

Cambridge

AS Level

Chemistry

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Chapter 7 and Chapter 8

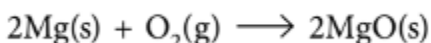
Redox reactions and Equilibrium



Chapter 7 – Redox reactions

What is a redox reaction?

Oxidation is the process by which an element gains oxygen, such as magnesium, by reacting with oxygen to form magnesium oxide.



A simple definition of **reduction** is loss of oxygen. When copper (II) oxide reacts with hydrogen, this is the equation for the reaction:



Oxidation and reduction always take place together. We call the reactions in which this happens **redox reactions**.

Oxidation is the process of removing hydrogen from a compound, often occurring in the reaction of organic compounds.

There are two other ways of finding out whether a substance has been oxidised or reduced during a chemical reaction:

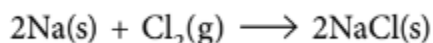
- Electron transfer
- Changes in oxidation number.

Redox and electron transfer

Half-equations

We can extend our definition of redox to include reactions involving ions.

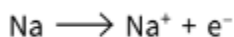
Sodium reacts with chlorine to form the ionic compound sodium chloride.



We can divide this reaction into two separate equations, one showing oxidation and the other showing reduction. We call these **half-equations**.

When sodium reacts with chlorine:

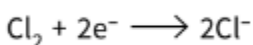
- Each sodium atom loses one electron from its outer shell. Oxidation is loss of electrons (OIL). The sodium atoms have been oxidised.



This half-equation shows that sodium is oxidised. It is also acceptable to write this half-equation as:



- Each chlorine atom gains one electron to complete its outer shell. Reduction is gain of electrons (RIG). The chlorine atoms have been reduced.



Oxidation Is Loss of electrons.
Reduction Is Gain of electrons.
The initial letters shown in bold spell **OIL RIG**. This may help you to remember these two definitions!

Balancing half-equations

A balanced ionic equation can be created by balancing the numbers of electrons lost and gained in a redox reaction, ensuring equal numbers.

Oxidation numbers

What are oxidation numbers?

We can extend our definition of redox even further to include oxidation and reduction in reactions involving covalent compounds. We do this by using oxidation numbers (**oxidation numbers** are also called **oxidation states**).

Oxidation number rules

Oxidation number rules help determine the oxidation number of any atom or ion, referring to a single atom in a compound.

1. The oxidation number of any uncombined element is zero.
2. In compounds many atoms or ions have fixed oxidation numbers.
3. The oxidation number of an element in a monatomic ion is always the same as the charge.
4. The sum of the oxidation numbers in a compound is zero.
5. The sum of the oxidation numbers in an ion is equal to the charge on the ion.
6. In either a compound or an ion, the more electronegative element is given the negative oxidation number.



Figure 7.2 This is part of a ship's hull. It is made of iron protected by bars of magnesium metal. The magnesium atoms (oxidation number = 0) are oxidised to Mg^{2+} ions (oxidation number = +2) in preference to iron atoms changing to Fe^{3+} . This is called sacrificial protection.

Applying the oxidation number rules

In the following examples we shall use 'ox. no.' as an abbreviation for oxidation number.

Compounds of a metal with a non-metal

The metal always has the positive ox. no. and the non-metal has the negative ox. no.

If we do not know the ox. no. of one of the atoms, we can often work it out using the invariable ox. nos.

Compounds of a non-metal with a non-metal

The sign of the ox. no. in compounds with two non-metals depends on the electronegativity of each atom, with the most electronegative element receiving the negative sign.

Sulfur dioxide, SO_2

- ox. no. of each O atom = -2
- for two oxygen atoms = $2 \times (-2) = -4$
- SO_2 has no charge, so the total ox. no. is zero (rule 4)
- ox. no. of S = +4

Iodine trichloride, ICl_3

- chlorine is more electronegative than iodine, so chlorine is – and iodine is +
- ox. no. of each Cl atom = –1
- for three chlorine atoms = $3 \times (-1) = -3$
- ICl_3 has no charge, so the total ox. no. is zero (rule 4)
- ox. no. of I = +3

Hydrazine, N_2H_4

- nitrogen is more electronegative than hydrogen, so nitrogen is – and hydrogen is +
- ox. no. of each H atom = +1 (rule 2)
- for four hydrogen atoms = $4 \times (+1) = +4$
- N_2H_4 has no charge, so the total ox. no. is zero (rule 4)
- ox. no. of two N atoms = –4
- ox. no. of each N atom = –2

Compound ions

Compound ions are ions with two or more different atoms.

Examples are the sulfate ion, SO_4^{2-} , and the nitrate ion, NO_3^- . We use rule 5 to work out the ox. no. that we do not know.

Nitrate ion, NO_3^-

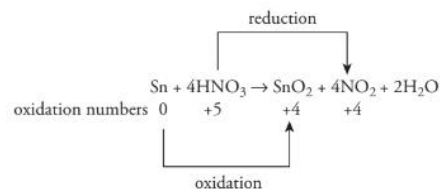
- ox. no. of each O atom = –2
- for three oxygen atoms = $3 \times (-2) = -6$
- NO_3^- has a charge of 1–, so the total ox. no. of N and O atoms is –1 (rule 5)
- ox. no. of the nitrogen atom plus ox. no. of the three oxygen atoms (–6) = –1
- ox. no. of N = +5

Redox and oxidation number

We can define oxidation and reduction in terms of the oxidation number changes of particular atoms during a reaction.

Oxidation is an increase of oxidation number.
Reduction is a decrease in oxidation number.

Tin atoms undergo oxidation, nitrogen reduction, oxygen and hydrogen oxidation/reduction, respectively, with tin atoms increasing by +4 and nitrogen decreasing by -1, and oxygen and hydrogen remaining unchanged.



In this reaction nitric acid is acting as an **oxidising agent**:

- Oxidising agents increase the ox. no. of another atom
- An atom in the oxidising agent decreases in ox. no.
- The oxidising agent is the substance which gets reduced – it gains electrons.

In this reaction tin is acting as a **reducing agent**:

- Reducing agents decrease the ox. no. of another atom
- An atom in the reducing agent increases in ox. no.
- The reducing agent is the substance that gets oxidised – it loses electrons.

Naming compounds

Roman numbers in brackets are used to name compounds, distinguishing between different elements like iron (II) chloride and iron (III) chloride, based on their oxidation numbers.

- In iron(II) chloride, the ox. no. of the iron is +2. The compound contains Fe^{2+} ions. The formula is FeCl_2 .
- In iron(III) chloride, the ox. no. of the iron is +3. The compound contains Fe^{3+} ions. The formula is FeCl_3 .

Oxides of nitrogen

There are several oxides of nitrogen, including N_2O , NO and NO_2 . We distinguish between these according to the ox. no. of the nitrogen atom. (The ox. no. of oxygen is generally -2.)

- The ox. no. of N in N_2O is +1. So this compound is nitrogen(I) oxide.
- The ox. no. of N in NO is +2. So this compound is nitrogen(II) oxide.
- The ox. no. of N in NO_2 is +4. So this compound is nitrogen(IV) oxide.

Nitrate ions

Sodium, nitrogen and oxygen can form two different compounds. The ox. no. of sodium is +1 and the ox. no. of oxygen is -2. So, it is the ox. no. of nitrogen that varies.

- The ox. no. of N in the NO_2^- ion is +3. So NaNO_2 is sodium nitrate(III).
- The ox. no. of N in the NO_3^- ion is +5. So NaNO_3 is sodium nitrate(V).

The names of inorganic acids containing oxygen end in -ic. The Roman number goes directly after the ion that contains the oxygen and another element.

- H_3PO_3 is phosphoric(III) acid because the ox. no. of phosphorus is +3.
- HClO_4 is chloric(VII) acid because the ox. no. of chlorine is +7.

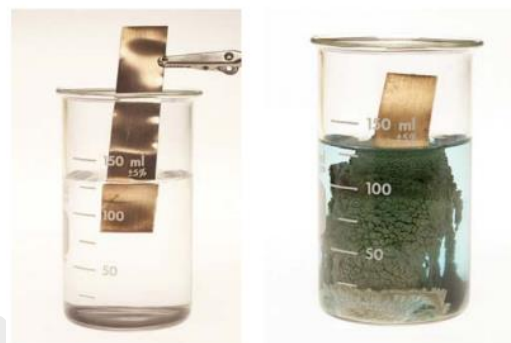


Figure 7.3 Copper reacts with silver nitrate to form silver and copper(II) nitrate. The ox. no. of each copper atom has increased by two. The ox. no. of each silver ion decreases by one.

Common acids' salts are named without non-metal ion ox. no., like magnesium nitrate(V) or potassium sulfate (VI). Metal ox. no. is not stated for one oxidation state.

From name to formula

You can work out the formula of a compound from its name.

Balancing chemical equations using oxidation numbers

We can use oxidation numbers to balance equations involving redox reactions. This method is especially useful where compound ions such as nitrate(V) or manganate (VII) is involved.

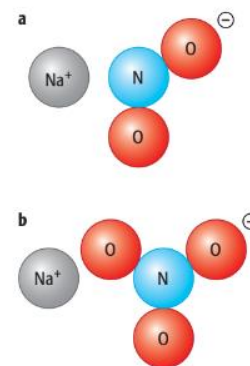


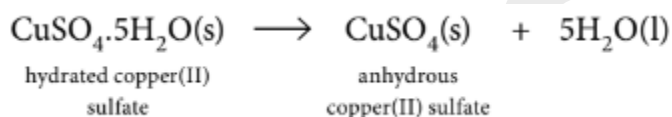
Figure 7.4 a One formula unit of 'sodium nitrate(III)' and b one formula unit of 'sodium nitrate(V)'.

Chapter 08 - Equilibrium

Reversible reactions and equilibrium

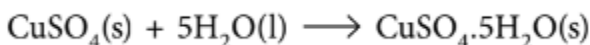
Reversible reactions

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.

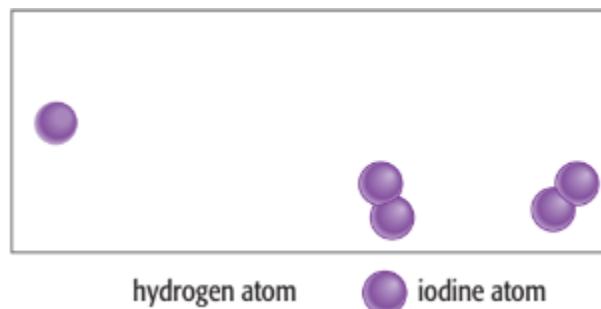


A reaction in which the products can react to re-form the original reactants is called a **reversible reaction**.

A chemical reaction occurs when both forward and backward reactions occur simultaneously, resulting in a mixture of products and reactants. This reversible reaction, known as an **equilibrium reaction**, occurs when reactants are not fully utilized, forming products.

Hydrogen iodide molecules are breaking down to hydrogen and iodine at the same rate as hydrogen and iodine molecules react to form hydrogen iodide.

Fizzy drinks create bubbles of carbon dioxide due to the equilibrium between the dissolution of carbon dioxide gas and the release of the liquid.



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.

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.

Figure 8.4 illustrates the reaction between hydrogen and iodine molecules at 500K in a 1dm³ vessel, revealing a purple iodine vapour until equilibrium.

Figure 8.5 demonstrates that 10.00mol of hydrogen iodide molecules can achieve the same equilibrium concentrations when they decompose into iodine and hydrogen iodide.

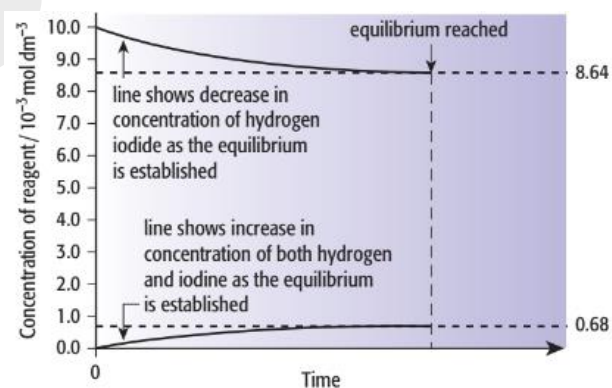
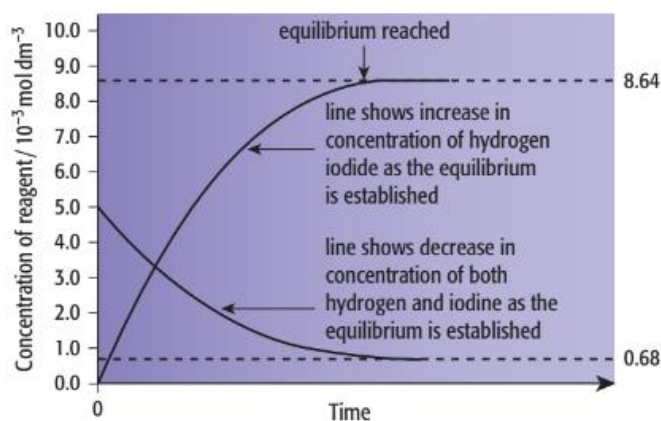


Figure 8.5 The changes in the concentrations of reagents as 10.00 mol of hydrogen iodide react to form an equilibrium mixture with hydrogen and iodine gases in a vessel of 1 m³.

4. Equilibrium requires a closed system

A **closed system** is one in which none of the reactants or products escapes from the reaction mixture. 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.

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.

Henri Le Chatelier, a French chemist, observed how changes in concentration, temperature, and pressure affect equilibrium positions, introducing **Le Chatelier's principle**.

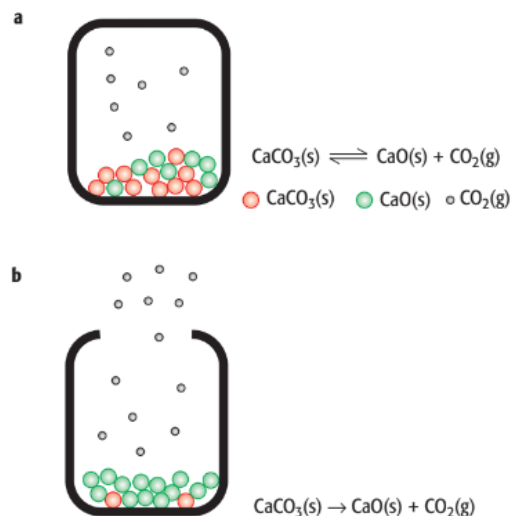


Figure 8.6 **a** A closed system. No carbon dioxide escapes. The calcium carbonate is in equilibrium with calcium oxide and carbon dioxide. **b** An open system. The calcium carbonate is continually decomposing as the carbon dioxide is lost. The reaction eventually goes to completion.

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.

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.

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

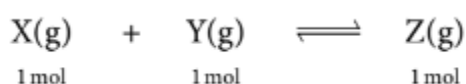
What happens when we remove some water?

- 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.

The effect of pressure on the position of equilibrium

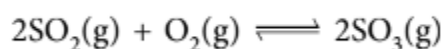
The molecules or ions in solids and liquids are packed closely together and cannot be compressed very easily. In gases, the molecules are far apart (Figure 8.8).

Figure 8.9 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.



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 .

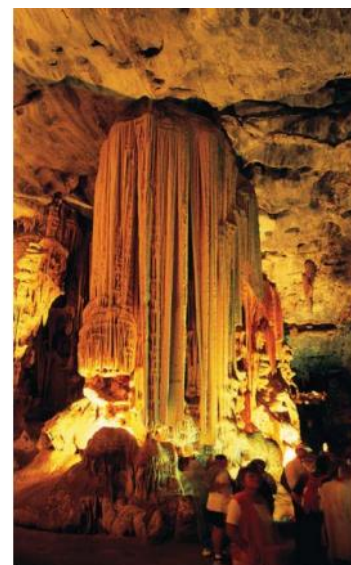


Figure 8.7 Stalactites and stalagmites are formed as a result of water passing through rocks containing calcium carbonate. The solution running through these rocks contains water, dissolved carbon dioxide and calcium hydrogencarbonate:

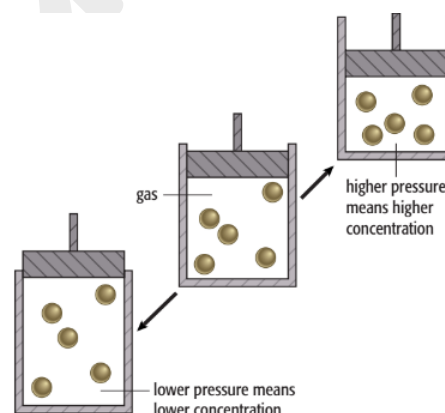
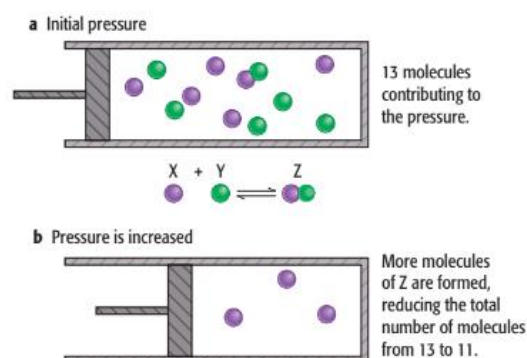


Figure 8.8 Pressure has a considerable effect on the concentration of gases.



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 SO₂ and O₂ molecules are formed by the decomposition of SO₃ 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.

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.

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 H₂ and I₂.

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.

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 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2$
pressure increase	equilibrium position shifts towards products: more NH ₃ forms	equilibrium position shifts towards reactants: more N ₂ O 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.

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.

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.

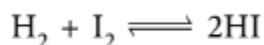
Do catalysts have any effect on the position of equilibrium?

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 500K, the following equilibrium is set up:



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 500K
- The concentrations of hydrogen, iodine and hydrogen iodide at equilibrium are determined.

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:

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

$$= 161$$

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)

concentration of product D

$$K_c = \frac{[\text{C}]^p [\text{D}]^q}{[\text{A}]^m [\text{B}]^n}$$

concentration of reactant B

(Arrows in the original image point from the text labels to the corresponding terms in the equation: from 'concentration of product D' to $[\text{D}]^q$, from 'number of moles of product D' to q , from 'number of moles of reactant B' to n , and from 'concentration of reactant B' to $[\text{B}]$.)

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}	$\frac{[HI]^2}{[H_2][I_2]}$
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 $H_2 + I_2 \rightleftharpoons 2HI$.

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.

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 are altered.

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 $[H_2]$ and $[I_2]$ increase and $[HI]$ 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.

K_c and temperature changes

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

So for the endothermic reaction $2HI \rightleftharpoons H_2 + I_2$:

- 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:

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

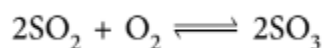
Table 8.5 shows how the value of K_c for this reaction changes with temperature.

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 $2HI \rightleftharpoons H_2 + I_2$ 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.

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

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.

Equilibria in gas reactions: the equilibrium constant, K_p

Partial pressure

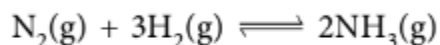
At constant temperature, each gas in the mixture contributes to the total pressure in proportion to the number of moles present (Figure 8.10). The pressure exerted by any one gas in the mixture is called its partial pressure.

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 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.

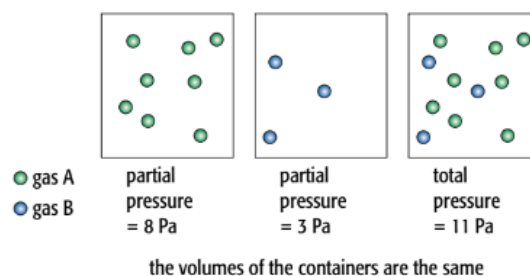


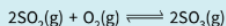
Figure 8.10 Each gas in this mixture contributes to the pressure in proportion to the number of moles present.

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 $\text{SO}_2 = 1.0 \times 10^6 \text{ Pa}$, $\text{O}_2 = 7.0 \times 10^6 \text{ Pa}$, $\text{SO}_3 = 8.0 \times 10^6 \text{ Pa}$. 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.

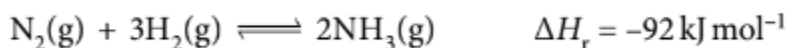
$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times 7.0 \times 10^6} = 9.1 \times 10^{-6} \text{ Pa}^{-1}$$

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:



■ 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?

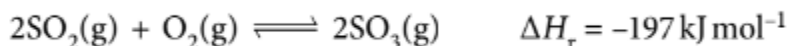
- A decrease in temperature decreases the energy of the surroundings.
- The reaction will go in the direction in which energy is released.
- Energy is released in the exothermic reaction, in which the position of equilibrium favours ammonia production.
- This shifts the position of equilibrium to the 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.

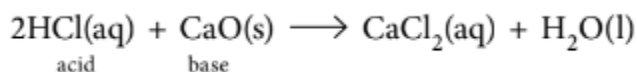
■ What happens if we decrease the temperature?

- 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.

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.



A **base** is a substance that neutralizes an acid, which contains hydrogen atoms. When dissolved in water, it ionizes and forms hydrogen ions, with organic acids like carboxylic acids having only some hydrogen atoms.



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.

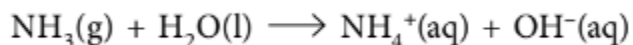
Name of acid	Formula	Ions formed in water
hydrochloric acid	HCl	$\text{H}^+ + \text{Cl}^-$
nitric acid	HNO_3	$\text{H}^+ + \text{NO}_3^-$
sulfuric acid	H_2SO_4	$2\text{H}^+ + \text{SO}_4^{2-}$
ethanoic acid	CH_3COOH	$\text{CH}_3\text{COO}^- + \text{H}^+$
benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	$\text{C}_6\text{H}_5\text{COO}^- + \text{H}^+$

Table 8.6 Formulae and ions of some common acids.

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

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**.

Alkalis are formed when a base reacts with water, releasing hydroxide ions when ammonia gas dissolves in water.



Aqueous ammonia is an alkali, accepting a hydrogen ion to become NH_4^+ , making it a base that accepts hydrogen ions.

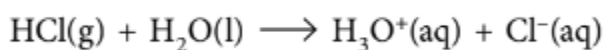
The Brønsted–Lowry theory of acids and bases

In 1923, Danish chemist J. Brønsted and English chemist T. Lowry proposed a more general definition of acids and bases, based on the transfer of a proton.

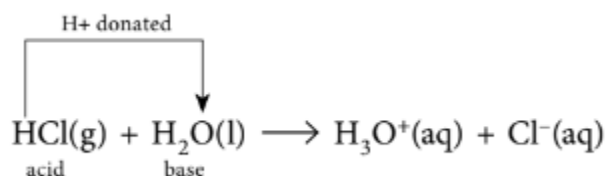
Name of base	Formula
calcium oxide	CaO
copper(II) oxide	CuO
sodium hydroxide	NaOH
calcium hydroxide	$\text{Ca}(\text{OH})_2$
ammonia	NH_3

Table 8.7 The formulae of some common bases.

When hydrochloric acid is formed, hydrogen chloride gas dissolves in water and reacts to form hydroxonium ions, H_3O^+ , and chloride ions (Figure 8.12). You can see that the water is involved in the reaction.

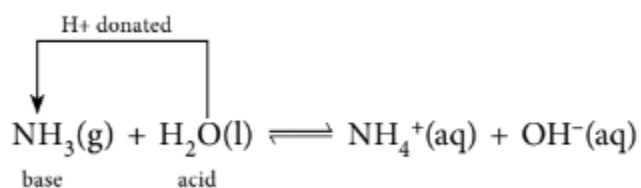


Hydrochloric acid is an acid because it donates a proton to water. This means that water is acting as a Brønsted–Lowry base. The water is accepting a proton.



A Brønsted–Lowry acid is a proton donor.
A Brønsted–Lowry base is a proton acceptor.

Water can also act as an acid. When ammonia reacts with water, it accepts a proton from the water and becomes an NH_4^+ ion (Figure 8.13).



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

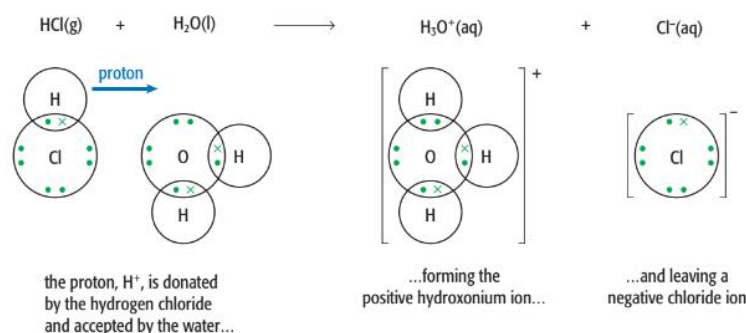


Figure 8.12 An acid is a proton donor. Hydrogen chloride is the acid in this reaction. A base is a proton acceptor. Water is the base in this reaction. Remember that a proton is a hydrogen ion, H^+ .

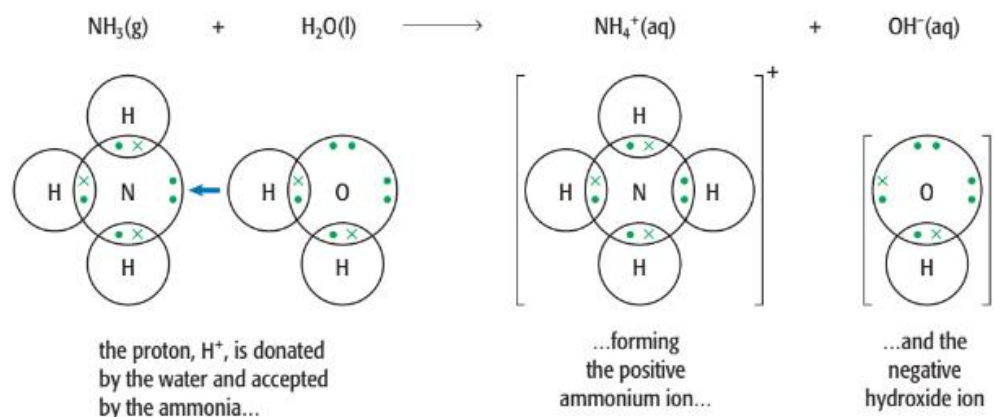


Figure 8.13 Water is the proton donor (it is the acid); ammonia is the proton acceptor (it is the base).

Brønsted–Lowry acids and bases do not have to involve aqueous solutions.

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.

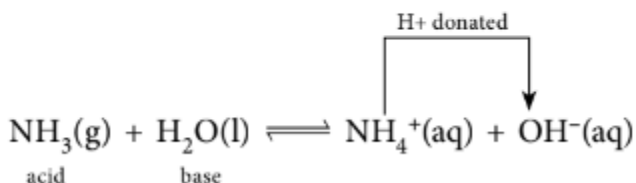
Conjugate acids and conjugate bases

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.

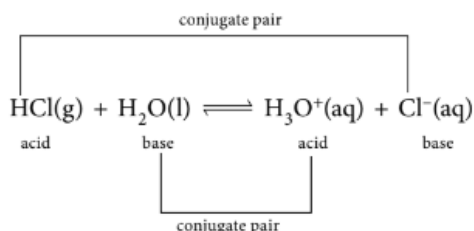
Consider the reaction:



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:



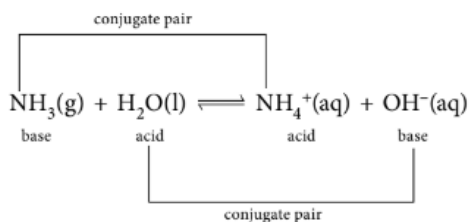
Looking at the forward reaction:

- 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^+

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.

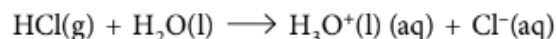


Figure 8.14 Many foods have high quantities of sugar in them. The sugar is converted to acid by bacteria in your mouth. This acid can attack the enamel on your teeth. By chewing sugar-free gum, more saliva is produced. Saliva is slightly alkaline. It neutralises the acid.

Strong and weak acids and bases

Strong acids

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



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

Weak acids

There are many more molecules of ethanoic acid in solution than ethanoate ions and hydroxonium ions. We say that the acid is partially dissociated.

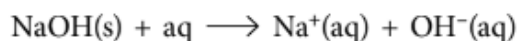


Acids that are only partially dissociated in solution are called **weak acids**.

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

Strong bases

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



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

Weak bases

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



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.

Revision questions

1. (a) (i) Define the term *Brønsted-Lowry acid*.
.....
- (ii) What is meant by the term *strong* when describing an acid?
.....
- (iii) Give the value of the ionic product of water, K_w , measured at 298K, and state its units.
Value.....
Units.....
- (b) At 298 K, 25.0 cm³ of a solution of a strong acid contained 1.50×10^{-3} mol of hydrogen ions.
 - (i) Calculate the hydrogen ion concentration in this solution and hence its pH.
Hydrogen ion concentration.....
.....
pH.....
 - (ii) Calculate the pH of the solution formed after the addition of 50.0 cm³ of 0.150 M NaOH to the original 25.0 cm³ of acid.
- (c) A solution of a strong acid was found to have a pH of 0.5
 - (i) Calculate the hydrogen ion concentration in this solution.
.....
 - (ii) Calculate the volume of water which must be added to 25.0 cm³ of this solution to increase its pH from 0.5 to 0.7

2. (a) The pH of a 0.15 M solution of a weak acid, HA, is 2.82 at 300 K.
- Write an expression for the acid dissociation constant, K_a , of HA, and determine the value of K_a for this acid at 300 K, stating its units.
 - The dissociation of HA into its ions in aqueous solution is an endothermic process. How would its pH change if the temperature were increased? Explain your answer.
- (b) Solution **A** contains n moles of a different weak acid, HX. The addition of some sodium hydroxide to **A** neutralises one third of the HX present to produce Solution **B**.
- In terms of the amount, n , how many moles of HX are present in Solution **B**?
 - Determine the ratio $\frac{[\text{HX}]}{[\text{X}^-]}$ in Solution **B**.
 - Solution **B** has a hydrogen ion concentration of $4.2 \times 10^{-4} \text{ mol dm}^{-3}$. Use this information and your answer to part (b)(ii) to determine the value of the acid dissociation constant of HX.
- (c) Why is methyl orange **not** suitable as an indicator for the titration of HX with sodium hydroxide?
- (d) Solution **B** can act as a buffer. Explain what this means and write an equation that shows how Solution **B** acts as a buffer if a little hydrochloric acid is added.
3. (a) Explain the terms *acid* and *conjugate base* according to the Brønsted-Lowry theory.
- (b) For each of the following reactions, give the formula of the acid and of its conjugate base
- $$\text{NH}_3 + \text{HBr} \rightarrow \text{NH}_4^+ + \text{Br}^-$$

Acid Conjugate base
 - $$\text{H}_2\text{SO}_4 + \text{HNO}_3 \rightarrow \text{HSO}_4^- + \text{H}_2\text{NO}_3^+$$

Acid Conjugate base
- (c) (i) Write an equation to represent the dissociation of water.
- Give the expression for the equilibrium constant, K_c , for the reaction in (c)(i) and use this to derive the expression for the ionic product of water, K_w .
 - The ionic product of water is $2.92 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 313K. Calculate the pH of water at this temperature.
 - Given that the pH of water is 7.00 at 298 K, state whether the dissociation of water is endothermic or exothermic. Give a reason for your answer.

- 4) (a) Samples of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ are reacted separately with an excess of aqueous sodium hydroxide or with an excess of aqueous ammonia.

Give the following information about these reactions.

(i) reaction 1: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with an excess of aqueous of sodium hydroxide

(ii) reaction 2: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ with an excess of aqueous ammonia

(b) Copper(I) oxide is added to hot dilute sulfuric acid. A blue solution, X, and a red-brown solid, Y, form.

Suggest the identities of X and Y. Name the type of reaction.

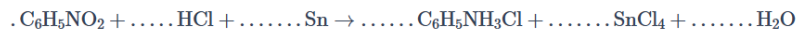
- 5) Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, in acid solution in a two step process.

(a) (i) Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.



(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to (i) useful.



(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, was produced.

Calculate the percentage yield.

(c) Following the reaction in (b), an excess of $\text{NaOH}(\text{aq})$ was added to liberate phenylamine from phenylammonium chloride.

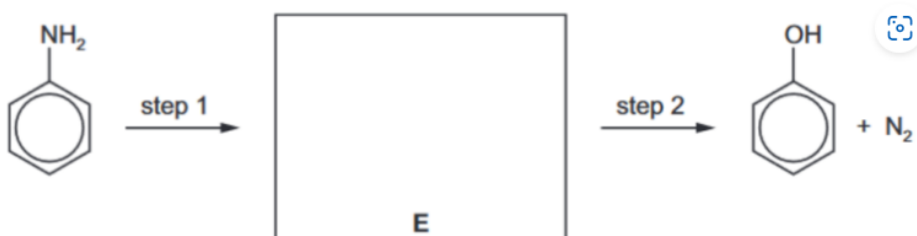
(i) Calculate the mass of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of $\text{NaOH}(\text{aq})$.

The final volume of the alkaline solution of phenylamine in (i) was 25.0 cm^3 . The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

(ii) Use the data to calculate the partition coefficient, $K_{\text{partition}}$, of phenylamine between dichloromethane and water.

d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

(e) Phenol can be synthesised from phenylamine in two steps



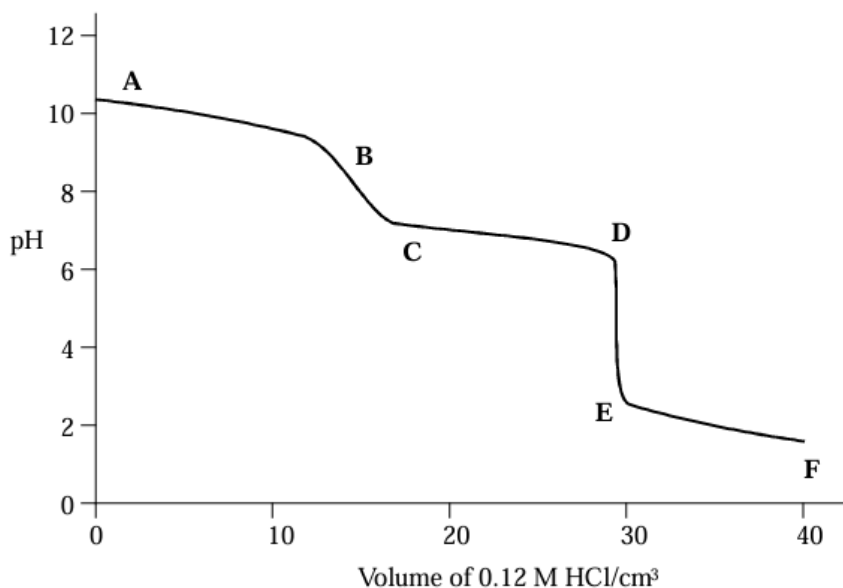
i) State the reagents and conditions for steps 1 and 2.

step 1

step 2 [2]

(ii) Draw the structure of the intermediate compound E in the box above. [1] [Total: 13]

6. The graph below shows how the pH changes as 0.12 M HCl(aq) is added to 25.0 cm³ of a solution of sodium carbonate. There are two end-points. The second end-point is at 30.0 cm³.



- (a) Write equations for the reactions which occur in the solution between point A and point B on the graph and between point C and point D on the graph.

Equation for reaction occurring between A and B.

.....

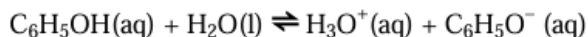
Equation for reaction occurring between C and D.

.....

- (b) Estimate the minimum volume of hydrochloric acid needed in this experiment for carbon dioxide to be produced from a well-stirred solution of sodium carbonate.
- (c) Name an indicator which can be used to determine the end-point occurring between points D and E. Explain why this indicator does not change colour between points B and C.
- (d) Use the end-point occurring between points D and E to calculate the concentration of sodium carbonate in the given solution.
- (e) If the original solution had contained, in addition to sodium carbonate, an equal molar concentration of sodium hydrogen carbonate, at what volumes of hydrochloric acid would the two end-points have been detected?

7. (a) Define the term *Brønsted-Lowry acid*.
- (b) Write an equation for the reaction between gaseous hydrogen chloride and water. State the role of water in this reaction, using the Brønsted-Lowry definition.
- (c) Write an equation for the reaction between gaseous ammonia and water. State the role of water in this reaction, using the Brønsted-Lowry definition.
- (d) The ion H_2NO_3^+ is formed in the first stage of a reaction between concentrated nitric acid and an excess of concentrated sulphuric acid. In this first stage the two acids react in a 1:1 molar ratio. In the second stage, the H_2NO_3^+ ion decomposes to form the nitronium ion, NO_2^+ . Write equations for these two reactions and state the role of nitric acid in the first reaction.
- (e) (i) Explain the term *weak acid*.
- (ii) Write an expression for the acid dissociation constant, K_a , of HA, a weak monoprotic acid.
- (iii) The value of the acid dissociation constant for the monoprotic acid HX is 144 mol dm^{-3} . What does this suggest about the concentration of undissociated HX in dilute aqueous solution?
- (iv) State whether HX should be classified as a strong acid or a weak acid. Justify your answer.
8. For acid HA, $K_a = 2.00 \times 10^{-4} \text{ mol dm}^{-3}$.
- (a) Write an equation for the reaction of HA with NaOH.
- (b) A solution was formed by adding 15 cm^3 of 0.34 M NaOH to 25 cm^3 of 0.45 M HA.
- (i) Calculate the number of moles of $\text{A}^-(\text{aq})$ and $\text{HA}(\text{aq})$ in this solution. (You should neglect the small number of moles of $\text{A}^-(\text{aq})$ formed by ionisation of the remaining $\text{HA}(\text{aq})$.)
- (ii) Calculate the concentration of $\text{A}^-(\text{aq})$ and $\text{HA}(\text{aq})$ in this solution.
- (iii) Using an expression for K_a , calculate the pH of this solution.

9. (a) Phenol is a *weak acid*. The dissociation of phenol in aqueous solution is represented by the following equation:



What is meant by the term *weak acid*?

- (b) (i) Write an expression for the acid dissociation constant, K_a , for phenol.
- (ii) Write an expression linking K_a with $\text{p}K_a$.
- (iii) The value of the acid dissociation constant, K_a , for phenol is $1 \times 10^{-10} \text{ mol dm}^{-3}$. Calculate the $\text{p}K_a$ value of phenol.
- (iv) Ethanoic acid is a stronger acid than phenol. State whether the $\text{p}K_a$ value for ethanoic acid will be greater or smaller than that of phenol.
10. (a) (i) Define the term *pH*.
- (ii) Write an expression for the dissociation constant K_a for the weak acid HX.
- (iii) For HX, $K_a = 4.25 \times 10^{-5} \text{ mol dm}^{-3}$. Calculate the pH of a 0.45 M solution of this acid.
- (b) In a 0.25 M solution, a different acid HY is 95% dissociated.
- (i) Calculate the pH of this solution.
- (ii) Calculate the value of K_a for the acid HY.