COOC}_2\text{H}_5$ is also $0.0654 \text{ mol dm}^{-3}$ (as we started with the same initial concentrations of ethyl ethanoate and water)
- the amount of water used in forming the products is $(0.1000 - 0.0654) = 0.0346 \text{ mol dm}^{-3}$.

The chemical equation shows that 1 mole of water formed 1 mole of ethanoic acid and 1 mole of ethanol. So the concentrations of both the products at equilibrium is $0.0346 \text{ mol dm}^{-3}$



Step 3 Write the equilibrium constant for this reaction in terms of concentrations:

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

Step 4 Substitute the equilibrium concentrations into the expression:

$$K_c = \frac{(0.0346) \times (0.0346)}{(0.0654) \times (0.0654)} = 0.280$$

(to 3 significant figures)

WORKED EXAMPLES (CONTINUED)

Step 5 Add the correct units by referring back to the equilibrium expression.

$$\frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

The units of mol dm^{-3} cancel, so K_c has no units.
Therefore $K_c = 0.280$.

QUESTION

- 7 Calculate the value of K_c for the following reaction using the information below:



initial concentration of $\text{H}_2(\text{g}) = 10.00 \text{ mol dm}^{-3}$.

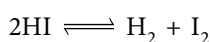
initial concentration of $\text{CO}_2(\text{g}) = 10.00 \text{ mol dm}^{-3}$.

equilibrium concentration of $\text{CO}(\text{g}) = 9.47 \text{ mol dm}^{-3}$.

 K_c and concentration changes

If all other conditions remain constant, the value of K_c does not change when the concentration of reactants or products is altered.

Take the example of the decomposition of hydrogen iodide.



The equilibrium constant at 500 K for this reaction is 6.25×10^{-3} .

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = 6.25 \times 10^{-3}$$

When more hydrogen iodide is added to the equilibrium mixture, the equilibrium is disturbed.

- The ratio of concentrations of products to reactants in the equilibrium expression decreases.
- To restore equilibrium, both $[\text{H}_2]$ and $[\text{I}_2]$ increase and $[\text{HI}]$ decreases.
- Equilibrium is restored when the values of the concentrations in the equilibrium expression are such that the value of K_c is once again 6.25×10^{-3} .

 K_c and pressure changes

Where there are different numbers of gas molecules on each side of a chemical equation, a change in pressure

alters the position of equilibrium. It is shifted in the direction that results in fewer gas molecules being formed. However, if all other conditions remain constant, the value of K_c does not change when the pressure is altered.

 K_c and temperature changes

We have seen on page 122 that for an endothermic reaction, an increase in temperature shifts the reaction in the direction of more products.

So for the endothermic reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$:

- the concentrations of H_2 and I_2 increase as the temperature increases
- the concentration of HI falls as the temperature increases.

Look at how these changes affect the equilibrium expression:

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

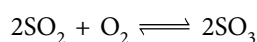
We see that the equilibrium constant must increase with increasing temperature. This is because $[\text{H}_2]$ and $[\text{I}_2]$ are increasing and $[\text{HI}]$ is decreasing. Table 8.5 shows how the value of K_c for this reaction changes with temperature.

Temperature / K	K_c (no units)
300	1.26×10^{-3}
500	6.25×10^{-3}
1000	18.5×10^{-3}

Table 8.5 Variation of K_c for the reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ with temperature.

For an exothermic reaction, an increase in temperature shifts the reaction in favour of more reactants.

Now look at the exothermic reaction:



- The concentrations of SO_2 and O_2 increase as the temperature increases.
- The concentration of SO_3 falls as the temperature increases.

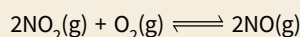
How do these changes affect the equilibrium expression?

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

We see that the equilibrium constant must decrease with increasing temperature. This is because $[\text{SO}_2]$ and $[\text{O}_2]$ are increasing and $[\text{SO}_3]$ is decreasing.

QUESTION

- 8 a Deduce the effect of increase in temperature on the value of K_c for the reaction:

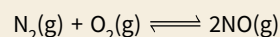


$$\Delta H_r = -115 \text{ kJ mol}^{-1}$$

- b Explain why increasing the concentration of oxygen in this reaction does not affect the value of K_c .

QUESTION

- 9 The reaction below was carried out at a pressure of $10.00 \times 10^4 \text{ Pa}$ and at constant temperature.



The partial pressures of nitrogen and oxygen are both $4.85 \times 10^4 \text{ Pa}$.

Calculate the partial pressure of the nitrogen(II) oxide, NO(g), at equilibrium.

Equilibria in gas reactions: the equilibrium constant, K_p

Partial pressure

For reactions involving mixtures of gases, it is easier to measure the pressure than to measure concentrations. The total pressure in a mixture of gases is due to each molecule bombarding the walls of the container. At constant temperature, each gas in the mixture contributes to the total pressure in proportion to the number of moles present (Figure 8.10). The pressure exerted by any one gas in the mixture is called its **partial pressure**.

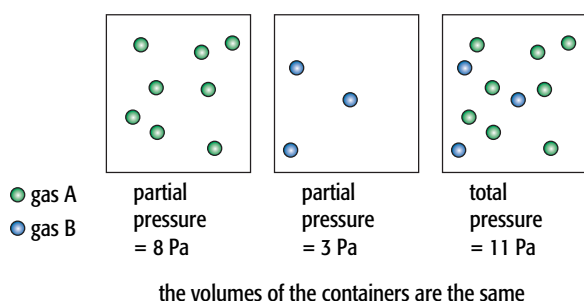


Figure 8.10 Each gas in this mixture contributes to the pressure in proportion to the number of moles present.

The total pressure of a gas equals the sum of the partial pressures of the individual gases.

$$p_{\text{total}} = p_A + p_B + p_C \dots$$

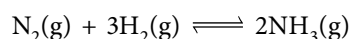
where p_A , p_B , p_C are the partial pressures of the individual gases in the mixture.

Equilibrium expressions involving partial pressures

We write equilibrium expressions in terms of partial pressures in a similar way to equilibrium expressions in terms of concentrations. But there are some differences:

- we use p for partial pressure
- the reactants and products are written as subscripts after the p
- the number of moles of particular reactants or products is written as a power after the p
- square brackets are not used
- we give the equilibrium constant the symbol K_p (the equilibrium constant in terms of partial pressures).

For example, the equilibrium expression for the reaction:



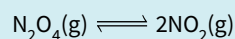
$$\text{is written as } K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} \times p_{\text{H}_2}^3}$$

What are the units of K_p ?

The units of pressure are pascals, Pa. The units of K_p depend on the form of the equilibrium expression.

WORKED EXAMPLES

- 8 For the reaction:



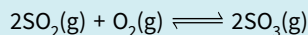
The equilibrium expression is:

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

$$\text{The units are } \frac{\text{Pa} \times \text{Pa}}{\text{Pa}} = \text{Pa}$$

WORKED EXAMPLES (CONTINUED)

9 For the reaction:



The equilibrium expression is:

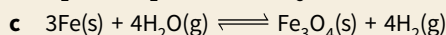
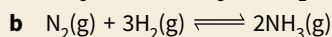
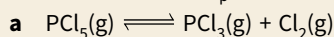
$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}$$

$$\text{The units are } \frac{\text{Pa} \times \text{Pa}}{\text{Pa} \times \text{Pa} \times \text{Pa}} = \frac{1}{\text{Pa}} = \text{Pa}^{-1}$$

Although the standard unit of pressure is the pascal, many chemists in industry use the atmosphere as the unit of pressure. 1 atmosphere = 1.01×10^5 Pa. Using 'atmospheres' as units simplifies calculations because the numbers used are not as large.

QUESTION

10 Deduce the units of K_p for the following reactions:



WORKED EXAMPLES (CONTINUED)

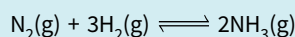
Step 3 Add the correct units.

$$\text{The units are } \frac{\text{Pa} \times \text{Pa}}{\text{Pa} \times \text{Pa} \times \text{Pa}} = \frac{1}{\text{Pa}} = \text{Pa}^{-1}$$

$$K_p = 9.1 \times 10^{-6} \text{ Pa}^{-1}$$

11 In this calculation we are given the partial pressure of two of the three gases in the mixture as well as the total pressure.

Nitrogen reacts with hydrogen to form ammonia.



The pressure exerted by this mixture of hydrogen, nitrogen and ammonia at constant temperature is 2.000×10^7 Pa. Under these conditions, the partial pressure of nitrogen is 1.490×10^7 Pa and the partial pressure of hydrogen is 0.400×10^7 Pa. Calculate the value of K_p for this reaction.

Step 1 Calculate the partial pressure of ammonia.

We know that the total pressure is the sum of the partial pressures.

$$P_{\text{total}} = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3}$$

$$2.000 \times 10^7 = (1.490 \times 10^7) + (0.400 \times 10^7) + P_{\text{NH}_3}$$

$$\text{So partial pressure of } \text{NH}_3 = 0.110 \times 10^7 \text{ Pa}$$

Step 2 Write the equilibrium expression for the reaction in terms of partial pressures.

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

Step 3 Substitute the equilibrium concentrations into the expression.

$$K_p = \frac{(0.110 \times 10^7)^2}{(1.490 \times 10^7) \times (0.400 \times 10^7)^3}$$

Step 4 Add the correct units.

$$\text{The units are } \frac{\text{Pa} \times \text{Pa}}{\text{Pa} \times \text{Pa} \times \text{Pa} \times \text{Pa}} = \frac{1}{\text{Pa}^2} = \text{Pa}^{-2}$$

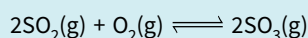
$$K_p = 1.27 \times 10^{-15} \text{ Pa}^{-2}$$

Calculations using partial pressures

WORKED EXAMPLES

10 In this example we are given the partial pressure of each gas in the mixture.

In the reaction



the equilibrium partial pressures at constant temperature are $\text{SO}_2 = 1.0 \times 10^6$ Pa, $\text{O}_2 = 7.0 \times 10^6$ Pa, $\text{SO}_3 = 8.0 \times 10^6$ Pa. Calculate the value of K_p for this reaction.

Step 1 Write the equilibrium expression for the reaction in terms of partial pressures.

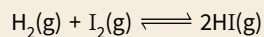
$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}$$

Step 2 Substitute the equilibrium concentrations into the expression.

$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times 7.0 \times 10^6} = 9.1 \times 10^{-6} \text{ Pa}^{-1}$$

QUESTION

- 11** The information below gives the data for the reaction of hydrogen with iodine at 500°C.



The table shows the initial partial pressures and the partial pressures at equilibrium of hydrogen, iodine and hydrogen iodide. The total pressure was constant throughout the experiment.

	Partial pressures / Pa		
	Hydrogen	Iodine	Hydrogen iodide
Initially	7.27×10^6	4.22×10^6	0
At equilibrium	3.41×10^6		7.72×10^6

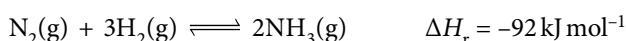
- Deduce the partial pressure of the iodine at equilibrium.
- Calculate the value of K_p for this reaction, including the units.

Equilibria and the chemical industry

An understanding of equilibrium is important in the chemical industry. Equilibrium reactions are involved in some of the stages in the large-scale production of ammonia, sulfuric acid and many other chemicals.

Equilibrium and ammonia production

The synthesis of ammonia is carried out by the Haber process. The equilibrium reaction involved is:



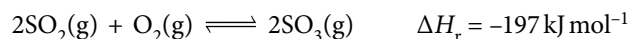
We can use Le Chatelier's principle to show how to get the best yield of ammonia. At high temperatures, when the reaction is faster, the position of equilibrium is to the left because the reaction is exothermic (ΔH is negative).

- What happens if we increase the pressure?
 - When we increase the pressure, the reaction goes in the direction that results in fewer molecules of gas being formed.
 - The equilibrium shifts in the direction that reduces the pressure.
 - In this case there are four molecules of gas on the left-hand side and two on the right-hand side. So the equilibrium shifts towards the right.
 - The yield of ammonia increases.

- What happens if we decrease the temperature?
 - A decrease in temperature decreases the energy of the surroundings.
 - The reaction will go in the direction in which energy is released.
 - Energy is released in the exothermic reaction, in which the position of equilibrium favours ammonia production.
 - This shifts the position of equilibrium to the right. The value of K_p increases.
- What happens if we remove ammonia by condensing it to a liquid? We can do this because ammonia has a much higher boiling point than hydrogen and nitrogen.
 - The position of equilibrium shifts to the right to replace the ammonia that has been removed.
 - More ammonia is formed from hydrogen and nitrogen to keep the value of K_p constant.

Equilibrium and the production of sulfuric acid

The synthesis of sulfuric acid is carried out by the Contact process. The main equilibrium reaction involved is:



We can use Le Chatelier's principle to show how to get the best yield of sulfur trioxide.

- What happens when we increase the pressure?
 - When we increase the pressure, the reaction goes in the direction that results in fewer molecules of gas being formed, to reduce the pressure.
 - There are three molecules of gas on the left-hand side and two on the right-hand side, so the equilibrium shifts towards the right.

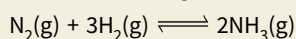
However, in practice, the reaction is carried out at just above atmospheric pressure. This is because the value of K_p is very high. The position of equilibrium is far over to the right even at atmospheric pressure. Very high pressure is unnecessary, and is not used as it is expensive.

- What happens if we decrease the temperature?
 - Decreasing the temperature shifts the position of equilibrium to the right.
 - A decrease in temperature decreases the energy of the surroundings so the reaction will go in the direction in which energy is released.
 - This is the exothermic reaction, in which the position of equilibrium favours SO_3 production. The value of K_p increases.

SO₃ is removed by absorbing it in 98% sulfuric acid. Although the SO₃ is absorbed in a continuous process, this does not affect the equilibrium significantly because the position of equilibrium is already far over to the right.

QUESTION

- 12** The Haber process for the synthesis of ammonia may operate at a temperature of 450 °C and pressure of 1.50×10^7 Pa using an iron catalyst.



$$\Delta H_r = -92 \text{ kJ mol}^{-1}$$

- Suggest why the temperature of more than 450 °C is not used even though the rate of reaction would be faster.
- Suggest why the reaction is carried out at a high pressure rather than at normal atmospheric pressure. Explain your answer.
- Explain why the removal of ammonia as soon as it is formed is an important part of this industrial process.
- When the ammonia has been removed, why doesn't it decompose back to nitrogen and hydrogen?



Figure 8.11 **a** The sour taste of lemons is due to citric acid and that of vinegar is due to ethanoic acid. **b** Washing soda is a base used to soften water prior to washing clothes. A solution of washing soda feels soapy.

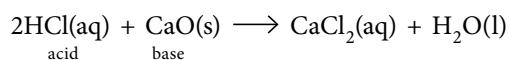
Name of acid	Formula	Ions formed in water
hydrochloric acid	HCl	H ⁺ + Cl ⁻
nitric acid	HNO ₃	H ⁺ + NO ₃ ⁻
sulfuric acid	H ₂ SO ₄	2H ⁺ + SO ₄ ²⁻
ethanoic acid	CH ₃ COOH	CH ₃ COO ⁻ + H ⁺
benzoic acid	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻ + H ⁺

Table 8.6 Formulae and ions of some common acids.

Acid–base equilibria

Some simple definitions of acids and bases

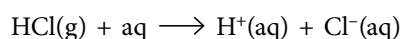
A very simple definition of an **acid** is that it is a substance which neutralises a base. A salt and water are formed.



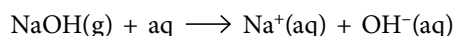
The equation above also shows us a very simple definition of a base. A **base** is a substance that neutralises an acid.

If we look at the formulae for a number of acids in [Table 8.6](#), we see that they all contain hydrogen atoms. When the acid dissolves in water, it ionises and forms hydrogen ions. Note that in organic acids such as carboxylic acids (see [page 231](#)) only some of the hydrogen atoms are capable of forming ions.

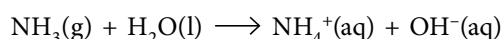
A better definition of an acid is a substance that releases hydrogen ions when it dissolves in water. For example:



The formulae for a number of bases are given in [Table 8.7](#). Many metal oxides or hydroxides are bases. Some bases dissolve in water to form hydroxide ions in solution. A base that is soluble in water is called an **alkali**. For example:



Some alkalis are formed by the reaction of a base with water. When ammonia gas dissolves in water, some of the ammonia molecules react with water molecules. Hydroxide ions are released in this reaction.



Aqueous ammonia is therefore an alkali. We can also see from the equation above that the ammonia has accepted a hydrogen ion to become NH₄⁺. So a wider definition of a base is a substance that accepts hydrogen ions.

Name of base	Formula
calcium oxide	CaO
copper(II) oxide	CuO
sodium hydroxide	NaOH
calcium hydroxide	Ca(OH) ₂
ammonia	NH ₃

Table 8.7 The formulae of some common bases.

QUESTION

- 13 a** Write an equation to show potassium hydroxide dissolving in water.
- b** Write an equation for liquid nitric acid dissolving in water.
- c** Write ionic equations for:
- the reaction in aqueous solution between sodium hydroxide and nitric acid
 - the reaction in aqueous solution between potassium hydroxide and hydrochloric acid.

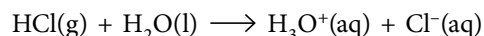
The Brønsted–Lowry theory of acids and bases

The definitions of acids and bases given above are limited to reactions taking place in water. In 1923 the Danish chemist J. Brønsted and the English chemist T. Lowry suggested a more general definition of acids and bases. This definition is based on the idea that in an acid–base reaction, a proton is transferred from an acid to a base (a proton is a hydrogen ion, H⁺).

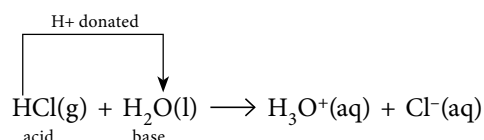
A Brønsted–Lowry acid is a proton donor.

A Brønsted–Lowry base is a proton acceptor.

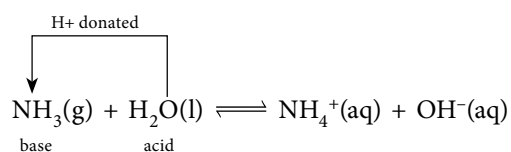
When hydrochloric acid is formed, hydrogen chloride gas dissolves in water and reacts to form hydroxonium ions, H₃O⁺, and chloride ions (Figure 8.12). You can see that the water is involved in the reaction.



Hydrochloric acid is an acid because it donates a proton to water. This means that water is acting as a Brønsted–Lowry base. The water is accepting a proton.



Water can also act as an acid. When ammonia reacts with water, it accepts a proton from the water and becomes an NH₄⁺ ion (Figure 8.13).



Substances like water, which can act as either acids or bases, are described as **amphoteric**.

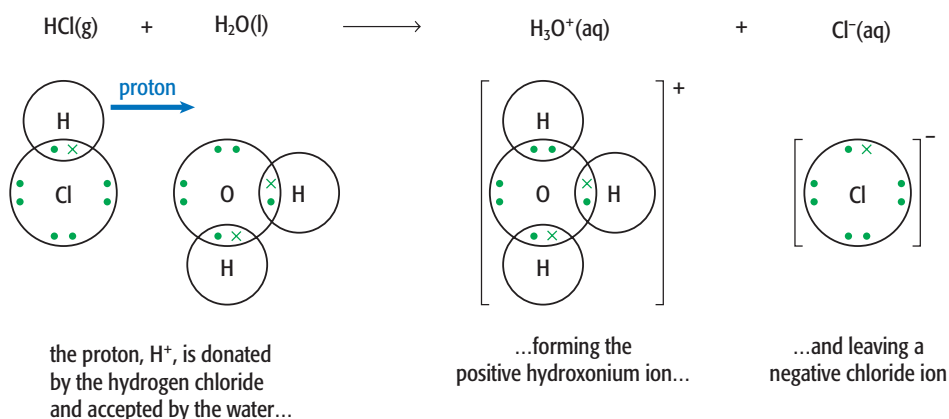


Figure 8.12 An acid is a proton donor. Hydrogen chloride is the acid in this reaction. A base is a proton acceptor. Water is the base in this reaction. Remember that a proton is a hydrogen ion, H⁺.

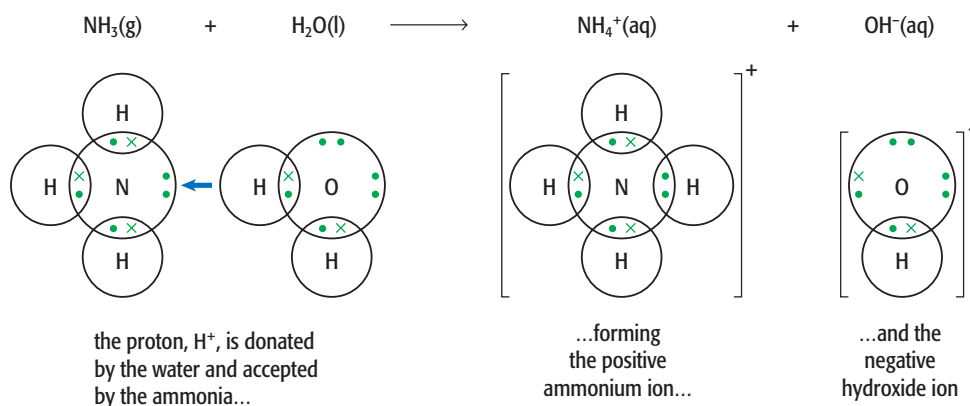
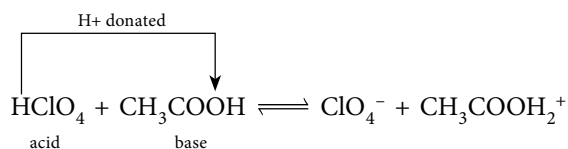


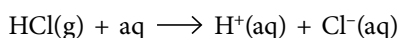
Figure 8.13 Water is the proton donor (it is the acid); ammonia is the proton acceptor (it is the base).

Brønsted–Lowry acids and bases do not have to involve aqueous solutions. For example, when chloric(VII) acid (HClO_4) reacts with ethanoic acid (CH_3COOH) in an inert solvent, the following equilibrium is set up:

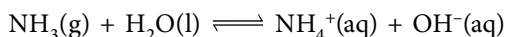


In this reaction HClO_4 is the acid because it is donating a proton to CH_3COOH . CH_3COOH is the base because it is a proton acceptor.

When an acid or base reacts with water, an equilibrium mixture is formed. For acids such as hydrochloric acid, the position of equilibrium is almost entirely in favour of the products. But for ammonia the position of equilibrium favours the reactants. The equations can be written to show this. For example:



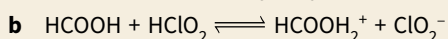
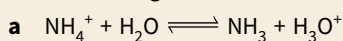
A forward arrow is used as this reaction goes to completion.



An equilibrium arrow is used as this reaction does not go to completion.

QUESTION

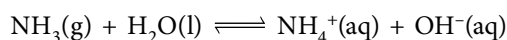
14 Identify which reactants are acids and which are bases in the following reactions:



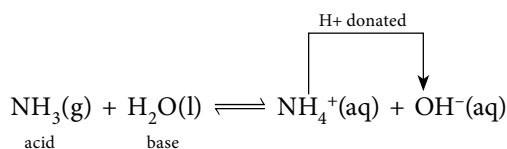
Conjugate acids and conjugate bases

In a reaction at equilibrium, products are being converted to reactants at the same rate as reactants are being converted to products. The reverse reaction can also be considered in terms of the **Brønsted–Lowry theory** of acids and bases.

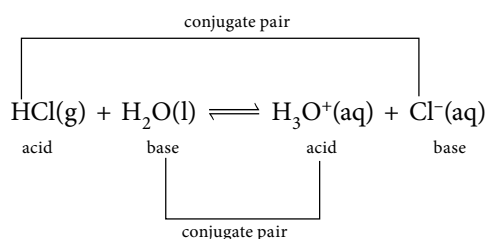
Consider the reaction:



In the reverse reaction, the NH_4^+ ion donates a proton to the OH^- ion. So NH_4^+ is acting as an acid and OH^- is acting as a base.



If a reactant is linked to a product by the transfer of a proton we call this pair a **conjugate pair**. Consider the following reaction:



Looking at the forward reaction:

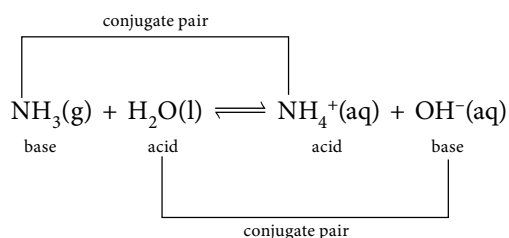
- Cl^- is the conjugate base of the acid HCl
- H_3O^+ is the conjugate acid of the base H_2O .

Looking at the reverse reaction:

- HCl is the conjugate acid of the base Cl^-
- H_2O is the conjugate base of the acid H_3O^+ .

In a conjugate pair, the acid has one proton more.

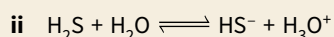
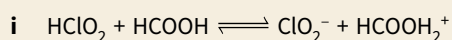
The conjugate pairs for the equilibrium between ammonia and water to form ammonium ions and hydroxide ions are:



The idea of conjugate acids and bases is sometimes called the acid–1 base–1, acid–2 base–2 concept.

QUESTION

- 15 a** Identify the acid and the base on the right-hand side of these equilibria.



- b** Identify the acid on the right-hand side of this equation which is conjugate with the base on the left-hand side.

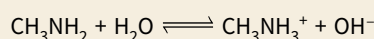
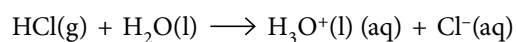


Figure 8.14 Many foods have high quantities of sugar in them. The sugar is converted to acid by bacteria in your mouth. This acid can attack the enamel on your teeth. By chewing sugar-free gum, more saliva is produced. Saliva is slightly alkaline. It neutralises the acid.

Strong and weak acids and bases

Strong acids

When hydrogen chloride dissolves in water to form a solution of concentration 0.1 mol dm^{-3} , it ionises almost completely. We say that the acid is almost completely **dissociated**.



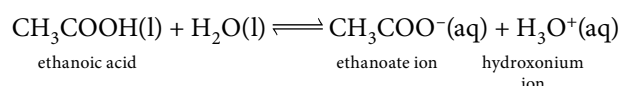
The position of equilibrium is so far over to the right that we can show this as an irreversible reaction. The pH of this solution is pH 1. The pH of a solution depends on the concentration of hydroxonium ions, H_3O^+ . The higher the concentration of hydroxonium ions, the lower the pH. The low pH shows that there is a high concentration of hydroxonium ions in solution.

Acids that dissociate almost completely in solution are called **strong acids**.

The mineral acids, hydrochloric acid, sulfuric acid and nitric acid, are all strong acids.

Weak acids

When ethanoic acid dissolves in water to form a solution of concentration 0.1 mol dm^{-3} , it is only slightly ionised. There are many more molecules of ethanoic acid in solution than ethanoate ions and hydroxonium ions. We say that the acid is partially dissociated.

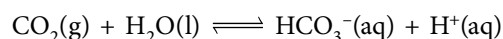


The position of equilibrium is well over to the left. The pH of this solution is pH 2.9. The pH is much higher compared with a solution of hydrochloric acid of the same concentration. This is because the concentration of hydroxonium ions in solution is far lower.

Acids that are only partially dissociated in solution are called **weak acids**.

Weak acids include most organic acids, hydrocyanic acid (HCN), hydrogen sulfide and 'carbonic acid'.

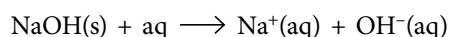
Although we sometimes talk about the weak acid, carbonic acid, you will never see a bottle of it. The acid is really an equilibrium mixture of carbon dioxide dissolved in water. The following equilibrium is set up:



The amount of CO_2 that forms undissociated carbonic acid, H_2CO_3 , is very small as H_2CO_3 ionises readily.

Strong bases

When sodium hydroxide dissolves in water to form a solution of concentration 0.1 mol dm^{-3} , it ionises completely.



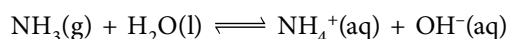
The position of equilibrium is far over to the right. The solution formed is highly alkaline due to the high concentration of hydroxide ions present. The pH of this solution is pH 13.

Bases that dissociate almost completely in solution are called **strong bases**.

The Group 1 metal hydroxides are strong bases.

Weak bases

When ammonia dissolves and reacts in water to form a solution of concentration 0.1 mol dm^{-3} , it is only slightly ionised. There are many more molecules of ammonia in solution than ammonium ions and hydroxide ions.



The position of equilibrium is well over to the left. The pH of this solution is pH 11.1. The pH is much lower compared with a solution of sodium hydroxide of the same concentration. This is because the concentration of hydroxide ions in solution is far lower.

Bases which dissociate to only a small extent in solution are called **weak bases**.

Ammonia, amines (see page 220) and some hydroxides of transition metals are weak bases.

Table 8.8 compares the pH values of some typical strong and weak acids and bases.

Acid or base	pH of 1.0 mol dm^{-3} solution	pH of 0.1 mol dm^{-3} solution	pH of 0.01 mol dm^{-3} solution
hydrochloric acid (strong acid)	0	1	2
ethanoic acid (weak acid)	2.4	2.9	3.4
sodium hydroxide (strong base)	14	13	12
ammonia (weak base)	11.6	11.1	10.6

Table 8.8 pH values of some typical strong and weak acids and bases.

QUESTIONS

16 Nitric acid is a strong acid but chloric(I) acid, HClO , is a weak acid.

- Explain the difference between a strong and a weak acid.
- Write equations showing the ionisation of each of these acids in water.
- Suggest relative pH values for 0.1 mol dm^{-3} aqueous solutions of:
 - chloric(I) acid
 - nitric acid.
- Hydrazine, N_2H_4 , is a weak base.
 - Write a chemical equation to show the equilibrium reaction of hydrazine with water.
 - State the relative concentrations (high or low) of the N_2H_4 molecules and the products.

17 a The pH of a solution depends on the hydrogen ion (hydroxonium ion) concentration. Which concentration of ethanoic acid in Table 8.8 has the highest concentration of hydrogen ions in solution?

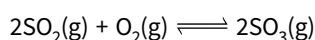
- Which acid or alkali in Table 8.8 has the highest concentration of hydroxide ions?
- Explain why a solution of 0.1 mol dm^{-3} ethanoic acid has a lower electrical conductivity than a solution of 0.1 mol dm^{-3} hydrochloric acid.
- Both hydrochloric acid and ethanoic acid react with magnesium. The rate of reaction of 1.0 mol dm^{-3} hydrochloric acid with magnesium is much faster than the rate of reaction of 1.0 mol dm^{-3} ethanoic acid. Explain why.

Summary

- A reversible reaction is one in which the products can be changed back to reactants.
- Chemical equilibrium is dynamic because the backward and forward reactions are both occurring at the same time.
- A chemical equilibrium is reached when the rates of the forward and reverse reactions are equal.
- Le Chatelier's principle states that when the conditions in a chemical equilibrium change, the position of equilibrium shifts to oppose the change.
- Changes in temperature, pressure and concentration of reactants and products affect the position of equilibrium.
- For an equilibrium reaction, there is a relationship between the concentrations of the reactants and products which is given by the equilibrium constant K .
- Equilibrium constants in terms of concentrations, K_c , and partial pressure, K_p , can be deduced from appropriate data.
- The quantities of reactants and products present at equilibrium can be calculated from the equilibrium expression and a value of K_c (or K_p), given appropriate data.
- A change in temperature affects the value of the equilibrium constant for a reaction but changes in concentration, pressure or the presence of a catalyst do not affect the value of the equilibrium constant.
- The conditions used in the Haber process and the Contact process are chosen so that a good yield of product is made.
- The Brønsted–Lowry theory of acids and bases states that acids are proton donors and bases are proton acceptors.
- Strong acids and bases are completely ionised in aqueous solution whereas weak acids and bases are only slightly ionised.
- Strong and weak acids and bases can be distinguished by the pH values of their aqueous solutions.

End-of-chapter questions

1 The reaction



reaches dynamic equilibrium in a closed vessel. The forward reaction is exothermic. The reaction is catalysed by V_2O_5 .

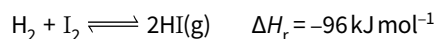
- a Explain the term **dynamic equilibrium**. [2]
- b What will happen to the position of equilibrium when:
 - i some sulfur trioxide, SO_3 , is removed from the vessel? [1]
 - ii the pressure in the vessel is lowered? [1]
 - iii more V_2O_5 is added? [1]
 - iv the temperature of the vessel is increased? [1]
- c State Le Chatelier's principle. [2]
- d Use Le Chatelier's principle to explain what will happen to the position of equilibrium in the reaction



when the concentration of hydrogen is increased. [5]

Total = 13

- 2 Hydrogen, iodine and hydrogen iodide are in equilibrium in a sealed tube at constant temperature. The equation for the reaction is:



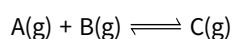
The partial pressures of each gas are shown in the table below.

Gas	Partial pressure / Pa
H_2	2.330×10^6
I_2	0.925×10^6
HI	10.200×10^6

- Explain the meaning of the term **partial pressure**. [2]
- Calculate the total pressure of the three gases in this mixture. [1]
- Write an equilibrium expression for this reaction in terms of partial pressures. [1]
- Calculate a value for K_p for this reaction, including the units. [1]
- Use Le Chatelier's principle to explain what happens to the position of equilibrium in this reaction when:
 - the temperature is increased [5]
 - some iodine is removed. [5]

Total = 15

- 3 The equilibrium between three substances, **A**, **B** and **C** is shown below.

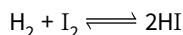


Initially there were 0.1 mol of **A** and 0.2 mol of **B** in the reaction mixture. **A** and **B** reacted together to produce an equilibrium mixture containing 0.04 mol of **C**. The total volume of the mixture was 2.00 dm^3 .

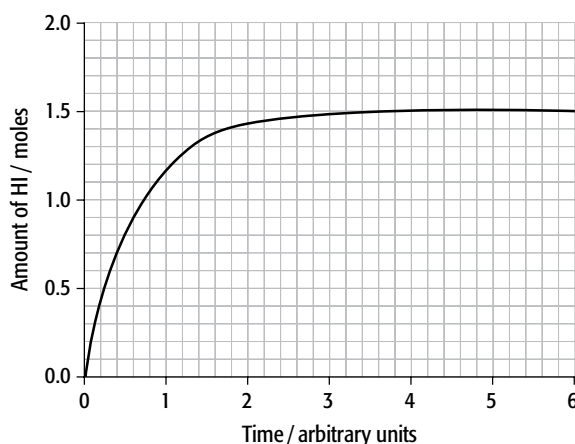
- Calculate the number of moles of **A** and **B** at equilibrium. [2]
- Calculate the concentrations of **A**, **B** and **C** at equilibrium. [3]
- Write the equilibrium expression for K_c . [1]
 - Calculate the value of K_c and give the units. [2]

Total = 8

- 4 Gaseous hydrogen and gaseous iodine react together to form hydrogen iodide.



- a The graph shows how the amount of hydrogen iodide varies with time in a 1.00 dm³ container.
The initial amounts of hydrogen and iodine were 1.00 mol H₂ and 1.00 mol I₂.



Draw a similar graph to show how the number of moles of hydrogen varies with time.

[5]

- b Calculate the number of moles of iodine present at equilibrium.

[1]

- c i Write the equilibrium expression for K_c for the reaction between gaseous hydrogen and iodine.

[1]

- ii Calculate the value of K_c and give the units.

[2]

Total = 9

- 5 a Describe three characteristic features of chemical equilibrium.

[3]

- b When 1 mol of N₂O₄ gas is allowed to come to equilibrium with NO₂ gas under standard conditions, only 20% of the N₂O₄ is converted to NO₂.



- i Give the equilibrium expression for this reaction.

[1]

- ii Calculate the value of K_c for the reaction. Assume that the volume of the reaction mixture is 1 dm³.

[4]

- c Explain the effect on K_c of an increase in:

- i pressure

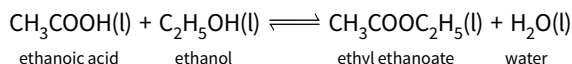
[2]

- ii temperature.

[2]

Total = 12

- 6 This question is about the following reaction:



9.20 g of ethanol are mixed with 12.00 g of ethanoic acid in an inert solvent. The total volume of solution is 250 cm³. The mixture is left to equilibrate for several days. At equilibrium 70% of the reactants are converted to products.

- a What is the concentration of each reactant at the start?

[2]

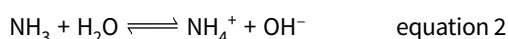
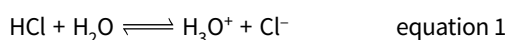
- b What is the concentration of each reactant at equilibrium?

[2]

- c What is the concentration of each product at equilibrium? [2]
- d i Write the equilibrium expression for this reaction. [1]
- ii Calculate the value of K_c for the reaction. [1]
- iii Explain why there are no units for K_c for this reaction. [1]
- e What will happen to the numerical value of K_c if 100 cm³ of water is added to the equilibrium mixture? [1]
- f What will happen to the yield of ethyl ethanoate if 100 cm³ of water is added to the equilibrium mixture? Explain your answer. [2]

Total = 12

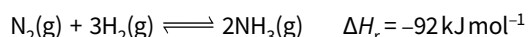
- 7 a Hydrogen chloride and ammonia both ionise in water:



- i State the name of the ion H_3O^+ . [1]
- ii Identify the acid and the base on the left-hand side of each equation. [2]
- iii By referring to equation 1 and equation 2, explain why water is described as being **amphoteric**. [5]
- b When dissolved in an organic solvent, hydrogen chloride reacts with hydrogen iodide as follows:
- $$\text{HCl} + \text{HI} \rightleftharpoons \text{H}_2\text{Cl}^+ + \text{I}^-$$
- i Use the Brønsted–Lowry theory of acids and bases to explain which reactant is the acid and which reactant is the base. [2]
- ii Identify which of the products is the conjugate acid and which is the conjugate base of the substances you have identified in part b i. [1]
- c Hydrochloric acid is a strong acid but ethanoic acid, CH_3COOH , is a weak acid.
- i Explain the difference between a strong acid and a weak acid. [2]
- ii Suggest a value of the pH for a 0.1 mol dm⁻³ solution of ethanoic acid in water. [1]
- iii Write a chemical equation to show the reaction when ethanoic acid donates a proton to water. [2]

Total = 16

- 8 This question is about the reaction:



120.0 mol of hydrogen gas are mixed with 40.0 mol of nitrogen gas then pressurised. The mixture of gases is passed at constant pressure over an iron catalyst at 450 °C until the mixture reaches equilibrium. The total volume of the mixture is 1.0 dm³. 20% of the reactants are converted to ammonia.

- a How many moles of nitrogen and hydrogen remain at equilibrium? [2]
- b How many moles of ammonia are formed? [1]
- c Write an equilibrium expression for K_c . [1]
- d Calculate a value for K_c , including units. [2]
- e What will happen to the numerical value of K_c when the pressure is raised? [1]
- f What will happen to the numerical value of K_c when the temperature is raised? [1]

Total = 8